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CHLORIDE ION CATALYSED REARRANGEMENT AND ISOTOPE EXCHANGE  
OF THE ISOMERIC METHYLALLYL CHLORIDES  
IN ACETONITRILE

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### ABSTRACT

The bromide ion catalysed rearrangement reaction of  $\alpha$ -methylallyl bromide in acetone was studied by England and Hughes and assigned an  $S_N2'$  mechanism, and this was the only isomeric rearrangement reaction proceeding by this mechanism which had been thoroughly investigated.<sup>79,120</sup>

The kinetics and mechanism of the chloride ion catalysed isomeric rearrangement reactions of  $\alpha$ - and  $\gamma$ -methylallyl chloride in acetonitrile have now been investigated and an  $S_N2'$  mechanism has been assigned to these reactions, various other possible mechanisms having been excluded.

The kinetics and mechanism of the isotope exchange reactions of the two isomers in acetonitrile have also been studied and these reactions have been assigned an  $S_N2$  mechanism.

The isotope exchange reactions of both the methylallyl bromides and the methylallyl chlorides in acetone were studied by England and Hughes, the reaction medium being unfavourable for a study of the  $S_N2'$  reactions of the latter substrates.

A comparison of the kinetic data for the rearrangement and isotope exchange reactions of the methylallyl chlorides in acetonitrile with that for the corresponding reactions of the methylallyl bromides in acetone is made. The two systems are similar in behaviour as may be seen from the data tabulated below.

Substrate	Mechanism	$k_2$ (25°C) (M <sup>-1</sup> sec. <sup>-1</sup> )	$\Delta H^\ddagger$ (kcal.mole <sup>-1</sup> )	$\Delta S^\ddagger$ (cal.deg. <sup>-1</sup> mole <sup>-1</sup> )
$\alpha$ -methylallyl chloride	S <sub>N</sub> 2	2.87x10 <sup>-6</sup>	20.8	-13.9
$\alpha$ -methylallyl chloride	S <sub>N</sub> 2'	1.33x10 <sup>-8</sup>	24.2	-13.4
$\gamma$ -methylallyl chloride	S <sub>N</sub> 2	3.15x10 <sup>-4</sup>	18.8	-11.6
$\gamma$ -methylallyl chloride	S <sub>N</sub> 2'	5.31x10 <sup>-9</sup>	24.3	-14.9
$\alpha$ -methylallyl bromide	S <sub>N</sub> 2	8.79x10 <sup>-4</sup>	15.9	-19.1
$\alpha$ -methylallyl bromide	S <sub>N</sub> 2'	1.49x10 <sup>-5</sup>	18.8	-17.7
$\gamma$ -methylallyl bromide	S <sub>N</sub> 2	1.41x10 <sup>-1</sup>	14.1	-15.0
$\alpha$ -methylallyl chloride	S <sub>N</sub> 2	2.30x10 <sup>-7</sup>	19.9	-22.1
$\gamma$ -methylallyl chloride	S <sub>N</sub> 2	2.88x10 <sup>-5</sup>	15.8	-26.2

A comparison of the kinetic data for the isotope exchange reactions of the methylallyl chlorides in acetonitrile and acetone is also made. England and Hughes' data for the latter solvent is shown above.

Relative rates of nucleophilic attack at saturated carbon,  $\pi$ -bonded carbon and hydrogen are discussed for these substrates, a minor concurrent elimination reaction accompanying the S<sub>N</sub>2' reaction of  $\alpha$ -methylallyl chloride in acetonitrile providing information on the latter.

The nucleophilic reactivity of the halide ions is much greater for attack at a saturated carbon atom than for attack at a  $\pi$ -bonded carbon atom, while towards hydrogen these ions are very weak nucleophiles

as shown by the rate ratios given below for the chloride ion catalysed reactions of  $\alpha$ -methylallyl chloride in acetonitrile.

$$\frac{k_2(S_N2)}{k_2(S_N2')} = 67(100^\circ\text{C}) \quad \frac{k_2(S_N2')}{k_2(E2)} \sim 12(96^\circ\text{C}) \quad \frac{k_2(S_N2)}{k_2(E2)} \sim 875(96^\circ\text{C})$$

In the absence of chloride ions a slow surface-catalysed elimination reaction takes place which promotes hydrogen chloride catalysed rearrangement. The addition of 0.05M  $\text{Et}_4\text{NCl}$  prevents the latter reaction from occurring and gives a rate ratio of 5.5 for the chloride ion catalysed and surface-catalysed elimination reactions.

By comparison with other dipolar aprotic solvents, acetonitrile appears to be particularly suitable for slow reactions requiring prolonged reaction times at elevated temperatures. Acetone, as mentioned above, and both dimethyl sulphoxide and dimethylformamide were found to be unsuitable for  $S_N2'$  studies, the latter two being investigated during the search for a suitable solvent in which to study the reactions of the methylallyl chlorides.

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# SYMBOLS USED IN THE TEXT

- $k_1'$  = the composite first-order or pseudo-first-order rate constant for rearrangement, the former being for uncatalysed rearrangement and the latter for catalysed.
- $k_2'$  = the composite second-order rate constant for rearrangement.  
 $= k_2'^{\alpha} + k_2'^{\gamma}$
- $k_2'^{\alpha}$  = the second-order rate constant for rearrangement of  $\alpha$ -methylallyl chloride.
- $k_2'^{\gamma}$  = the second-order rate constant for rearrangement of  $\gamma$ -methylallyl chloride.
- $k_1^E$  = the rate constant for uncatalysed elimination.
- $k_1^E(\text{obs.})$  = the pseudo-first-order rate constant for the overall elimination reaction.
- $k_2^E$  = the rate constant for catalysed elimination.
- $k_2^{\alpha}$  = the second-order rate constant for the isotope exchange reaction of  $\alpha$ -methylallyl chloride.
- $k_2^{\gamma}$  = the second-order rate constant for the isotope exchange reaction of  $\gamma$ -methylallyl chloride.
- $K(\text{eq.})$  = the equilibrium constant for the rearrangement reaction.
- $K(\text{cal.})$  = the calibration constant of the GLC's detector.

SYMBOLS USED IN THE TEXT (cont.)

GLC = gas-liquid chromatography or chromatograph.

v.p.c. = vapour phase chromatography.

$\left| \frac{\alpha}{\gamma} \right|$  = the peak area ratio of  $\alpha$ -methylallyl chloride to  
 $\gamma$ -methylallyl chloride on v.p.c. chromatograms.

$\alpha$ -( $\gamma$ -)MAC =  $\alpha$ -( $\gamma$ -)methylallyl chloride.

But. = butadiene.

AN = acetonitrile.

$\chi_R$  see Appendix II.

CHAPTER IINTRODUCTIONSOLVENT EFFECTS, SOLVENT CLASSIFICATIONAND NUCLEOPHILIC SUBSTITUTIONI Solvent Effects and Solvent Classification(1) The Hughes-Ingold Theory

Hughes, Ingold and co-workers were largely responsible for creating from the data of early organic chemistry and from extensive investigations of their own, a theory of organic chemistry based on a fundamental understanding of the nature of the atom and chemical bonding. Chemical reactions were divided into types, reagents were classified, mechanisms were postulated or clarified and the effect on rates and mechanism, of varying different parameters, was investigated.<sup>1</sup>

Much of their experimental work involved the use of the solvents ethanol, methanol, formic acid, acetone and aqueous mixtures of these. For example, the alcohols, or alcohol-water mixtures, were the usual solvent employed for studies of nucleophilic aliphatic substitution reactions with the anions phenoxide, hydroxide and

alkoxide, while for halide ion exchange reactions, acetone was often used.<sup>2</sup>

Their theory of solvent effects on nucleophilic substitution and olefin-forming elimination reactions of various charge types, which states that "a change to a more polar solvent will decrease or increase the enthalpy of activation according to whether the transition state is more or less polar than the initial state", (where solvent polarity is correlated with the molecular dipole moment of the solvent and the shielding of the dipole charges), derives most of its experimental support from data in alcohol-water mixtures.<sup>3</sup>

In common with attempts to relate the effect of solvent changes on ion-ion or ion-molecule reactions to the dielectric constant of the solvent,<sup>4</sup> this theory ignores specific solute-solvent interactions such as hydrogen bonding, and also entropy effects.<sup>5</sup>

The limited success of such theories, which hold for very restricted sets of data, has been superseded by other treatments.<sup>4,6</sup>

#### (ii) Linear Free-Energy Relationships

Linear free-energy relationships such as the Grunwald-Winstein equation:<sup>7</sup>

$$\log \frac{k}{k_0} = mY$$

where Y represents the capacity of the solvent to facilitate ionisation of a covalent halide, (and which uses t-butyl chloride at 25°C in 80%

ethanol-water as reference reaction and is extended to non-hydroxylic solvents using *p*-methoxyneophyl toluene-*p*-sulphonate),<sup>8</sup> have considerable success in correlating, for example, solvolysis rates, while at the same time indicating specific interactions and differing mechanisms.<sup>6</sup>

### (iii) Spectral Relationships

An easily obtainable measure of solvent ionising power has been proposed by Kosower.<sup>10</sup> A parameter *Z*, based on the transition energy derived from the c.-t. band position in the spectrum of 1-ethyl-4-carbomethoxypyridinium iodide, is dependent upon the solvation of the ground state of the compound. Correlation with *Y* values is good and measurements can be made in both hydroxylic and non-hydroxylic solvents.<sup>8,10</sup>

In ion-molecule reactions, neglect of solvent effects on anion nucleophilicity, ion-pairing and the nature of the nucleophile (e.g., proton transfer with the solvent), has added to the confusion caused by ignoring specific solute-solvent interactions.<sup>12,13,14</sup>

### (iv) Hydrogen-Bonding Solvation and Solvent Classification

It was however the review by Parker of dipolar aprotic solvents which focussed attention on the very different effects of the solvents commonly used for kinetic studies, due to their capacity or incapacity

to participate in certain specific solvent-solute interactions.<sup>15</sup>

Thus, considering the following two groups of solvents:

<u>Group I</u>		<u>Group II</u>	
<u>Solvent</u>	<u>D<sup>16</sup></u>	<u>Solvent</u>	<u>D<sup>16</sup></u>
H <sub>2</sub> O	78.3	DMSO	46.7
MeOH	32.6	DMF	36.7
EtOH	24.3	MeCN	36.7
ROH/H <sub>2</sub> O	-	PhNO <sub>2</sub>	34.8
		Me <sub>2</sub> CO	20.7

(D = dielectric constant)

transfer of an ion-molecule reaction from a solvent in Group I to one in Group II of similar dielectric constant can produce a 10<sup>5</sup>-fold increase in rate<sup>17</sup> and a reversal of nucleophilicity order,<sup>13</sup> while transfer of an ion-forming reaction may cause a large change in the position of equilibrium.<sup>17</sup> The effects on electrolyte and non-electrolyte solubility, acid-base properties, spectra and conductance can also be dramatic.<sup>19</sup>

Therefore, the knowledge that macroscopic solvent properties are inadequate for relating observed behaviour and that specific solute-solvent interactions must be considered, has resulted in the separation of polar solvents into two groups, where polar applies to those solvents which have a dielectric constant greater than 15. Group I comprises those solvents which have hydrogen atoms which they

can donate to form strong hydrogen bonds, i.e., protic solvents such as methanol and Group II comprises those solvents which do not have suitable hydrogen atoms, i.e., dipolar aprotic solvents such as dimethylformamide.<sup>20</sup>

There are four kinds of strong solvent-solute interaction: ion-dipole, dipole-dipole,  $\pi$ -complex-forming and hydrogen-bonding. Parker has shown, that it is the difference in anion solvation in the two groups, which is mainly responsible for the enormous differences in solute behaviour. While anion solvation in protic solvents is due to hydrogen bonding, greatest for small ions, superimposed on ion-dipole interactions, anion solvation in dipolar aprotic solvents is due to the latter with a superimposed mutual polarisability interaction, which is greatest for large ions.<sup>20</sup>

Whereas behaviour in various members of a group, or binary mixtures of solvents from the same group, is similar, behaviour in binary mixtures consisting of one member from each group can be dependent upon specific interactions between one member and solutes, which make interpretation impossible without considering these interactions.<sup>21,22,23</sup>

(v) The Effect of Hydrogen-Bonding Solvation on the Behaviour of Solutes

Data on the degree of cation and anion solvation comes from solubility measurements, polarography, spectroscopy, conductance measurements and dissociation constants.<sup>24</sup>

For example, the solubility of electrolytes depends on the solvation energy of the ions, and, while cations tend to be well solvated in dipolar aprotic solvents having a negative charge located on a bare oxygen atom (e.g., dimethyl sulphoxide) anions tend to be poorly solvated with solvation increasing with anion size, so that salts of small anions such as chloride have a lower solubility in these solvents relative to protic solvents, which increases with increasing anion size. Chlorides tend to be weak electrolytes in dipolar aprotic solvents, while iodides are much stronger. In protic solvents the dissociation constants are similar.<sup>25</sup>

Further evidence for the poor solvation of anions in the absence of hydrogen bonding comes from the dissociation constants of acids. The hydrogen halides are weak acids in most dipolar aprotic solvents and have the strength order:



this being the reverse of that in protic solvents, which level acid strength. Many acids hydrogen bond to solvent molecules or their conjugate base.<sup>26</sup>

(vi) The Effect of Hydrogen-Bonding Solvation on Reaction Rates and Mechanism

However, it is in the field of reaction kinetics that recognition of the importance of hydrogen-bonding solvation has proved most fruitful.

The reactivity of an anion towards hydrogen is very much greater in dipolar aprotic solvents than in protic, due to the absence of hydrogen-bonding stabilisation. For example, methoxide catalysed H-D exchange is  $10^9$  times faster in dimethyl sulphoxide than in methanol, at carbon  $\alpha$  to CN, CO.NR<sub>2</sub> and CO<sub>2</sub>R.<sup>27</sup> Similarly, halide ions, conventionally regarded as very poor eliminating agents in protic solvents, are, as far as the limited data available can reveal, good eliminating agents for olefin formation, especially if the acid produced is prevented from back adding by either self-scavenging or added weak base scavenging.<sup>28,29,30</sup>

The protic to dipolar aprotic solvent change for S<sub>N</sub>2 and S<sub>N</sub>Ar reactions involving anionic nucleophiles can cause an increase in reaction rate of the order of  $10^5$  times. The change in rate is greatest for small anions of low polarisability.<sup>17</sup>

Miller and Parker have attributed this enormous change in the reactivity of small anions to the removal of hydrogen-bonding stabilisation, and to possible steric hindrance to solvation of small anions in dipolar aprotic solvents.<sup>32</sup> They consider that the bulky solvent dipoles may not be able to fit closely round a small anion but may fit much better round a large, polarisable one, so that the solvent can be envisaged as having holes in which a small anion is poorly solvated and a large anion better solvated. Thus, not only is the change in stabilisation greatest for small anions, but also, large, polarisable transition states should be well solvated, so there is the possibility that these are more stabilised in dipolar aprotic than in

protic solvents, resulting in the enthalpy of activation being lowered both by destabilisation of the anion and stabilisation of the transition state.

In a recent series of papers, Parker and co-workers have attempted to put the theory of hydrogen-bonding solvation on a semi-quantitative basis, utilising hydrogen-bonding activity coefficients for anions and transition states derived mainly from comparative rate studies in solvent members from the two groups.<sup>33a-e</sup>

The effects of solvent group change on the rates of reactions not involving anions are much smaller, but the equilibrium position may be greatly altered. Again, these effects can be explained in terms of hydrogen-bonding solvation.<sup>34</sup>

Dipolar aprotic solvents do not solvate anions, especially small anions, effectively, so that  $S_N1$  reactions are less promoted by these solvents than by protic solvents of comparable dielectric constant. The effect of the absence of hydrogen-bonding solvation is reflected in the "Y values" for these solvents.<sup>8</sup>

#### (vii) The Effect of Hydrogen-Bonding Solvation on Nucleophilicity

The vexed problem of nucleophilicity, reviewed recently by Bunnett,<sup>12</sup> requires careful consideration of hydrogen-bonding solvation. A nucleophilicity order towards carbon of  $CN^- > I^- > SCN^- > N_3^- > Br^- > Cl^-$ , based on Swain and Scott's nucleophilic constants,<sup>36</sup> is sometimes quoted for some substrates in protic solvents,<sup>12,37</sup> while

for some substrates in dipolar aprotic solvents, an order of  $\text{Cl}^- > \text{Br}^- > \text{I}^-$  has been observed.<sup>13,37,21</sup> Therefore, a correlation with "polarisability" in one solvent group could be due to a correlation with "basicity" distorted by hydrogen-bonding solvation.

However, nucleophilicity is so dependent on external factors, one such being the solvent and others the type of carbon attacked and the displaced group, that these attempts to define reactivity orders are of very restricted validity.<sup>33b</sup>

The foregoing discussion has been an attempt to emphasize how profoundly the solvent chosen for a particular kinetic and mechanistic study can affect the rate and mechanism, due to its capacity or incapacity for certain specific interactions, which affect, for example, solvation of ions, molecules and transition states and ionisation and dissociation of solutes.

The work of Hughes, Ingold and co-workers for each reaction type, and that of subsequent workers, needs therefore to be considered in terms of solvent classification.

## II Mechanisms of Nucleophilic Substitution

The reaction types initially relevant to the present project were (a) nucleophilic substitution at saturated carbon, and (b) nucleophilic substitution with anionotropic rearrangement. Both of these types have been studied in a range of solvents drawn from the classes protic, dipolar aprotic and low polarity aprotic.

### (a) Nucleophilic Substitution at Saturated Carbon

There are two mechanisms of nucleophilic substitution at saturated carbon available to the majority of substrates. These are the  $S_N1$  and  $S_N2$  mechanisms, first proposed by Hughes and Ingold<sup>2</sup> and refined by subsequent workers.

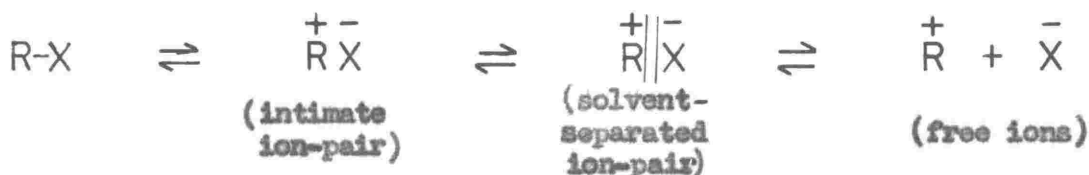
#### (1) The $S_N1$ Mechanism

The  $S_N1$  mechanism involves rate-determining heterolysis of a substrate to form a carbonium ion, which rapidly reacts with available nucleophiles to form the products.



While the concept of a "free" carbonium ion may be adequate to describe behaviour in protic solvents of fairly high dielectric constant, reactions in low polarity protic solvents and members of the other

solvent classes require the use of more subtle concepts. Thus the ionisation-dissociation scheme of Winstein and co-workers, which involves a sequence of ion-pairs culminating in the free carbonium ion:



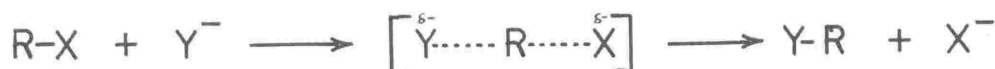
has had considerable success in interpreting salt effects in solvolysis reactions and substitution reactions in which the rate of stereochemical change is greater than that of substitution.<sup>42a,b</sup>

Hughes, Ingold and co-workers have postulated a quadrupole intermediate for halide exchange reactions in benzene.<sup>43</sup>

If the rate of reversal of the heterolysis is much greater than the rate of reaction with other nucleophiles, then the rate-determining step becomes the bimolecular attack of a nucleophile on the carbonium ion and the mechanism is designated  $\text{S}_{\text{N}}2\text{C}^{+}$ .<sup>44,45</sup>

#### (11) The $\text{S}_{\text{N}}2$ Mechanism

The  $\text{S}_{\text{N}}2$  mechanism involves concerted attack by the nucleophile and departure of the leaving group.



This mechanism has been developed in terms of a transition state in which bond-making and bond-breaking are not necessarily equally far advanced and in which the relative extents of these processes are widely different for various reactions and reaction conditions.<sup>46</sup>

The use of linear free-energy relationships and kinetic isotope effects to probe transition state character is yielding valuable information.<sup>46,47,48,49,50,51</sup>

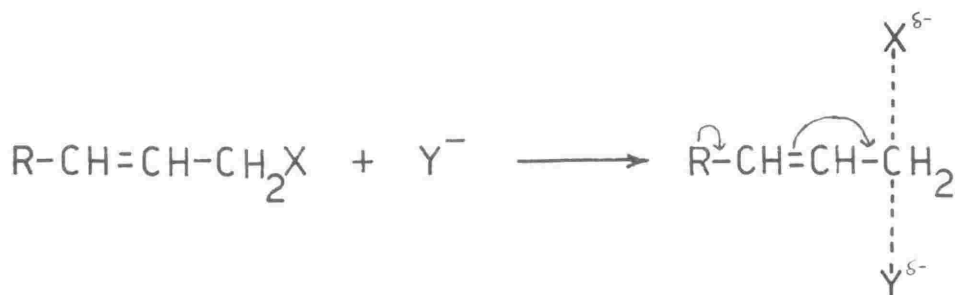
The S<sub>N</sub>2 mechanism is more favoured by dipolar aprotic solvents, than it is by protic, because of their lesser ability to promote ionisation.<sup>8,52</sup>

#### (iii) The S<sub>N</sub>2 and S<sub>N</sub>1 Reactivity of Allylic Compounds

An allylic compound, i.e., one having a vinylic substituent on the saturated α-carbon atom, or the basic structure  $\text{>C=C-}\overset{\cdot}{\underset{\cdot}{\text{C}}}\text{-X}$ , differs from its alkyl analogue in being considerably more reactive in nucleophilic substitution reactions proceeding by either the S<sub>N</sub>1 or the S<sub>N</sub>2 mechanism.<sup>54</sup> Correlation of γ-carbon substituent effects by a Hammett-type plot is not good, but the effects on S<sub>N</sub>2 reactivity

are closely similar to, though smaller than, those on  $S_N1$ .<sup>54</sup>  
 The facilitating effects of  $\alpha$ -alkyl substituents follow the  
 hyperconjugation order  $Me > Et > Bu^t > H$ .<sup>55</sup>

Therefore, the transition states for reactions of allylic  
 compounds proceeding by both the  $S_N1$  and  $S_N2$  mechanisms are considered  
 to be stabilised by conjugative and hyperconjugative electron release.  
 In the case of the  $S_N2$  mechanism, facilitation of the bond-breaking  
 process takes precedence over the electronic requirements for  
 facilitating bond-making.<sup>55</sup> e.g.



(b) Nucleophilic Substitution with Rearrangement in Allylic Compounds

Nucleophilic substitution with three-carbon anionotropic  
 rearrangement is an additional mode of reaction available to allylic  
 compounds, which differentiates them from their saturated analogues.

(1) The  $S_N1'$  and  $S_Ni'$  Mechanisms

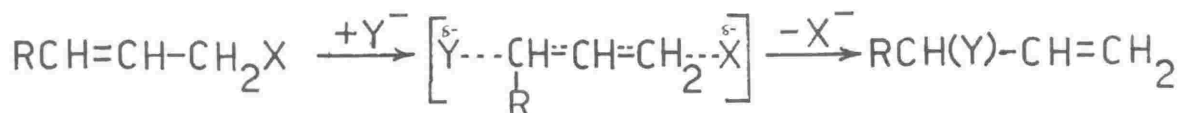
The carbonium ion intermediate of the  $S_N1$  mechanism can be  
 regarded as a resonance hybrid of the two structures:<sup>56</sup>



concept of a concerted cyclic mechanism with bond-breaking and making equally far advanced in the transition state (although hypothetical), for placing a reaction, according to the degree of bond-breaking in the transition state, along a carbonium ion-cyclic continuum of transition states.<sup>51</sup> The rearrangement of allylic thionbenzoates apparently involves a transition state of very low polarity.<sup>60</sup>

#### (ii) The S<sub>N</sub>2' Mechanism

The possibility of anionotropic rearrangement by a bimolecular mechanism, analogous to the S<sub>N</sub>2 mechanism, was postulated independently by Hughes and Winstein in 1938.<sup>63,64</sup> This mechanism is designated S<sub>N</sub>2' and it may be formulated as follows:



#### (iii) Demonstrations of the Operation of the S<sub>N</sub>2' Mechanism Prior to 1956

Early attempts to establish examples of the mechanism were fruitless, e.g., ethoxide ion in ethanol gave only the normal product with α-methylallyl chloride.<sup>65</sup>

In 1942, Roberts, Young and Winstein studied the reactions of the above substrate with ethoxide and acetate anions, and also obtained only normal products.<sup>66</sup>

Meisenheimer and Link (1930) were the first to obtain rearranged products from the reaction of an amine with an allylic halide.<sup>67</sup>

In 1944, Webb obtained only the rearranged product from  $\alpha$ -methylallyl chloride and diethylamine,<sup>68</sup> and in 1945, Kepner, Young and Winstein found that both  $\alpha$ -methyl and  $\alpha$ -ethylallyl chloride, with the diethyl-malonate ion in ethanol, gave some rearranged product - 10% and 23% respectively.<sup>69</sup> The reaction was shown to be second-order.

Jones, Lacey and Smith, in 1946, obtained abnormal products from the reaction of diethylamine with  $R-C\equiv C-CH=CH-CH(Cl)CH_3$ .<sup>70</sup>

In 1948, the reaction of  $\alpha$ -phenylallyl *p*-nitrobenzoate, with the lithium salt in acetonitrile and acetic anhydride, was shown to fit the  $S_N1'$  mechanism, while preliminary work with  $\alpha$ -methylallyl bromide and lithium bromide in acetone, indicated an exchange to rearrangement rate ratio of the order of  $10^2$ .<sup>71,72</sup>

At this stage, Hughes and Ingold considered reaction by the  $S_N2'$  mechanism to be too slow to be important experimentally.<sup>73</sup>

However, in 1949, Winstein, Kepner and Young took the view that the rearranged products obtained with amines were significant and in 1951, Young, Webb and Goering found that  $\alpha$ -methylallyl chloride gave rearranged product with diethylamine in benzene and followed kinetics which were in accord with an  $S_N2'$  mechanism.<sup>69,75</sup> The former authors considered preliminary hydrogen bonding could aid the operation of the mechanism,<sup>69</sup> but it was argued by the London group that such a mechanism more resembled an  $S_N1'$  than an  $S_N2'$  mechanism.<sup>76a,b</sup>

The demonstration<sup>69</sup> of the formation of rearranged products in a second-order reaction with the diethylmalonate ion was considered ambiguous, because the rearranged products could result from attack on the  $\alpha$ -carbon atom by nucleophilic oxygen and subsequent rearrangement.<sup>77,78</sup>

In 1951, England and Hughes published their work on the reactions of  $\alpha$ - and  $\gamma$ -methylallyl bromide with lithium bromide in acetone,<sup>76b,79</sup> showing, under relatively unambiguous conditions, (a) that the mechanism was realisable, and (b) that it could not compete to a significant extent with the  $S_N2$  mechanism for either of these halides, but that the rate ratio for the secondary halide favoured the  $S_N2'$  mechanism far more than did that for the primary halide. This work was of considerable value in indicating the conditions necessary to promote the operation of the  $S_N2'$  mechanism. Consequently, between 1951 and 1954, de la Mare and Vernon published results for the sterically hindered compounds 3,3-dichloropropene, 3,3,3-trichloro-2-methylpropene and 1,1-dimethylallyl chloride reacting with thiophenoxide, phenoxide and ethoxide ions in ethanol.<sup>80a-c</sup> The latter two compounds gave the rearranged product almost exclusively, while the first gave a mixture of the normal and abnormal products.

It was also shown, between 1951 and 1956, that preliminary hydrogen bonding is not necessary for the operation of the mechanism in reactions using amines as nucleophiles. Thus,  $\alpha$ -methylallyl chloride with trimethylamine in acetone gave 70% of the rearranged product in a second-order process,<sup>81a,b</sup> while even allyl chloride gave 7% with trimethylamine in benzene.<sup>82</sup>

The operation of the mechanism in cyclohexenyl compounds was demonstrated by Stork and White in 1953, in the reactions of trans-6-alkyl-2-cyclohexen-1-yl 2,6-dichlorobenzoates with piperidine, in xylene or the amine as solvent.<sup>83</sup> Only trans products were obtained, in accordance with the cis relationship of entering and leaving groups postulated by Young, Webb and Coering in 1951.<sup>75</sup>

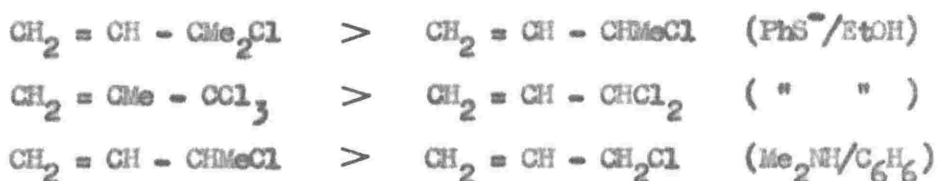
A number of other reactions, not investigated kinetically, which give rearranged products and thus may also utilise the  $S_N2'$  mechanism, have been enumerated by De Wolfe and Young in their review.<sup>85</sup>

#### (iv) Factors Influencing the Operation of the $S_N2'$ Mechanism

Up to 1956, knowledge about the effect of various factors on the operation of the  $S_N2'$  mechanism was confined to that outlined in the following discussion.

(1) Substituents on the  $\alpha$ -carbon atom, by sterically hindering attack by the  $S_N2$  mechanism, allow the  $S_N2'$  mechanism to assume prominence.<sup>80a-c</sup> Thus, while primary halides, except in special circumstances,<sup>79,82</sup> undergo only  $S_N2$  attack, secondary halides may give a mixture of products and tertiary halides give almost exclusive rearrangement. It was suggested, that chlorine substituents on the  $\alpha$ -carbon atom activated the  $\gamma$ -carbon atom for nucleophilic attack, by inductively shifting the  $\pi$ -electron cloud of the double bond away from it.<sup>86</sup>

(2) Electron-releasing substituents, which can release electrons to the  $\alpha$ -carbon atom by either the inductive or mesomeric mechanism, were considered to increase the rate of reaction by the  $S_N2'$  mechanism by stabilising the transition state, as for  $S_N2$  reactions.<sup>87</sup> For example, the following rate orders were observed:<sup>87</sup>



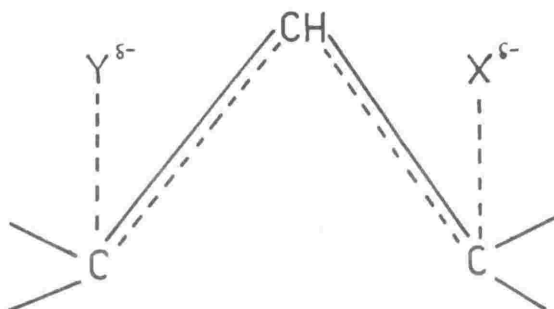
(3) The nature of the nucleophile has a considerable effect on the  $S_N2:S_N2'$  product ratio, with uncharged nucleophiles such as amines being considerably less discriminating than anionic nucleophiles in their position of attack.<sup>88</sup>

Amines capable of hydrogen bonding seemed more effective than tertiary amines in promoting rearrangement,<sup>82</sup> and it was also suggested that anionic nucleophiles in which the charge is delocalised (e.g., the diethyl malonate ion) may be more effective than other anions.<sup>88</sup>

For anionic nucleophiles, the rate of reaction by both the  $S_N2$  and  $S_N2'$  mechanisms appeared to be more dependent on the nucleophile than did the product ratio. Thus, 3,3-dichloropropene with ethoxide, phenoxide and thiophenoxide ions in ethanol gave approximately the same product ratio, while the overall rate constant for the reactions with the thiophenoxide ion was about 260 times greater than that for the other two.<sup>80b,c</sup>

Electrostatic facilitation of leaving group departure by anionic attack at the  $\alpha$ -carbon atom,<sup>88</sup> and electrostatic repulsion between the entering and leaving groups in the cis transition state for the  $S_N2'$  reaction with anionic nucleophiles,<sup>75</sup> were suggested to explain the less discriminating attack by uncharged nucleophiles.

(4) The cis transition state postulated by Young, Webb and Goering, mentioned above:



in which the electrons being transferred to the  $\alpha$ -carbon atom enter from the opposite side to that from which the leaving group is departing, was considered to best satisfy the electronic requirements of the  $\alpha$ -carbon atom.<sup>75</sup>

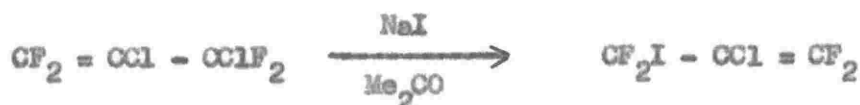
(5) From the small amount of data on solvent effects, it appeared that the Hughes-Ingold theory for ion-neutral substrate charge-type reactions was not valid. For example, 3,3-dichloropropene and 3,3,3-trichloro-2-methyl-1-propene react more than twice as fast with thiophenoxide ions in 75% ethanol-water than they do in 100%

ethanol.<sup>92a</sup> This is similar to the behaviour of the  $S_N2$  reactions of allylic halides, which frequently contradicts the above theory.<sup>92a,b</sup>

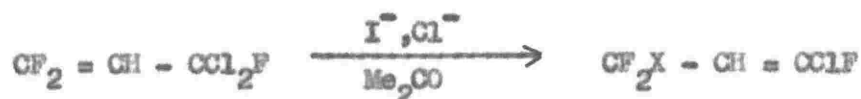
(v) Progress Since 1955

Progress since 1955 involving further demonstrations of the operation of the  $S_N2'$  mechanism, the effect of various factors on the operation of the mechanism and the nature of the transition state is outlined in the following pages, but not necessarily in chronological order.

Fried and Miller (1959) confirmed their suspicions that perhalo compounds react with halide ions by the  $S_N2'$  mechanism, e.g.



by studying compounds which do not give identical products by both the  $S_N2$  and  $S_N2'$  mechanisms, e.g.



and found that these gave rearranged products exclusively.<sup>93</sup>

A qualitative estimation of nucleophilicity order was made from reaction conditions using a variety of salts and solvents, but was later confirmed for the tetraethylammonium salts in chloroform.<sup>94</sup> The order obtained was  $\text{F}^- > \text{Cl}^- > \text{I}^-$ .

An interesting observation was the inertness of compounds with two chlorine substituents, or one chlorine and one fluorine substituent, on the  $\gamma$ -carbon atom, as opposed to two fluorine substituents.

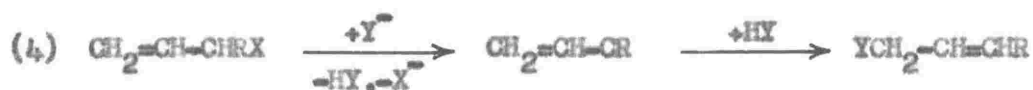
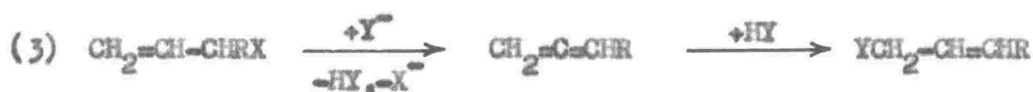
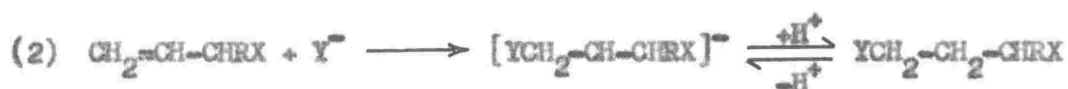
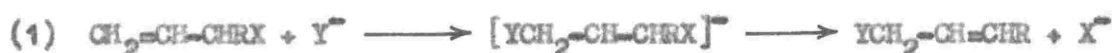
In 1958, de la Mare, Vernon and co-workers showed that 1-tert.-butylallyl chloride with ethoxide ions in ethanol gives essentially exclusive rearrangement.<sup>95</sup>

A reactivity order by the  $S_N2'$  mechanism of:



could be deduced from data on the reactions of the above substrates with ethoxide or thiophenoxide ions in ethanol.<sup>96</sup> Two opposing polar effects of substituents operate in members of this series of sterically hindered compounds, (a) hyperconjugative electron release for the  $\alpha$ -alkyl substituted compounds, and (b) inductive electron withdrawal for the  $\alpha$ -halogen substituted ones. It appears therefore that facilitation of the bond-breaking process by effect (a), or facilitation of the attack of the nucleophile by effect (b), (attributed to polarisation of the  $\pi$ -bond electron cloud), promotes the operation of the  $S_N2'$  mechanism, the  $S_N2$  mechanism being retarded by steric hindrance to bond-making for both types of substituents and also by polar hindrance to bond-breaking for the halogen substituents.<sup>96</sup> Thus the operation of the mechanism in poly-halogenated compounds is not unexpected.

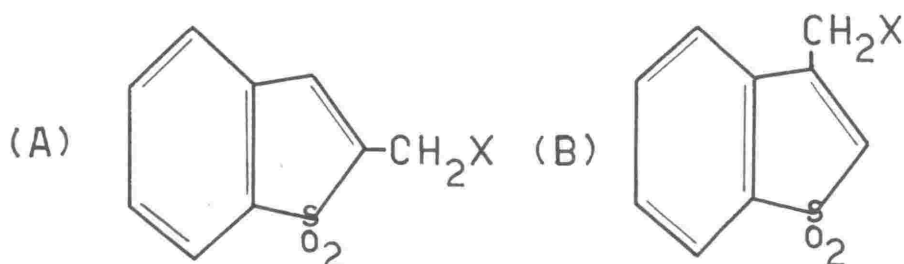
De la Mare<sup>97</sup> has suggested some other possible base-catalysed modes of anisotropic rearrangement:



His view is that, as these mechanisms could fulfil the conditions stated by De Wolfe and Young as having to be met before a reaction can be designated  $\text{S}_{\text{N}}2'$ ,<sup>98</sup> these conditions are not an unambiguous criterion of mechanism.

Little is known about such reactions, but, for carbanion formation followed by expulsion of a terminal substituent, which is analogous to the mechanism of attack on suitably activated ethylenic derivatives,<sup>99</sup> the work of Bordwell and co-workers<sup>100,100a</sup> is relevant (1960).

They found that compound (A) reacts with piperidine, thiourea and thiophenoxide ions to give only normal products, while compound (B) gives only rearranged products.



By varying the leaving group ( $X = \text{Cl}, \text{Br}, \text{I}$ ) and comparing the rate of reaction of these compounds,  $\text{ArSO}_2\text{CH}=\text{CH}-\text{CH}_2\text{X}$ ,  $\text{CH}_2=\text{CH}-\text{CH}_2\text{X}$  and  $\text{CH}_3-\text{CH}_2-\text{CH}_2\text{X}$  with thiourea in methanol, they showed that the effect of varying the leaving group was large and similar for all types of compound, irrespective of the mechanism. This was considered proof against an addition-elimination type mechanism, and for a concerted mechanism in general for the  $\text{S}_{\text{N}}2'$  process, as the  $\text{ArSO}_2-$  group is strongly electron withdrawing.

The work of Fry (1964) is in accord with concerted bond-making and bond-breaking rather than a carbanion-type mechanism, as he observed kinetic isotope effects for chlorine and successive carbon-14 labelling of the  $\text{C}_1$ ,  $\text{C}_2$  and  $\text{C}_3$  carbon atoms in the reaction of  $\alpha$ -methylallyl chloride with diethylamine, which indicated that bonding changes were taking place at all positions.<sup>50</sup>

Thiourea and substituted thioureas in acetone, like thiophenoxide ions in ethanol, react with 1,1-dimethylallyl chloride by the  $\text{S}_{\text{N}}2'$  mechanism (1957).<sup>41</sup>

Dittmer and Marcantonio have investigated the theory that hydrogen bonding between secondary amines and allylic halides assists the operation of the  $S_N2'$  mechanism, by using N-deuterated amines.<sup>102a,b</sup> Only with N-methylaniline-N-d and  $\alpha$ -methylallyl chloride in n-heptane was an isotope effect observed and it was in the third-order term of a mixed-order kinetic expression, of which a second-order term was attributed to the  $S_N2'$  mechanism and the third-order term to an  $S_N2C+$  mechanism. The isotope effect was considered to arise from electrophilic catalysis of the ionisation step by a molecule of the amine.

The absence of an isotope effect in these  $S_N2'$  reactions does not necessarily mean that hydrogen-bonding assistance to leaving group departure is unimportant.<sup>103</sup>

The promotion of the  $S_N2'$  mechanism at the expense of other mechanisms by secondary amines compared with tertiary (demonstrated with  $\alpha$ -methylallyl chloride and allyl chloride)<sup>81b,82</sup> gains another example in the work of Cignarella, Testa and co-workers (1964).<sup>105</sup> They found that secondary amines, in acetone, ethanol, carbon tetrachloride or the absence of additional solvent, gave with  $\alpha$ -(p-nitrophenyl)-allyl chloride, products consistent with the operation of the  $S_N2'$  and  $B-S_E1'$  mechanisms of rearrangement. No  $S_N2'$  product was obtained with a tertiary amine.

Although prototropic rearrangements in allylic systems which undergo anionotropic rearrangements are quite possible, because of the inductive electron-withdrawing effects of many substituents,<sup>106</sup> they are

not common and the above is reported to be the first example in an  $\alpha$ -substituted allylic halide. (e.g., 3,3-dichloro-1-propene, when reacted with ethoxide ions in ethanol, shows no significant rearrangement to 1,1-dichloro-1-propene).<sup>80b</sup>

The stereochemical course for the  $S_N2'$  mechanism, involving the cis relationship of entering and leaving groups, found further support in additional work by Stork and White (1956).<sup>108</sup>

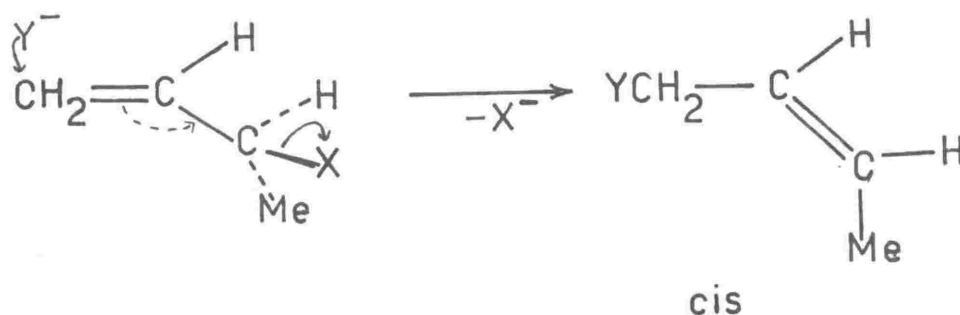
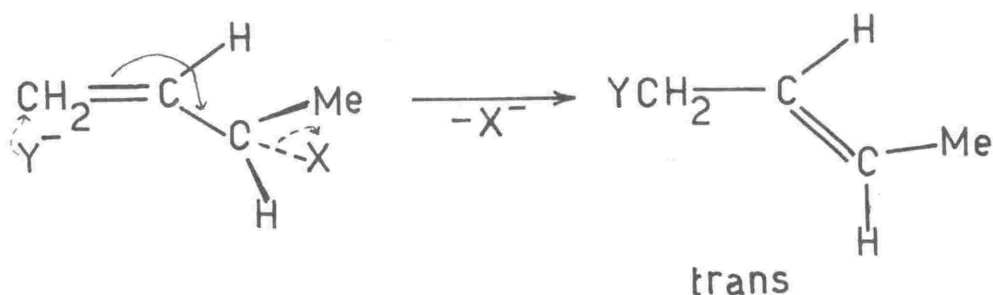
The trans-6-alkyl-2-cyclohexen-1-yl 2,6-dichlorobenzoates with piperidine in *m*-xylene and sodium di-*n*-butyl malonate in *n*-butyl alcohol gave, as far as could be ascertained, exclusively  $S_N2'$  products with  $R = \text{Me}$ ,  $\text{Me}_2\text{CH}$  and  $\text{Me}_3\text{C}$  except, significantly, for the methyl compound and the malonic ester anion, which gave  $S_N2$ . The kinetics were shown to be second-order and the trans product was obtained from all the  $S_N2'$  reactions.  $\alpha$ - and  $\beta$ -Chlorocodide have also been shown to react by a cis  $S_N2'$  mechanism.<sup>109</sup>

Application of the "frontier electron theory" of Fukui,<sup>110</sup> to the stereochemistry of  $S_N2'$  reactions, has predicted the cis relationship of entering and leaving groups for an allylic system, a trans relationship for a system of two conjugated double bonds and alternate cis and trans for still longer chains.<sup>111</sup> Little mechanistic work has been done on extended conjugated systems.

The work of Bordwell and co-workers (mentioned earlier) provides some information about the structure of the transition state in the reactions of allyl compounds.<sup>100a</sup>

The geometry of the chloromethylbenzothiophene 1,1-dioxide structure allows  $S_N2$  substitution only in conformations in which the axis of the carbon-halogen bond is parallel to the  $\pi$ -bond orbitals, i.e., in conformations suiting the stereochemical requirements for  $S_N2'$  attack. The absence of any appreciable differences between  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  for this and less demanding systems was considered to show that this transition state geometry is general for allyl halides. Such a transition state geometry should also be fairly insensitive to nucleophile bulk in  $S_N2'$  reactions and  $\gamma$ -substituents cis to the  $-\text{CH}_2\text{X}$  group in  $S_N2$  reactions.

The cis transition state of the  $S_N2'$  mechanism can be formed from either of the two conformations given below:



and therefore the product of the reaction is a mixture of the geometrical isomers in which the trans predominates, reflecting the difference in thermodynamic stability between the two isomers.<sup>81b,102a</sup>

Nesmeyanov and co-workers (1956) have reported some work with  $\gamma$ -substituted allylic halides of the type  $RR'C=CH-CCl_3$ .<sup>112</sup> The  $-CCl_3$  group is inert to nucleophilic attack so that reaction is confined to attack at the  $\gamma$ -carbon atom. Using the substituents  $R = H, H, Me, H$  and  $R' = Me, Ph, Me, t-Bu$  and the nucleophiles  $R_1ONa, Et_2NH, Na_2S$  in an alcohol, or in the absence of additional solvent where appropriate, it was qualitatively shown that the  $t-Bu$  group sterically hinders nucleophilic attack and that the capacity for O-alkylation, i.e., reaction with the solvent, increases to the exclusion of S- and N-alkylation along the series:



i.e., in the order of decreasing electrophilicity of the  $\gamma$ -carbon atom.

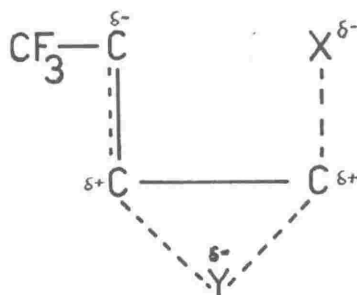
Andrac and Prevost (1964) allow the  $S_N2'$  and  $S_N1'$  mechanisms a negligible contribution to the mechanisms available for the reactions of allylic compounds, which they suggest to be the  $S_N1$ , the  $S_N2$  and a range of intermediate mechanisms involving considerable rupture of the bond to the departing group before interaction of the nucleophile with the positions of substitution occurs. Electrophilic assistance to the bond-breaking step is stressed.<sup>58</sup>

Their work on extended conjugated systems to refute the concerted cyclic six-centred ( $S_N1'$ ) mechanism, shows that attack is by no means confined to the  $C_3$  carbon atom, and may also occur at further positions along the chain.

(vi) Additional Knowledge About the  $S_N2$  Mechanism in Allylic Halides

Two further types of substituent effects on the  $S_N2$  reactions of allylic compounds are of interest.

In some reactions, an electron-withdrawing substituent such as  $CF_3$ - or  $ArSO_2$ - on the  $\beta$ - or  $\gamma$ -carbon atom facilitates bimolecular substitution. For example,  $\gamma$ -trifluoromethylallyl chloride is more reactive than  $\gamma$ -methylallyl chloride and allyl chloride with iodide ions in acetone, and 3-bromo-1-p-toluenesulphonyl-1-propene and 2-bromomethylbenzothiophene 1,1-dioxide are more reactive, with thiourea in methanol, than allyl bromide.<sup>100a,114</sup> These substituents are strongly electron withdrawing so stabilisation of the transition state by electron release to the  $\alpha$ -carbon atom cannot be invoked to explain their activating effect. In the former case the increased reactivity is attributed to facilitation of nucleophilic attack to form a transition state of the following type:



similar to that suggested for substitution in  $\alpha$ -halo ketones. In the latter case it is attributed to decreased carbon-halogen and  $\pi$ -bond repulsions and an increased extent of conjugation.

It also appears that the reaction of  $\alpha$ -trifluoromethylallyl *p*-bromobenzenesulphonate with iodide ions in acetone and azide ions in 70% acetone-water goes by the  $S_N2'$  mechanism.<sup>114</sup>



It has been observed by Hatch and co-workers that a  $\gamma$ -alkyl substituent cis to the chloromethyl group of an allylic chloride increases the reactivity, over that for the unsubstituted chloride, appreciably more than it does in the trans position.<sup>116</sup> The effect is considerably greater with iodide ions in acetone than with ethoxide ions in ethanol and applies to  $\gamma$ -Me, Et, *i*-Pr and *t*-Bu substituents. An inverse effect with ethoxide ions was obtained for the *t*-Bu group. A suggested explanation is that the enhanced reactivity is due to London interactions between the cis-alkyl group and the attacking nucleophile, which result in a reduction in the free energy of the transition state.<sup>117</sup>

Although the foregoing outline of the development of knowledge about the  $S_N2'$  mechanism is confined almost exclusively to allylic halides, which the majority of the published work involves, in general, the factors applicable to these have their parallels in the reactions of allylic esters and other compounds.

(vii) Classification of  $S_N2'$  Studies on the Basis of Substrate Type and Nucleophile Charge-Type


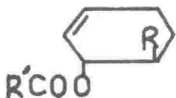
The reactions of allylic halides discussed in the preceding sections are tabulated below.

TABLE I

Group	Reaction	Solvent	Kinetic Order	% R	Ref. No.
C	$\text{CH}_2:\text{CH}.\text{CH}(\text{Et})\text{Cl}/\text{R}_2\text{NH}$	-	-	100	67
C	$\text{CH}_2:\text{CH}.\text{CH}(\text{Me})\text{Cl}/\text{Et}_2\text{NH}$	$\text{C}_6\text{H}_6$	second	100	75
C	$\text{CH}_2:\text{CH}.\text{CH}(\text{Me})\text{Cl}/\text{Et}_3\text{N}$	$\text{C}_6\text{H}_6$	-	100D	75
C	$\text{CH}_2:\text{CH}.\text{CH}(\text{Me})\text{Cl}/\text{Me}_3\text{N}$	$\text{Me}_2\text{CO}$	second	70	81b
C	$\text{CH}_2:\text{CH}.\text{CH}_2\text{Cl}/\text{Me}_3\text{N}$	$\text{C}_6\text{H}_6$	-	7	82
C	$\text{CH}_2:\text{CH}.\text{CH}_2\text{Cl}/\text{Me}_2\text{NH}$	$\text{C}_6\text{H}_6$	second	25	82
C	$\text{CH}_2:\text{CH}.\text{CH}(\text{Me})\text{Cl}/\text{PhNMe}$	$n\text{-C}_7\text{H}_{16}$	second + third	91	102b
C	$\text{CH}_2:\text{CH}.\text{CH}(\text{Me})\text{Cl}/\text{Et}_2\text{NH}$	$\text{C}_6\text{H}_6$	second	100	102a
C	$\text{CH}_2:\text{C}(\text{CH}_3)_2.\text{CH}(\text{Me})\text{Cl}/\text{Et}_2\text{NH}$	$\text{MeCN}$	second	$\sim 16$	118
C	$\text{CH}_2:\text{C}(\text{CH}_3)_2.\text{CH}(\text{Me})\text{Cl}/\text{EtNH}_2$	$\text{MeCN}$	second	0	118
D	$\text{CH}_2:\text{CH}.\text{CHCl}/$ <div style="display: inline-block; vertical-align: middle; text-align: center;">             (a) <math>i\text{-Pr}_2\text{NH}</math>            (b) <math>\text{Et}_3\text{N}</math>            (c) <math>\text{C}_5\text{H}_{11}\text{N}</math> </div>	$i\text{-Pr}_2\text{NH}$ $\text{Et}_3\text{N}$ $\text{C}_5\text{H}_{11}\text{N}$	- - -	15 0 > 15	105 " "
E	<div style="display: inline-block; vertical-align: middle; text-align: center;">   <math>\text{XCH}_2-\text{C}(\text{SO}_2)-</math> </div> / (a) $\text{C}_5\text{H}_{11}\text{N}$ (b) $\text{CS}(\text{NH}_2)_2$ (c) $\text{PhS}^-$	$\text{C}_5\text{H}_{11}\text{N}/\text{C}_6\text{H}_6$ $\text{MeOH}$ $\text{C}_6\text{H}_6/\text{EtOH}$	- second -	$\sim 100$ 100 100	100 100a 100
D	$\text{CH}_2:\text{CH}.\text{COOMe}_2/\text{CS}(\text{NH}_2)_2$	$\text{Me}_2\text{CO}$	second	100	41


/continued...

Table I continued

Group	Reaction	Solvent	Kinetic Order	% R	Ref. No.
E	 CH <sub>2</sub> Cl /MeO <sup>-</sup>	MeOH	second	40	191
A	RR'C:CH.CCl <sub>3</sub> / (a) Na <sub>2</sub> S	ROH	-	100	112
D	(b) Et <sub>2</sub> NH	ROH	-	100	"
D	(c) Et <sub>2</sub> NH	Et <sub>2</sub> NH	-	100	"
A	(d) RNa	ROH	-	100	"
A	CH <sub>2</sub> :CH.CCl <sub>2</sub> } CH <sub>2</sub> :CMe.CCl <sub>3</sub> } CH <sub>2</sub> :CH.CO <sub>2</sub> Me <sub>2</sub> }	EtOH	second	~ 50	80b-e
A	PhS <sup>-</sup>		second	100	"
A	PhO <sup>-</sup>		second	100	"
A	EtO <sup>-</sup>		second	100	"
A	CH <sub>2</sub> :CH.CHBu <sup>3</sup> Cl/EtO <sup>-</sup>	EtOH	second	100	95
B	CH <sub>2</sub> :CH.CH(Me)Cl/CH(CO <sub>2</sub> Et) <sub>2</sub>	EtOH	-	10	69
B	CH <sub>2</sub> :CH.CH(Et)Cl/CH(CO <sub>2</sub> Et) <sub>2</sub>	EtOH	second	23	69
A	CF <sub>2</sub> :CH.CFCl <sub>2</sub> /X <sup>-</sup>	{ Me <sub>2</sub> CO HCONH <sub>2</sub> CHCl <sub>3</sub>	-	100	93
M	 / (a) C <sub>5</sub> H <sub>11</sub> N (b) CH(CO <sub>2</sub> C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub>	m-C <sub>6</sub> H <sub>4</sub> Me <sub>2</sub> n-BuOH	second second	100 100	108 "
B	CH <sub>2</sub> :CH.CH(Me)Br/Br <sup>-</sup>	Me <sub>2</sub> CO	second	~ 2	79
A	CH <sub>2</sub> :CH.CHORs/I <sup>-</sup>   CF <sub>3</sub>	Me <sub>2</sub> CO	second	100	114

It may be seen that these  $S_N2'$  reactions can be divided into groups on the basis of substrate type and nucleophile charge-type, and discussed in terms of these and solvent groups or classes, e.g.

TABLE II

Group	Nucleophile Type	Solvent	Substrate Type
A	Anions e.g. $\text{PhS}^-$	EtOH	highly activated $\text{CH}_2=\text{CH}-\text{CHCl}_2$
B	Anions e.g. $\text{Br}^-$	$\text{Me}_2\text{CO}$	poorly activated $\text{CH}_2=\text{CH}-\text{CHMeCl}$
C	Uncharged e.g. $\text{Et}_2\text{NH}$	$\text{C}_6\text{H}_6$	poorly activated $\text{CH}_2=\text{CH}-\text{CHMeCl}$
D	Uncharged e.g. $\text{R}_2\text{NH}$	-	highly activated $\text{CH}_2=\text{CH}-\text{CH}-\text{Cl}$ <div style="text-align: center;">  </div>

A highly activated substrate is one in which there are strong -I effect substituents such as halogen, or one or more alkyl substituents, other than a single methyl or ethyl, on the  $\alpha$ -carbon atom.

(viii) Prerequisite for Nucleophilic Attack on  $\pi$ -Bonded Carbon

Considering first the reactions with anionic nucleophiles, if it is postulated that nucleophilic attack on the  $\gamma$ -carbon atom becomes easier as the  $\pi$ -electron cloud-density decreases, because of reduced

repulsive interaction between the nucleophile and the  $\pi$ -electron cloud,<sup>76a</sup> then substituent effects or mechanisms of substitution involving polarisation of the double bond over the small amount due to a single halogen substituent on the  $\alpha$ -carbon atom, should facilitate nucleophilic attack. In other words, a prerequisite for the operation of the  $S_N2'$  mechanism is polarisation of the double bond. This could be achieved in two ways. (a) Strong  $-I$  effect substituents on the  $\alpha$ -carbon atom produce polarisation of the double bond in the initial state. By analogy with the mechanism of nucleophilic attack on ethylenic derivatives, which requires activation by electron-withdrawing substituents and involves the formation of an unstable carbanion intermediate, which may then eject a substituent,<sup>99</sup> nucleophilic attack on the polarised allylic compound could result in bond-making being ahead of bond-breaking and consequently, a transition state on the carbanion side of a symmetrical one in which bond-making and breaking are advanced to the same extent. This type of mechanism in which bond-making and breaking are concerted but not equally far advanced would be in accordance with the results discussed in Section (v).

(b) Alkyl substituents on the  $\alpha$ -carbon atom by hyperconjugative electron release can facilitate departure of a leaving group and the developing carbonium ion is stabilised by electron release from the double bond, which reduces the electron cloud density on the  $\gamma$ -carbon atom. Therefore, a mechanism involving bond-breaking running ahead of bond-making would polarise the double bond for nucleophilic attack and

result in a transition state on the carbonium ion side of symmetrical. Thus a spectrum of transition states for  $S_N2'$  substitution can be envisaged ranging from a carbanion extreme type through a symmetrical one to a carbonium ion extreme type with the symmetrical one being of low probability.

(ix) Discussion of Reaction Groups and Correlation with Solvent Class

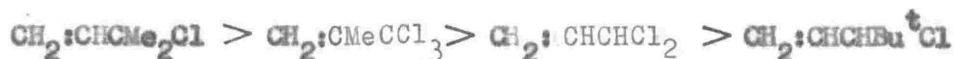
Now, considering Groups A and B of the classification above, Group A reactions of substrates with -I effect substituents should have a carbanion-type transition state; therefore the ability of a particular solvent class to facilitate departure of the leaving group should be less important than its effect on the reactivity of the nucleophile, the nearer the transition state is to the carbanion extreme. Table I shows that protic solvents and nucleophiles which are very reactive in these solvents with respect to attack at saturated carbon, or halide ions in dipolar aprotic or aprotic solvents, which are also very reactive in these solvents with respect to attack at saturated carbon, have been used. Data on the effectiveness of various nucleophiles in nucleophilic attack at ethylenic carbon is scarce but the conventional nucleophilic reagents in their conventional solvent class appear to be reasonably effective.<sup>12</sup> Group A reactions of substrates activated by  $\alpha$ -alkyl substituents should have a transition state on the carbonium ion side of symmetrical and therefore specific

solvent effects assisting the departure of the leaving group should be important. As these reactions have been studied in protic solvents hydrogen-bonding assistance is readily available.

In these Group A substrates the  $S_N2$  mechanism is suppressed by steric hindrance to nucleophilic attack and also polar hindrance to bond-breaking in the case of -I effect substituents.<sup>96</sup>

Examples of Group B are scarce, which is not unexpected considering that polarisation of the double bond by carbonium ion-type transition state formation is dependent upon a single methyl substituent which is only moderately efficient in suppressing the  $S_N2$  mechanism. The reaction of  $\alpha$ -methylallyl bromide with bromide ions in acetone gains some assistance from the  $\alpha$ -methyl group, but little from the poor anion-solvating solvent, to form a carbonium ion-type transition state. The examples with the malonic ester anion involve protic solvents, which can better assist leaving group departure and this, together with increased steric effects, increases the contribution of the  $S_N2'$  reaction to the overall reaction.

Rate data for comparison is scarce but the reactivity order:<sup>96</sup>



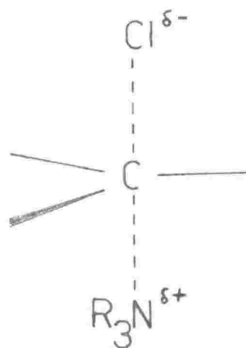
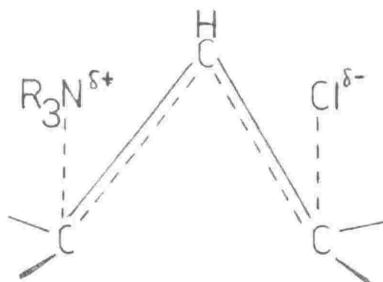
is in accord with facilitation of nucleophilic attack by either of the processes of double-bond polarisation described above.

The solvents used for Group A and B type reactions have fairly high dielectric constants, i.e., they belong to the dipolar aprotic or protic classes so that electrostatic repulsion between the cis entering

and leaving groups is much smaller than it would be in aprotic solvents of low dielectric constant.

The low polarity aprotic solvents usually used for Group C type reactions are not capable of much assistance to leaving group departure, and polarisation of the double bond is dependent upon initial state polarisation and usually a single methyl or ethyl substituent on the  $\alpha$ -carbon atom, to assist the formation of a carbonium ion-type transition state.

However, the production of an electrostatic interaction between the developing charges of the oppositely charged cis entering and leaving groups in the transition state, which in these low polarity solvents should be strong, may result in a self-stabilised transition state from which formation of the products as an ion-pair should require little further charge separation. The energetic advantage of this over an  $S_N2$  transition state, in which the developing charges are separated by a greater distance and the reaction centre, with formation of an ion-pair requiring the migration of one of the ions formed, may be considerable.



This may be partly the reason for the efficiency of uncharged nucleophiles such as amines in promoting  $S_N2'$  reactions at the expense of  $S_N2$ ; increasing the polarity and ion-solvating power of the solvent should reduce this advantage.<sup>8</sup> There is no suitable data for unambiguous comparison, but while  $\alpha$ -methylallyl chloride with diethylamine in benzene gives 100% rearrangement, trans-5-chlorohex-3-en-1-yne with diethylamine in acetonitrile gives only 16%.<sup>75,118</sup> The latter reaction in the amine as solvent gives 82% of the rearranged product, while dimethylamine and piperidine give 19% and 34% respectively, the amine being the solvent in each case and addition of water to the amine solvent lowers the proportion of rearranged product. The polarity order of the amines is  $Me_2NH$ ,  $(CH_2)_5NH$ ,  $Et_2NH$ , while their basicity order is  $(CH_2)_5NH \gg Et_2NH > Me_2NH$  and the decrease in the proportion of rearranged product with increase in solvent polarity is attributed by the authors (Bell, Madroñero and Whiting) to greater stabilisation of the  $S_N2$  transition state than of the  $S_N2'$ .<sup>118</sup>

The use of primary and secondary amines as both nucleophile and solvent constitutes a situation in which hydrogen-bonding solvation is available in a solvent of low polarity and therefore these solvents should be classified as "low polarity protic". e.g.

<u>Group III</u> (low polarity aprotic)		<u>Group IV</u> (low polarity protic)	
<u>Solvent</u>	<u>D</u> <sup>196,90</sup>	<u>Solvent</u>	<u>D</u> <sup>196,90</sup>
CHCl <sub>3</sub>	4.81	MeNH <sub>2</sub>	9.4
C <sub>6</sub> H <sub>6</sub>	2.28	n-BuNH <sub>2</sub>	5.3
n-C <sub>7</sub> H <sub>16</sub>	1.92	Me <sub>2</sub> NH	5.26
C <sub>5</sub> H <sub>5</sub> N	12.0	Et <sub>2</sub> NH	3.6
Me <sub>3</sub> N	2.44	n-Pr <sub>2</sub> NH	2.9
Et <sub>3</sub> N	2.42	C <sub>5</sub> H <sub>11</sub> N	5.8

The role of the hydrogen atom of secondary amines is not clear. Secondary amines show a tendency to be more effective than tertiary amines in promoting the S<sub>N</sub>2' reaction and stabilisation of the product by decomposition of the quaternary ammonium ion to a neutral amine occurs in low polarity aprotic solvents.<sup>75,82,102a,b</sup> For example, α-methylallyl chloride reacts with diethylamine in benzene to give 100% rearrangement and a stable product, while with triethylamine in benzene the products, though rearranged, are not stable.<sup>75</sup> However, with trimethylamine in acetone the product is stable and 70% rearranged,<sup>81b</sup> which is in accord with the better capacity of the dipolar aprotic solvent for solvating and stabilising ions.

The factors which may influence promotion of the S<sub>N</sub>2' mechanism at the expense of the S<sub>N</sub>2 mechanism, by secondary amines compared with tertiary in low polarity aprotic solvents, are as follows:

(a) hydrogen-bonding assistance to leaving group departure and subsequent decomposition to neutral products, and greater dispersion of charge in the transition state, (b) less shielding of the  $\overset{\delta+}{\text{N}} - \overset{\delta-}{\text{X}}$  dipole interaction by a hydrogen atom than by an alkyl group, and (c) steric hindrance to an  $\text{S}_{\text{N}}2$  reaction being greater for tertiary amines, which have three bulky groups on the nitrogen atom compared with two for secondary amines.

The association of quaternary ammonium salts having a partially substituted ammonium ion is much greater than that of tetra-alkyl-ammonium salts in dipolar aprotic solvents<sup>119a-d</sup> and has been attributed to hydrogen bonding between the anion and cation.<sup>15</sup> This suggests such an interaction could assist the operation of the  $\text{S}_{\text{N}}2'$  mechanism with partially substituted amines, while the concurrent mechanisms observed by Dittmer and Marcantonio with  $\alpha$ -methylallyl chloride and *N*-methylaniline in *n*-heptane, suggest that, if one path involves an ion-pair intermediate formed with hydrogen-bonding assistance to leaving group departure, then the more concerted path could also involve some hydrogen-bonding facilitation of bond-breaking.<sup>102b</sup>

Steric hindrance to  $\text{S}_{\text{N}}2$  attack may divert uncharged nucleophiles such as secondary and tertiary amines to the  $\gamma$ -carbon atom, in comparison with primary amines and anionic nucleophiles, as the former have two or three large groups attached to the nucleophilic atom compared with one or none for many anions. For example, the primary amines ethylamine and *n*-butylamine with trans-5-chlorohex-3-en-1-yne give almost exclusively normal products in the amine itself as solvent, and also

in acetonitrile for the former,<sup>118</sup> while secondary and tertiary amines give some rearranged product in members of any of the solvent classes-II, III or IV.

Similar considerations apply to Group D reactions, which differ from Group C in that the  $\gamma$ -carbon atom of the substrate is more accessible to nucleophilic attack, while the  $\alpha$ -carbon is sterically protected.

A substrate type that does not fit into either substrate group is that of primary halides with strongly electron-withdrawing substituents on the  $\gamma$ - or  $\epsilon$ -carbon atom. These are labelled E in Table I. The substrates are extended conjugated systems and electron withdrawal through both the  $\gamma$ , or  $\epsilon$ , and  $\beta$  positions can occur to activate the system for  $S_N2'$  attack.

The cyclic ester system classified M, is included for comparison. In this substrate, an alkyl substituent, other than methyl, sterically prevents an  $S_N2$  reaction.

#### (x) Future Progress

Some systematic studies of selected nucleophiles with a number of substrates in members of the various solvent groups would help to clarify some of the above points.

Therefore, although the volume of work reporting rearranged products, possibly formed in an  $S_N2'$  reaction, is considerable, the proportion involving a kinetic and mechanistic study is relatively small

and unsystematic from the point of view of present knowledge.

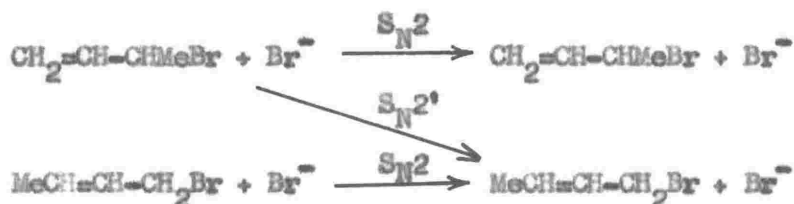
Modern techniques of analysis such as infra-red spectroscopy and gas chromatography have made analysis of isomeric mixtures much simpler and much valuable information could be gained from some systematic studies and the use, for example, of specific solvent effects, linear free-energy relationships and kinetic isotope effects.

### III Bimolecular Isomeric Rearrangement Reactions of Allylic Halides

(1) Only one reaction of this type has been thoroughly investigated, namely, the reaction of  $\alpha$ -methylallyl bromide with lithium bromide in acetone.



The study by England and Hughes of the following system:<sup>76b,79</sup>



provided valuable information about the conditions necessary to observe bimolecular non-isomeric rearrangement.

By using radioactive bromide ions, the kinetics of the  $\text{S}_\text{N}2$  reactions could be studied without affecting the identity of the substrate and therefore the much slower  $\text{S}_\text{N}2'$  reaction could be studied without  $\text{S}_\text{N}2$

complications. Use of the dipolar aprotic solvent acetone, which has a poor capacity for nucleophilic intervention with substrates and which does not particularly favour  $S_N1$  reactions, but in which the bromide ion is highly nucleophilic, eliminated solvolysis problems.<sup>15</sup> Therefore, the  $S_N2'$  mechanism could be isolated in a poorly activated substrate unaccompanied by the  $S_N1$  and multiple reaction complications associated with polyhalogeno- and polyalkyl- $\alpha$ -substituents.<sup>80,95</sup> This meant that the relative rates of nucleophilic attack at vinylic and saturated carbon could be determined under conditions of low initial polarity of the double bond and moderate steric hindrance at the  $\alpha$ -carbon atom.

Their technique involved following the  $S_N2$  reactions by means of a radioactive, isotopically-labelled nucleophile and the  $S_N2'$  by estimation of the relative amounts of each isomer present versus time, using a kinetic analysis method. By determining the rate of  $S_N2$  exchange of an isomeric mixture of unknown composition and comparing it with data on the rates of exchange of mixtures of known composition, the relative amounts of the two isomers could be estimated. The composition of equilibrium mixtures of the two isomers was similarly determined.

As the free energy difference between the two isomers is small, appreciable amounts of both are present at equilibrium.<sup>157</sup> The equilibrium composition in acetone was 75%  $\gamma$ -isomer and 25%  $\alpha$ -isomer.

Substitution of the data into the appropriate integrated rate equations:

$$k_2 = \frac{2.303}{(a+b)t} \log_{10} \frac{(X_{\infty} - X_0)}{(X_{\infty} - X_t)} \quad (S_N2)$$

$$k_2^{\alpha} \text{ or } k_2^{\gamma} = \frac{2.303 X_e}{10^2 b t} \log_{10} \frac{(X_e - X_0)}{(X_e - X_t)} \quad (S_N2')$$

(which are derived in Appendixes I and II) enabled the rate constants to be calculated.

This technique applies simply only when exchange, i.e., the  $S_N2$  reaction, is much faster than rearrangement, i.e., the  $S_N2'$  reaction.

England and Hughes determined the  $S_N2$  rate constants for both isomers reacting with bromide ions in acetone and the  $S_N2'$  rate constant for the  $\alpha$ -isomer. However, the kinetic analysis method, while accurate for low (up to 50%) percentages of the  $\gamma$ -isomer, due to the large difference in the  $S_N2$  reaction rates for the two isomers, which makes the method feasible, becomes increasingly inaccurate at high percentages of the fast-exchanging  $\gamma$ -isomer. For this reason, together with the fact that there is only a small proportion of the  $\alpha$ -isomer present in the equilibrium mixture (25%), the rate constant for the  $S_N2'$  reaction of the  $\gamma$ -isomer could not be determined directly. It was obtained from the overall  $S_N2'$  rate constant determined with the  $\alpha$ -isomer and the equilibrium constant;  $K_{(eq.)} = \frac{[\gamma]}{[\alpha]}$ .

England and Hughes' results are tabulated below:

TABLE III

Substrate	Mechanism	$E_a$ (kcal.mole <sup>-1</sup> )	$\log_{10} A$ (M <sup>-1</sup> sec. <sup>-1</sup> )	$10^6 k_2$ (25°C) (M <sup>-1</sup> sec. <sup>-1</sup> )
$\alpha$ -methylallyl bromide	$S_N2$	16.5	9.06	879
" " "	$S_N2'$	19.4	9.40	14.9
$\gamma$ -methylallyl bromide	$S_N2$	14.7	9.93	141,000
" " "	$S_N2'$	~19	~9	~5

This demonstration of the operation of the  $S_N2'$  mechanism has been criticised in De Wolfe and Young's review, on the grounds that neither a lithium ion catalysed  $S_N1'$  or  $S_Ni'$  mechanism was ruled out, and this will be discussed in Chapter V.<sup>77</sup>

Some preliminary work on the  $S_N2$  reactions of the corresponding isomeric chlorides with lithium chloride in acetone was also carried out, but decomposition of the substrate and polymerisation of the acetone, at the temperatures necessary for the rearrangement to go at a reasonable rate, precluded a study of the  $S_N2'$  reaction.<sup>120</sup> Their  $S_N2$  results are tabulated below.

TABLE IV

Substrate	$E_a$ (kcal.mole <sup>-1</sup> )	$\log_{10} A$ (M <sup>-1</sup> sec. <sup>-1</sup> )	$10^7 k_2$ (25°C) (M <sup>-1</sup> sec. <sup>-1</sup> )
$\alpha$ -methylallyl chloride	20.6	8.47	2.30
$\gamma$ -methylallyl chloride	16.5	7.56	288

(ii) The Aim of this Project

The aim of this project was to study the isomeric chlorides in a suitable solvent and obtain the rate constants for the reactions of both isomers by both mechanisms, thus extending the data on isomeric rearrangements and providing a system for comparison with that of the isomeric bromides.

It has therefore involved finding a suitable reaction medium, establishing the mechanisms of the reactions and determining the rate constants and activation parameters for them.

CHAPTER IICHOICE OF A SUITABLE SOLVENT IN WHICH TO STUDY THE ISOMERIC  
REARRANGEMENT REACTIONS OF THE METHYLALLYL CHLORIDESI Introduction

The initial problem of this project was to find a dipolar aprotic solvent in which the isomeric  $\alpha$ - and  $\gamma$ -methylallyl chlorides were stable, with respect to both decomposition and rearrangement, at the temperatures required for the chloride ion catalysed rearrangement reaction to go at a rate suitable for study.

The first solvent considered was dimethyl sulphoxide.

II Reactions of Allylic Chlorides in Dimethyl Sulphoxide

The work carried out in this solvent may be divided into three sections:- (a) a preliminary study of the reaction of allyl chloride with chlorine- $^{36}$  labelled lithium chloride, (b) a study of the solvolysis reactions of the allylic chlorides, and (c) a study of the reactions of  $\alpha$ -methylallyl chloride in the presence of lithium chloride, using qualitative analysis by gas chromatography to follow the rearrangement reaction.

(a) Preliminary Work on the Allyl Chloride/Lithium Chloride  
Exchange Reaction

(i) Introduction

Dimethyl sulphoxide is a dipolar aprotic solvent with a high boiling-point ( $189^{\circ}\text{C}$ )<sup>211</sup> and a fairly high dielectric constant (46.7)<sup>16</sup>, and it is also a good solvator of cations.<sup>15</sup> Lithium and tetra-alkylammonium salts are reported to be the most readily soluble in these solvents.<sup>15</sup> Considering the fairly high temperatures that would probably be necessary to observe a chloride ion catalysed rearrangement reaction by the  $\text{S}_{\text{N}}2'$  mechanism and the advantage of having a highly dissociated nucleophilic reagent, a solvent of fairly high dielectric constant and boiling-point seemed suitable.

The  $\text{S}_{\text{N}}2$  reactions of  $\alpha$ -methylallyl chloride,  $\gamma$ -methylallyl chloride and allyl chloride, with lithium chloride in acetone, have been studied by England and Vernon using lithium chloride labelled with the radioactive isotope of chlorine, chlorine-36.<sup>92b,120</sup> Therefore, a knowledge of the rate of the reaction of an allylic chloride with lithium chloride in dimethyl sulphoxide would enable an estimate to be made, from the data for the allylic chlorides in acetone and for the  $\text{S}_{\text{N}}2$  and  $\text{S}_{\text{N}}2'$  reactions of  $\alpha$ -methylallyl bromide with lithium bromide in acetone, of the probable rate of the rearrangement reaction of  $\alpha$ -methylallyl chloride with lithium chloride in dimethyl sulphoxide and hence a suitable temperature range for preliminary work on this reaction.

To enable this estimate to be made and to try out a technique for following exchange reactions in a solvent of low volatility and high boiling-point, some preliminary work on the exchange reaction of allyl chloride with chlorine-36 labelled lithium chloride in dimethyl sulphoxide, was carried out.

(ii) Procedure

Runs with allyl chloride and chlorine-36 labelled lithium chloride in dimethyl sulphoxide were carried out at 25.0°C, 35.0°C and 45.0°C. The solvent was dried using "Linde" molecular sieves (type 4A).

(iii) Experimental

The purification of allyl chloride and dimethyl sulphoxide and the preparation of lithium chloride labelled with chlorine-36 is described in Chapter VI. The salt was heated to fusion-point in a silica flask flushed with dry nitrogen, cooled, and dissolved up in dimethyl sulphoxide. The solution was then filtered and stored in a tightly stoppered flask. Precautions against the uptake of atmospheric moisture were taken during the above procedure, as both dimethyl sulphoxide and lithium chloride are extremely hygroscopic. A solution of allyl chloride in dimethyl sulphoxide was prepared by adding approximately the required weight to a given volume of solvent.

All the glass apparatus used was baked in an oven and cooled in a desiccator or a stream of dry nitrogen.

The runs were carried out by the "Y tube" technique used for studying moderately fast reactions. Reaction tubes shaped like an inverted "Y", with side-arms of 8 ml. capacity and ground-glass joints, were used. Aliquots (5 ml.) of each reagent solution were placed, one in each side-arm, in the tubes, which were then stoppered with stoppers lightly greased with silicone grease and placed in a thermostat at the required temperature to come to thermal equilibrium. The reaction was initiated by rapidly inverting the tubes a number of times and replacing them in the thermostat. Reaction tubes were then removed from the thermostat at suitable intervals and the reaction was quenched by pouring their contents into a 50 ml. conical flask containing a slight excess of a solution of silver nitrate in dimethyl sulphoxide (ca. 0.4 ml.). The tubes were washed with about 2 ml. of ethanol and the samples were shaken and left for 3 minutes. The precipitated silver chloride was then collected by filtration through a Gooch crucible containing an asbestos mat supported on a disc of filter paper and the precipitate was washed with small volumes of ethanol.

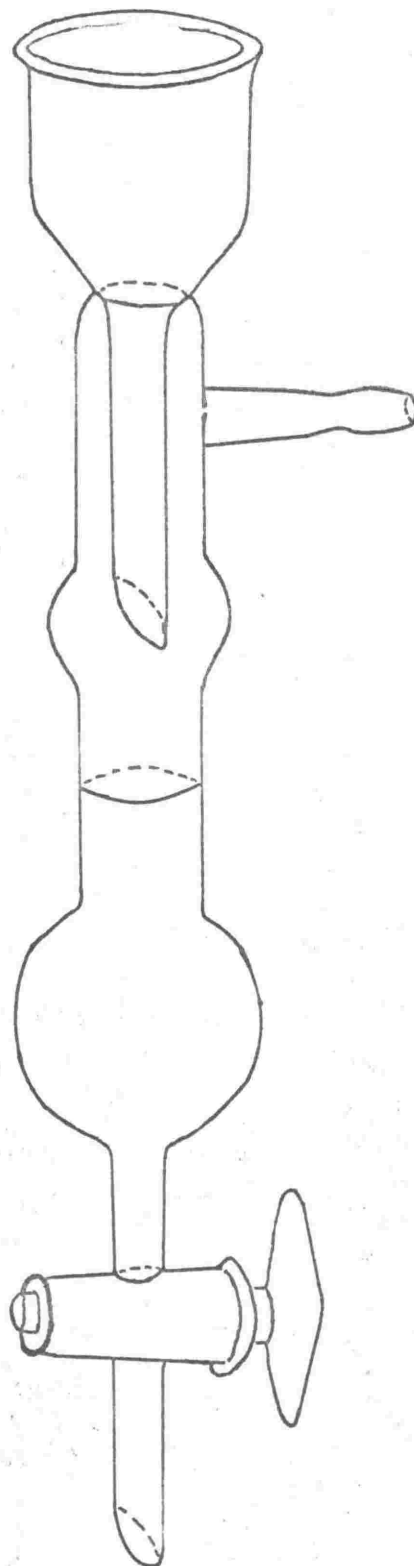
To ensure precipitation of lithium chloride was complete using this procedure, 5 ml. aliquots of the labelled salt in dimethyl sulphoxide were treated as above and the filtrate was tested for activity. There was no residual activity. Reaction of silver nitrate with allyl chloride during the precipitation of the chloride ions of the salt was also tested for, by treating aliquots of allyl chloride

in dimethyl sulphoxide as above. No sign of the formation of silver chloride was observed during the time interval used for runs (3 minutes). On standing, reaction occurred slowly. The reaction was much faster in the presence of water, the solutions becoming quite cloudy in a few minutes.

The Gooch crucible was then transferred to the special filtration apparatus shown in Fig. 1 and portions of sodium thiosulphate solution (2-3M) were added to the crucible and stirred to dissolve up the silver chloride, before being sucked through into the calibrated bulb. The crucible and flask were washed thoroughly and the solution was made up to the mark. It was then run out into a 50 ml. flask, shaken and an M6H (20th Century Electronics Ltd.) liquid counter was filled. The activity of the sample was then determined in the conventional counting assembly described in Chapter IV.

This method of separating labelled chloride ions from reaction mixtures, by precipitating them with silver nitrate solution and then dissolving up the precipitated silver chloride in concentrated sodium thiosulphate solution, to enable its activity to be determined, was developed by Millar for studying the exchange reactions of N-chloro-compounds.<sup>212</sup> As the high boiling-point of dimethyl sulphoxide made isolation of the lithium chloride by other methods difficult, and as counting of volatile organic solutions also has problems, this method was considered to have possibilities.

FIG. 1  
Millar's Apparatus



Subtraction of the background counting rate from the counting rate of the sample gave Y - the activity of the lithium chloride, and subtraction of this value from Z - the initial activity of the lithium chloride (determined by treating 5 ml. aliquots of the reagent solution as above) gave X - the activity of the substrate.

The initial concentration of lithium chloride was determined by titrating 5 ml. aliquots with standard silver nitrate by the potentiometric titration method, while that of allyl chloride was obtained by reacting aliquots to "infinity" with excess of a solution of sodium methoxide in methanol and titrating the liberated chloride ions with standard silver nitrate by the same method. (See Section VII, Chapter III). Dimethyl sulphoxide did not interfere with these analyses.

Substitution of the data into the integrated rate equation for an exchange reaction:

$$k_2 = \frac{2.303}{(a+b)t} [\log X_{\infty} - \log(X_{\infty} - X)]$$

which is derived and defined in Appendix II, enabled the rate constants to be calculated.

Corrections for solvent expansion were made using the data reported by Murto for dimethyl sulphoxide.<sup>23</sup> Errors in the activation parameters were calculated by the method given in a paper by Peterson, Markgraf and Ross.<sup>195</sup>

The solvent used for these runs was dried with "Linde" type 4A molecular sieves and had a freezing-point of 18.45-18.50°C. The literature value is 18.52-18.55°C and the molal freezing-point-depression constant is 4.36°C/mole, so that this corresponds to 0.012-0.025M impurities, these being most probably traces of water.<sup>210,213</sup>

#### (iv) Results and Discussion

The results are shown in Tables V-VIII and a plot of  $\log_{10} k_2$  versus  $\frac{1}{T}$  is shown in Fig. 2. The rate constants corrected for solvent expansion and the activation parameters are given in the Table below.

The standard deviation of the rate constants from the mean value is shown in the tables and an error of 5% in the rate constants, based on this, was assumed in calculating the errors in the activation parameters.

TABLE IX

$10^4 k_2$ (M <sup>-1</sup> sec. <sup>-1</sup> )	2.28	6.34	17.2
T (°C)	25.00	34.99	44.95
E <sub>a</sub> (kcal.mole <sup>-1</sup> )	19.0 ± 0.9		
log <sub>10</sub> A (M <sup>-1</sup> sec. <sup>-1</sup> )	10.32 ± 0.6		

The method of analysis for activity was not, at this stage, producing very good rate constants. Those near the beginning of the reaction showed large errors, with reasonable values only being

TABLE V

Run 1. The Allyl Chloride/LiCl Reaction in Dimethyl Sulphoxide (25°C)

Time (min.)	Y (ct./min.)	X (ct./min.)	$\log_{10}(X_{\infty}-X)$ ( $X_{\infty} = 619$ )	% R	$10^4 k_2$ ( $M^{-1} \text{ sec.}^{-1}$ )
60.6	767	65	2.7435	10.5	2.39
116.8	699	133	2.6866	21.5	(2.70)
205.5	637	195	2.6274	31.5	2.40
295.4	583	249	2.5682	40.2	2.27
478.2	498	334	2.4548	53.9	2.12
594.0	439	393	2.3541	63.4	2.21
513.6	340	492	2.1038	79.4	2.26

52

[Allyl Chloride] = 0.0950M      Z = 832 ct./min.      Mean (6)  $k_2 = 2.27 \pm 0.11 \times 10^{-4} M^{-1} \text{ sec.}^{-1}$ 

[LiCl] = 0.0328M      T = 25.00°C

LiCl = lithium chloride-36      Z = X + Y

TABLE VI

Run 2. The Allyl Chloride/ $\text{AlCl}_3$  Reaction in Dimethyl Sulphoxide ( $35^\circ\text{C}$ )

Time (min.)	Y (ct./min.)	X (ct./min.)	$\log_{10}(X_\infty - X)$ ( $X_\infty = 503$ )	% R	$10^4 k_2$ ( $\text{M}^{-1} \text{sec.}^{-1}$ )
26.2	574	71	2.6355	14.1	(8.19)
50.0	553	92	2.6138	18.3	5.71
80.6	491	154	2.5428	30.7	6.41
117.2	436	209	2.4683	44.6	6.48
180.7	366	279	2.3502	55.4	6.33
258.9	293	352	2.1790	70.0	6.57
359.3	254	391	2.0492	77.8	5.91
476.9	202	443	1.7782	88.1	6.26

[Allyl Chloride] = 0.0920M      Z = 645 ct./min.      Mean (7)  $k_2 = 6.24 \pm 0.31 \times 10^{-4} \text{M}^{-1} \text{sec.}^{-1}$

[ $\text{AlCl}_3$ ] = 0.0260M      T =  $34.99^\circ\text{C}$

TABLE VII

Run 3. The Allyl Chloride/LiCl Reaction in Dimethyl Sulphoxide (45°C)

Time (min.)	Y (ct./min.)	X (ct./min.)	$\log_{10}(X_{\infty}-X)$ ( $X_{\infty} = 622$ )	% R	$10^3 k_2$ ( $M^{-1} \text{sec.}^{-1}$ )
5.4	788	38	2.7664	6.1	(1.53)
12.3	720	106	2.7126	17.0	(1.99)
21.2	667	159	2.6656	25.6	1.81
30.1	610	216	2.6085	34.7	1.85
48.7	534	292	2.5185	46.8	1.70
70.6	454	372	2.3979	59.7	1.69
98.0	387	439	2.2625	70.6	1.63
130.4	324	502	2.0792	80.6	1.65
" $\infty$ "	210	615			

[Allyl Chloride] = 0.0961M      Z = 826 ct./min.      Mean (6)  $k_2 = 1.72 \pm 0.09 \times 10^{-3} M^{-1} \text{sec.}^{-1}$   
 [LiCl] = 0.0346M      T = 44.95°C

%

TABLE VIII

Run 4. The Allyl Chloride/LiCl Reaction in Dimethyl Sulphoxide (45°C)

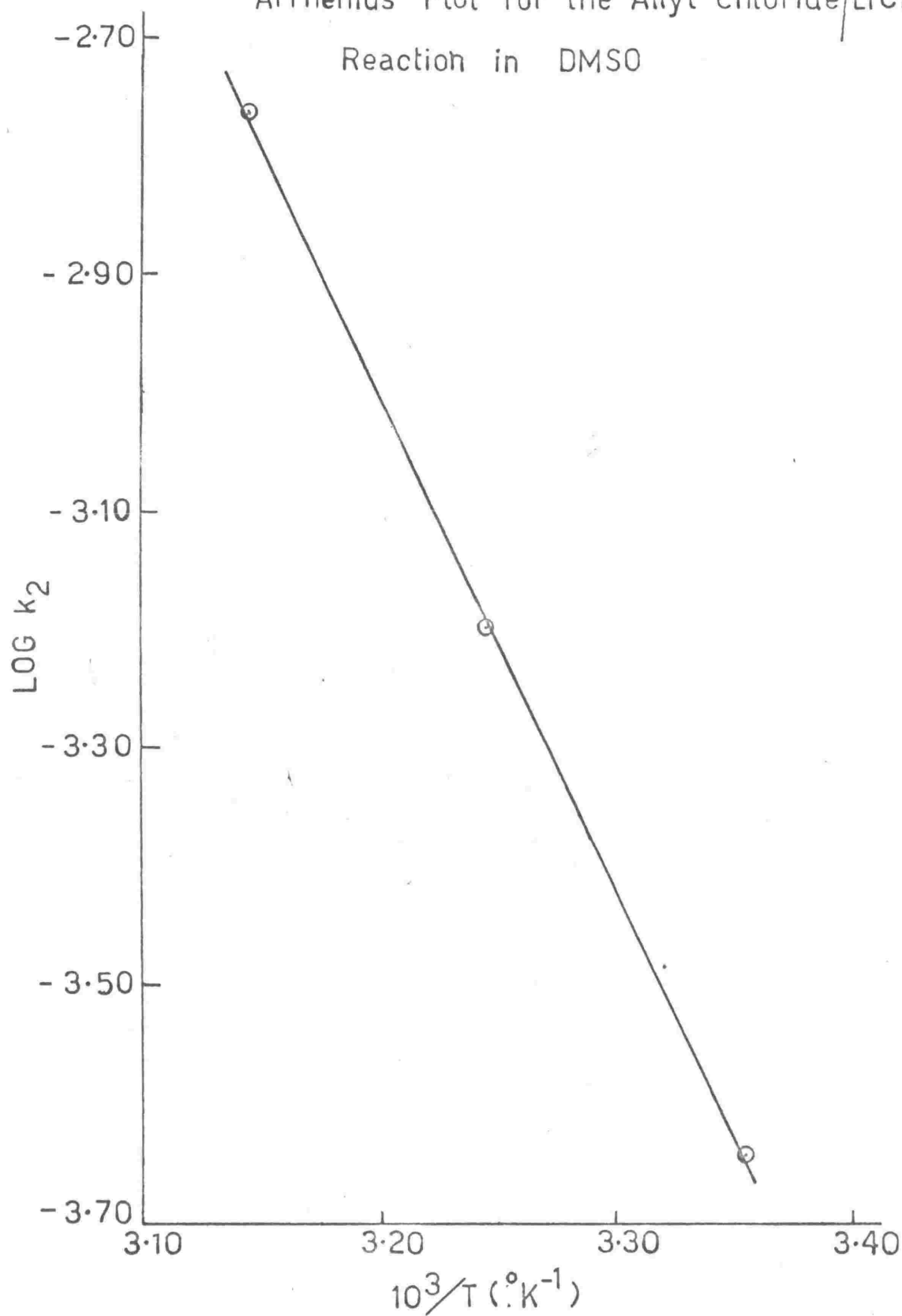
Time (min.)	Y (ct./min.)	X (ct./min.)	$\log_{10}(X_{\infty}-X)$ ( $X_{\infty} = 510$ )	% R	$10^3 k_2$ ( $M^{-1} \text{sec.}^{-1}$ )
12.2	653	71	2.6425	13.9	1.61
32.2	553	171	2.5302	33.5	1.67
45.1	498	226	2.4533	44.3	1.71
69.1	437	267	2.3483	56.3	1.58
87.2	382	342	2.2253	67.0	1.68
122.1	320	404	2.0253	79.2	1.69
150.0	302	422	1.9443	82.7	1.54

57.

$[\text{Allyl Chloride}] = 0.0892M$   
 $[\text{LiCl}] = 0.0374M$   
 $Z = 724 \text{ ct./min.}$   
 $T = 44.95^\circ C$   
 $\text{Mean (7) } k_2 = 1.64 \pm 0.06 \times 10^{-3} M^{-1} \text{sec.}^{-1}$

FIG. 2

Arrhenius Plot for the Allyl Chloride/LiCl<sup>36</sup>  
Reaction in DMSO



obtained after about 20% of the theoretical exchange had occurred. However, although the precision needed improving, some reasonably reliable rate constants were available, from data over the 20-80% theoretical exchange range, for an estimation of a suitable reaction temperature for an  $S_N2'$  study.

The rate constant for the exchange reaction of allyl chloride and lithium chloride- $\text{36}$  in acetone at  $44.6^\circ\text{C}$  (it has been studied at only one temperature) is  $5.87 \times 10^{-5} \text{ M}^{-1} \text{ sec.}^{-1}$ ,<sup>92b</sup> and the rate constant at  $44.6^\circ\text{C}$  in dimethyl sulphoxide, obtained from the Arrhenius plot, is  $1.65 \times 10^{-3} \text{ M}^{-1} \text{ sec.}^{-1}$ . Therefore, assuming the latter reaction to be an  $S_N2$  reaction, the rate constant in dimethyl sulphoxide is 28 times that in acetone.

As the  $S_N2$  reaction of  $\alpha$ -methylallyl chloride in acetone went at a convenient rate for study at  $60-80^\circ\text{C}$  with similar reagent concentrations, then, by assuming that the rate of this reaction would be increased by a similar factor on transference to dimethyl sulphoxide, and that the rate of the  $S_N2'$  reaction of this compound would be approximately  $1/60$  that of the  $S_N2$ , it appeared that at  $60-80^\circ\text{C}$  an  $S_N2'$  reaction of  $\alpha$ -methylallyl chloride in dimethyl sulphoxide might go at a suitable rate for study.<sup>120</sup>

It is interesting to note that the absolute rate constant ratio is not that above, because of the different dissociation constants for lithium chloride in dimethyl sulphoxide and acetone. In the former solvent the value for the dissociation constant at  $30^\circ\text{C}$  is reported to be  $2.59 \times 10^{-1}$ ,<sup>163</sup> while in the latter at  $25^\circ\text{C}$  it is  $3.3 \times 10^{-6}$ .<sup>178</sup>

Therefore, for a lithium chloride concentration of 0.03M, the value for the degree of dissociation is 0.905 in dimethyl sulphoxide at 30°C and 0.010 in acetone at 25°C, from calculations assuming activity coefficients to be unity.

Assuming ion-pairs to be kinetically unreactive and the values to be not greatly altered by a change in temperature from 25°C or 30°C to 44.6°C, a rough comparison of the absolute rate constants at this temperature can be made. The corrected rate constant ratio is now inverted with the rate constant in acetone being approximately three times that in dimethyl sulphoxide.

Therefore the rate constant is little altered by the solvent change, being slightly greater in the solvent of lower dielectric constant (20.7 compared with 46.7)<sup>16</sup>, a result which is in accord with the Hughes-Ingold theory of solvent effects<sup>2</sup>, and the main effect is a large increase in the degree of dissociation of lithium chloride on going to the more polar solvent.

(b) Solvolysis Reactions of the Allylic Chlorides

(1) Introduction

Besides the possibility of elimination of hydrogen chloride from  $\alpha$ -methylallyl chloride to form butadiene, on heating the compound with lithium chloride in dimethyl sulphoxide at the fairly high temperatures estimated to be required for studying an  $S_N2'$  reaction, reactions of the type reported by Smith and Winstein<sup>214</sup> and Kornblum and Blackwood,<sup>215</sup> which involve nucleophilic intervention by the solvent with alkyl halides to form salts or dehydrohalogenation products, were a possible complication.

As the product of elimination of hydrogen chloride from allyl chloride is allene - an unstable compound not easily formed<sup>92b</sup> - allyl chloride appeared a suitable substrate to test for solvolysis reactions other than elimination.

(11) Procedure

A preliminary test of the stability of allyl chloride in dimethyl sulphoxide at  $35.0^\circ\text{C}$  was carried out, which showed solvolysis as indicated by the production of chloride ions to occur. Consequently, further work at various temperatures up to  $75.0^\circ\text{C}$  was carried out.

(iii) Experimental

Solutions of allyl chloride in dimethyl sulphoxide were prepared and aliquots (5 ml.) were added to a series of constricted test tubes, each one being stoppered with a dried rubber bung immediately after being filled. The tubes were then cooled and sealed, before being immersed simultaneously in a thermostat at the required temperature. At intervals, ampoules were removed from the thermostat and cooled in ice water to quench any reaction.

Each ampoule was opened and its contents were added to 20 ml. each of hexane and water in a separating funnel, which was then vigorously shaken to extract the allyl chloride into the organic phase. The aqueous layer was then run off and titrated for chloride ions with standard silver nitrate by the potentiometric titration method. As a check on the method, ampoules kept at 0°C were treated as above and titrated, or an aliquot of standard potassium chloride solution was added to an extracted aliquot, which was then titrated. The average concentration of chloride ions in these blanks was  $1 \times 10^{-3}$  M.

The reaction times were chosen on the basis of the probable  $S_N2$  reaction rate of  $\alpha$ -methylallyl chloride.

(iv) Results and Discussion

The results for the solvolysis runs with allyl chloride at temperatures 35.0°C, 45.0°C and 65.0°C are shown in Table X. The preliminary observation at 35°C was confirmed by these subsequent runs, concentrations of chloride ions of 0.03-0.04M being produced

TABLE XRuns 5, 6, 7. Solvolysis of Allyl Chloride in Dimethyl Sulphoxide(dimethyl sulphoxide dried with type 4A molecular sieves)

Time (hr.)	$[Cl^-]$ ( $10^2 M$ )	Time (hr.)	$[Cl^-]$ ( $10^2 M$ )
264	2.22	24.0	2.47
432	3.09	72.0	2.82
		96.0	2.97
[Allyl Chloride] = 0.185M		168	3.08
T = 35.0°C		384	2.82
<hr/>		[Allyl Chloride] = 0.186M	
48.0	1.29	T = 65.0°C	
120	2.94	<hr/>	
240	3.04	2.4	0.27
360	3.40	24.0	1.81
480	3.68	48.0	2.14
696	3.97	96.0	2.52
[Allyl Chloride] = 0.228M		288	3.21
T = 45.0°C		432	3.27
<hr/>		[Allyl Chloride] = 0.259M	
		T = 65.0°C	
		<hr/>	

by interaction of allyl chloride with the solvent.

With the possibility of an elimination reaction ruled out, two other possible reasons for the solvolytic production of chloride ions were considered. These were (a) salt formation due to nucleophilic intervention by the solvent, and (b) hydrolysis of the allyl chloride by small quantities of water not removed from the solvent during the drying process or picked up during the preparation of runs, although precautions to avoid against the latter were taken.

The production of chloride ions showed signs of reaching equilibrium at about 15-20% reaction, which would be in accord with either a reversible salt-forming reaction, or hydrolysis by a limited quantity of water in the solvent. As the salt-forming reaction gives a product usually hydrolysed by water,<sup>214</sup> the presence of acid in the aqueous layer of extracted aliquots of the reaction mixture was no indication of whether either mechanism was operative. The concentration of impurities (probably water) in the solvent, which was estimated from the freezing-point depression (as described previously) was 0.012-0.025M, so that the concentration of solvolytic chloride ions could be due, or partially due, to a specific reaction of the substrate with water in the solvent.

To test these possibilities further, a run with  $\gamma$ -methylallyl chloride in dimethyl sulphoxide, dried with calcium oxide instead of molecular sieves, was carried out at 65.0°C, and to test the effect of water on the solvolysis reaction, 0.55M water was added to half of the reaction tubes.

The results are shown in Table XI.

TABLE XI

Run 8. Solvolysis of  $\gamma$ -Methylallyl Chloride in Dimethyl  
Sulphoxide and Dimethyl Sulphoxide + Water  
(dimethyl sulphoxide dried with calcium oxide)

Time (hr.)	$[\text{Cl}^-]_A$ ( $10^2 M$ )	$[\text{Cl}^-]_B$ ( $10^2 M$ )	V.P.C.
24.0	1.56	-	
72.0	1.63	6.08	Unknown peak formed and rearrangement to $\alpha$ -isomer
120	1.30	6.19	
168	1.39	6.20	
240	1.35	6.15	

$$[\gamma\text{-Methylallyl Chloride}] = 0.117M$$

$$[\text{H}_2\text{O}] = 0.55M$$

$$T = 65.0^\circ\text{C}$$

A denotes the run in the anhydrous solvent.

B denotes the run in the solvent +  $0.55M \text{H}_2\text{O}$ .

The solvolysis reaction in the "anhydrous" solvent is rapid at 65.0°C, producing<sup>a</sup> concentration of chloride ions which remains fairly constant over a ten-fold change in time. The concentration is lower than that observed in the allyl chloride runs and corresponds to about 12% solvolysis of the substrate. The reaction in the "aqueous" solvent behaves similarly in that a fairly constant concentration of chloride ions is formed rapidly, but this concentration is about 4.5 times that observed in the "anhydrous" solvent and corresponds to about 55% solvolysis of the substrate. Therefore, there is some correlation between the amount of water in the solvent and the extent of solvolysis. It was not possible to tell if the increased amount of solvolysis in the presence of added water was due to a specific hydrolysis reaction between the substrate and water, which did not go to completion because hydrogen chloride is a strong acid in dimethyl sulphoxide,<sup>216</sup> or whether the small amount of added water in the solvent stabilised a salt formed by reaction of the substrate with the solvent.

In a further attempt to establish the minimum concentration of solvolysis product attainable, dimethyl sulphoxide was dried with calcium oxide until its freezing-point was 18.5°C and another run was prepared. Finally, a few reaction tubes were prepared in a dry-box, tested for efficiency by determining the freezing-point of a sample of dimethyl sulphoxide, exposing it to the atmosphere of the dry-box for 1 hour and redetermining its freezing-point. No change was observed. The freezing-point of a sample of dimethyl sulphoxide drops rapidly on exposure to atmospheric moisture. The concentration of allyl chloride

was also increased in these runs to see if the position of "equilibrium" was concentration dependent.

The results are shown in Table XII.

TABLE XII

Runs 9,10. Solvolysis of Allyl Chloride in Dimethyl Sulphoxide  
(dimethyl sulphoxide dried with calcium oxide)

Time (hr.)	$[Cl^-]$ ( $10^2 M$ )	Time (hr.)	$[Cl^-]$ ( $10^2 M$ )
24.0	1.45	2.4	0.81
48.0	1.87	48.0	1.91
72.0	1.88	72.0	1.93
96.0	1.70		
120	1.90	[Allyl Chloride] = 0.373M	
144	2.10	T = 75.0°C	

[Allyl Chloride] = 0.337M

T = 75.0°C

Run 10 reaction tubes prepared in a dry-box.

Both runs gave an equilibrium concentration of chloride ions of about 0.02M, rather less than that obtained in the previous runs using allyl chloride. This corresponded to 5-6% solvolysis of the

substrate, compared with 15-20% observed previously, so that a concentration of solvolysis product independent of substrate concentration, but dependent upon the concentration of some other reagent appeared feasible. These results were more in accord with a reaction involving solvolysis by water, in which the percentage of reaction would depend on the amount of water in the solvent rather than the substrate concentration, than with salt-formation, as the percentage of solvolysis for the latter should be less dependent on substrate concentration, being determined by  $K = \frac{[\text{RO}^+\text{Me}_2][\text{X}^-]}{[\text{RX}]}$ . However, the results of other experiments suggested that the behaviour of the system was more complex than this and these results will be discussed in the next section.

(c) The  $\alpha$ -Methylallyl Chloride/Lithium Chloride Reaction in Dimethyl Sulphoxide

(i) Introduction

A qualitative investigation of the rearrangement of  $\alpha$ -methylallyl chloride in dimethyl sulphoxide in the presence of lithium chloride, using analysis by gas chromatography to follow the reaction, was carried out. The stability of  $\alpha$ -methylallyl chloride with respect to solvolysis and decomposition was also investigated. This work was in progress simultaneously with that in Section (b).

(ii) Experimental

Runs were carried out at 85.0°C and 65.0°C. Reaction mixtures containing  $\alpha$ -methylallyl chloride and lithium chloride in dimethyl sulphoxide were prepared and aliquots (>5 ml.) were placed in a series of constricted test tubes, which were stoppered with dried rubber bungs, cooled and sealed. Dimethyl sulphoxide dried with type 4A molecular sieves was used and the procedure for preparing a solution of lithium chloride in dimethyl sulphoxide was the same as that described for the exchange runs with the labelled salt. Precautions against the uptake of atmospheric moisture were taken. The reaction tubes for the run at 65.0°C were flushed out with dry nitrogen before being filled.

The tubes were then placed simultaneously in the thermostat and at various times one was removed and quenched for analysis.

Samples of the reaction mixture were injected onto the column of a gas chromatograph to test for rearrangement. (Analysis by gas chromatography, or v.p.c. analysis, is described in detail in Chapter III).

A FFE Argon model with a  $\beta$ -ray/argon-ionisation detector was used with a 4 foot column packed with tritolyl phosphate on celite. The operating temperature used was either ambient or 50°C. As dimethyl sulphoxide caused a large detector response and took several hours to come off the column, it was prevented from reaching the detector by injecting the samples onto a 3 inch precolumn, which was then back-flushed, after sufficient time had elapsed for the volatile methylallyl chlorides to be well onto the main column.

Aliquots (5 ml.) were then added to 20 ml. each of hexane and water in a separating funnel, which was vigorously shaken, and the aqueous layer was titrated for chloride ions by the potentiometric method, as described in Section (b). The initial concentrations of the reagents were determined by extracting the allylic chloride and titrating the inorganic chloride, and by reacting aliquots to "infinity" with excess of a solution of sodium methoxide in methanol and titrating the total chloride. Subtraction of the inorganic chloride concentration from the total chloride concentration gave the concentration of the substrate.

TABLE XIIIRuns 11,12. The  $\alpha$ -Methylallyl Chloride/ $\text{LiCl}$  Reaction in DimethylSulphoxide

Time (hr.)	$\Delta[\text{Cl}^-]$ ( $10^2 \text{M}$ )	V.P.C. (% R)
24.0	1.94	peak for $\alpha$ -isomer
48.0	1.74	merged with unknown
72.0	1.49	peak

[  $\alpha$ -Methylallyl Chloride ] = 0.141M[  $\text{LiCl}$  ] = 0.0373M

T = 85.0°C

---

24.0	1.80	-
72.0	3.46	~ 40
120	3.51	~ 55
192	3.87	~ 85
336	3.07	~ 85

[  $\alpha$ -Methylallyl Chloride ] = 0.158M[  $\text{LiCl}$  ] = 0.0566M

T = 65.0°C

---

 Dimethyl sulphoxide dried with molecular sieves.

(iii) Results and Discussion

The results are shown in Table XIII.

Assuming the response of the detector of the gas chromatograph to be the same for both isomers, some approximate estimations of the extent of reaction at various times could be made for the run at 65.0°C and these are shown in Table XIII. The probable equilibrium percentage of the  $\gamma$ -isomer was 70-75%, so the figures in the table give the percentage of the theoretical reaction, or

$$\frac{\% \gamma\text{-isomer} \times 100}{\% \gamma\text{-isomer at equilibrium}}, \text{ assuming the denominator to be } 75\%.$$

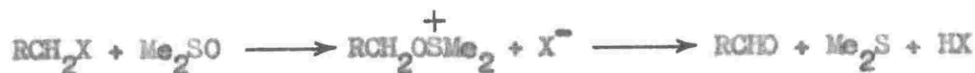
Therefore at 65.0°C, about 55% rearrangement has occurred in five days - a rate in accord with that expected. However, this reaction is accompanied by the production of chloride ions and apparently, also by decomposition of the solvent. The gas chromatograms of the reaction mixture showed a large peak just in front of the  $\alpha$ -methylallyl chloride peak and the solvent smelt of sulphides. Discoloration of the solvent also occurred as it turned from colourless to pale yellow. The peaks for the isomeric chlorides were smaller than expected, by comparison with the size of the peak for the  $\alpha$ -isomer at zero time, while at 85.0°C the unknown peak merged completely with that for the  $\alpha$ -isomer and the solvent turned dark yellow.

It appeared probable that the solvent was decomposing to dimethyl sulphide (b.p. 37.5-38°C)<sup>207</sup>, as this compound would account for the smell and the position of the extra peak, which would probably be due to a compound of boiling-point less than 64°C, i.e. that of the

$\alpha$ -isomer.<sup>200</sup> As the solvent is stable at these temperatures in the absence of allylic halides, the decomposition appeared to arise from interaction of the solvent with the allylic compound. Other decomposition products could have been lost through the back-flushing procedure used for the v.p.c. analyses, which would prevent compounds with a retention time greater than that of  $\gamma$ -methylallyl chloride, from reaching the detector.

At the time that this work was in progress (1964), there were various reports in the literature of oxidations of alcohols, tosylates and activated halides by dimethyl sulphoxide,<sup>217</sup> but the properties of this compound as a reactant, now well documented in various reviews,<sup>139,211</sup> were then only in the process of becoming widely known.

The mechanism proposed for the oxidation of most tosylates and activated halides involves nucleophilic attack by dimethyl sulphoxide as follows:<sup>9,217</sup>



Halides less reactive than benzyl bromides were reported to be less easily oxidised by dimethyl sulphoxide alone, although details of just how reactive they were under various conditions were not given.<sup>101</sup> A reactivity order of OTs > I > Br > Cl was deduced,<sup>9,139</sup> and facile oxidations of halides by conversion to the tosylate and oxidation in the presence of an acid scavenger were reported.<sup>101</sup> Secondary compounds often gave elimination products as well as, or to the exclusion of, oxidation products.<sup>139</sup>

Alcohols could sometimes be oxidised in the presence of oxygen but often needed an activating agent.<sup>31,139</sup> Hydrogen halides were also reported to be oxidised by dimethyl sulphoxide, to the halogen and water.<sup>9</sup> A recent review by Epstein and Sweat on dimethyl sulphoxide oxidations contains much information.<sup>139</sup>

It therefore appeared that the allylic chlorides could be sufficiently reactive to undergo oxidation by the solvent when kept at 60-80°C for the reaction times given in Table XIII.

Rearrangement of  $\alpha$ -methylallyl chloride and  $\gamma$ -methylallyl chloride in dimethyl sulphoxide in the absence of lithium chloride also occurred, at rates comparable with that of the "catalysed" reaction and these reactions were accompanied by the formation of "sulphides" and the production of the large extra peak observed above. As chloride ions were produced and as hydrogen chloride is a strong acid in dimethyl sulphoxide,<sup>216</sup> rearrangement in the absence of lithium chloride was not unexpected.

It therefore became obvious, that the chances of reducing the production of chloride ions to a negligible amount, or an amount small compared with a reasonable concentration of reactants, were not good, and that the concentration of chloride ions produced was not necessarily an indication of the real extent of decomposition of the substrate. As salt formation or hydrolysis could be followed by oxidation by dimethyl sulphoxide, and as the acid produced could be further oxidised to chlorine, which could then react further, a very

complex system was possible. The small size of the peaks for the methylallyl chlorides on gas chromatograms and the observation that, in the run for which the concentration of chloride ions (produced by solvolysis) was least, the unknown peak was large, were in accord with the above possibility. (Run 8A).

So, although the nature of the reactions occurring was far from clear and the exact role of water in the solvent was ambiguous, further more refined investigations of this solvent were abandoned in the hope of finding a less reactive and ambiguous one.

Other work, to be described in the next section, indicated that the unknown peak observed on gas chromatograms was not due to butadiene.

### III Reactions of Allylic Chlorides in Dimethylformamide

#### (i) Introduction

Another dipolar aprotic solvent of high boiling-point ( $153^{\circ}\text{C}$ )<sup>15</sup> and fairly high dielectric constant ( $36.7$ )<sup>16</sup> is dimethylformamide. This solvent does not have the oxidizing ability of dimethyl sulphoxide, but suffers from the disadvantage of being sufficiently nucleophilic to participate in salt-forming and dehydrohalogenation reactions with certain substrates.<sup>215</sup>

The possibility that it might be a suitable solvent for studying the rearrangement reaction of  $\alpha$ -methylallyl chloride was considered during the work in Section II and a run with  $\alpha$ -methylallyl chloride and lithium chloride in dimethylformamide was carried out at  $83.0^{\circ}\text{C}$ .

#### (ii) Experimental

The solvent was dried with type 4A molecular sieves as described in Chapter VI. The procedure for preparing and performing the run was identical to that described for the runs in dimethyl sulphoxide. Analysis by gas chromatography<sup>for</sup> rearrangement and decomposition products was carried out using the back-flushing procedure, to prevent the solvent, which has a similar effect to that of dimethyl sulphoxide, from reaching the detector. Analyses for the production of chloride ions were also carried out.

#### (iii) Results and Discussion

The results are shown in Table XIV.

TABLE XIV

Run 13. The  $\alpha$ -Methylallyl Chloride/LiCl Reaction in Dimethyl-  
formamide

Time (hr.)	$\Delta[\text{Cl}^-]$ ( $10^2\text{M}$ )	V.P.C. (% R)
43.0	0.60	-
89.0	1.56	~ 40
137	2.72	~ 65
192	3.46	peaks small
257	-	rearrangement near equilibrium
276	4.14	no extra peaks

$$[\alpha\text{-Methylallyl Chloride}] = 0.133\text{M}$$

$$[\text{LiCl}] = 0.0630\text{M}$$

$$T = 83.0^\circ\text{C}$$

Rearrangement occurred readily at this temperature and some 65% of the theoretical amount was reached in about 6 days. No extra peaks were observed and no obvious decomposition of the solvent was detected, except for discoloration to pale yellow. However, production

of chloride ions was again observed with about 20% decomposition of the substrate being observed in about 6 days.

Although no peak which might be attributed to butadiene (b.p. =  $-4.51^{\circ}\text{C}$ )<sup>115</sup> was observed, the possibility that chloride ion production might be due to an elimination reaction or water in the solvent, was checked by carrying out two solvolysis runs using allyl chloride alone in the solvent. Other methods of drying the solvent were also used.

#### (iv) Experimental

Solvent dried with barium oxide was used for the first run and dried with calcium oxide for the second. (See Chapter VI). The reaction mixtures were prepared and the reaction tubes were filled in a dry-box. Samples from the reaction tubes were analysed by gas chromatography for extra peaks and 5 ml. aliquots of reaction mixture were extracted and titrated for chloride ions using the Volhard titration procedure.<sup>104</sup> Dimethylformamide had no effect on the end-point determination. The "ferric indicator" was used and "Analar" nitrobenzene was added to the titration mixture.

Two runs were carried out, one at  $93.0^{\circ}\text{C}$  and one at  $96.0^{\circ}\text{C}$ .

#### (v) Results and Discussion

The results for both runs are shown in Table XV.

TABLE XVRuns 14, 15. Solvolysis of Allyl Chloride in Dimethylformamide

Time (hr.)	$\Delta[\text{Cl}^-]$ ( $10^2\text{M}$ )	Time (hr.)	$\Delta[\text{Cl}^-]$ ( $10^2\text{M}$ )
23.5	0.48	3.5	0.22
47.2	0.71	22.1	0.56
71.8	1.02	46.2	0.81
146	1.77	73.8	1.03

[Allyl chloride] = 0.377M

T = 93.0°C

dimethylformamide dried

with barium oxide.

reaction tubes prepared

in a dry-box for both runs.

120 1.64

121 1.80

145 1.84

195 2.22

336 3.70

[Allyl chloride] = 0.415M

T = 96.0°C

dimethylformamide dried with

calcium oxide.

No extra peaks were observed but discoloration of the solvent to yellow and then brown occurred, probably because of polymerisation reactions. Chloride ions were produced steadily as far as the reaction was followed.

It therefore appeared that the salt-forming reaction observed by Kornblum and Blackwood with other halides in dimethylformamide was taking place with allyl chloride and also with the  $\alpha$ -methyl compound.<sup>215</sup> Consequently, this solvent was also too reactive to allow a chloride ion catalysed rearrangement reaction to proceed without complications from side reactions.

The less reactive solvent acetonitrile was also being investigated at this stage and the results obtained for it will be described in the next chapter.

CHAPTER IIITHE KINETICS AND MECHANISM OF THE ISOMERIC REARRANGEMENT  
REACTIONS OF  $\alpha$ - AND  $\gamma$ -METHYLALLYL CHLORIDE IN ACETONITRILEI Investigation of the Stability of Allyl Chloride in Acetonitrile(i) Introduction

The preceding work on the stability of allylic chlorides in dimethyl sulphoxide and dimethylformamide has shown that allyl chloride is a useful compound for detecting substrate-solvent interactions other than elimination of hydrogen chloride. Therefore, a preliminary study of its interactions with acetonitrile was considered a suitable initial test of the merits of the solvent.

(ii) Procedure

The solvent - acetonitrile - was purified and dried as described in Chapter VI.

A solution of allyl chloride in acetonitrile was prepared in the dry-box which was used for all subsequent work (see Section VII), and slightly greater than 5 ml. aliquots were placed in a series of constricted test tubes, which were then stoppered with dried rubber bungs. The tubes, after removal from the dry-box, were cooled, sealed and placed simultaneously in a thermostat at  $96.0^{\circ}\text{C}$ . Ampoules were

removed from the thermostat at various times, plunged into an ice-water bath to quench any reaction, broken open and after removing a 1-2  $\mu$ l. sample for v.p.c. analysis (see Section VII), a 5 ml. aliquot was added to a 100 ml. separating funnel containing 25 ml. of hexane and 20 ml. of water. This was shaken vigorously to extract the unreacted allyl chloride into the hexane. The aqueous layer was then extracted with a further 10 ml. of hexane before being run off into a 150 ml. conical flask. After the addition of 10 ml. of water and sufficient sodium hydroxide solution to make it faintly alkaline, the aqueous extract was evaporated down to a small volume ( $\sim$ 5 ml.). The flask was flushed with nitrogen during this operation.

This procedure was necessary to remove acetonitrile which would have interfered with the subsequent "Volhard titration" for chloride ions,<sup>104</sup> and also to remove traces of unextracted allyl chloride and organic phase.

To the cold evaporated solution was added 20 ml. of water, 5 ml. of nitric acid (6N), 10 ml. of silver nitrate solution (0.01925N), 1 ml. of " $\text{Fe}^{3+}$  indicator" and 1 ml. of "Analar" nitrobenzene. The excess silver ions were then titrated with potassium thiocyanate (0.02376N). A "blank" was analysed to correct for chloride ions produced by solvolysis of unreacted allyl chloride during the extraction and evaporation procedure, i.e., a reaction tube kept at  $0^{\circ}\text{C}$  was treated as above.

Each ampoule, before analysis, was examined for discoloration of the reaction mixture.

(iii) Results and Discussion

The results are shown in Table XVI.

The low concentration of chloride ions produced and the slight degree of discoloration of the reaction mixture after 42 days at 96°C, suggested that substrate-solvent interactions producing chloride ions and polymer are not favoured in acetonitrile. The gas chromatograms showed only the substrate and solvent peaks.

These results were a promising indication that acetonitrile might be a suitable solvent for a study of the rearrangement reactions of  $\alpha$ - and  $\gamma$ -methylallyl chloride.

TABLE XVIRun 16. Solvolysis of Allyl Chloride in Acetonitrile(96°C)

Time (hr.)	ml. KCNS (0.02376N)	[Cl <sup>-</sup> ] (10 <sup>3</sup> M)	Colour of Sol'n
0.0	7.93	0.0	Colourless
22.3	7.70	1.1	"
47.9	7.77	0.8	"
98.2	7.73	0.9	"
168.1	7.47	2.2	Pale yellow
215.1	7.50	2.0	"
310.3	7.62	1.5	"
503.1	7.58	1.7	"
1010.8	7.39	2.6	"

[Allyl Chloride] = 0.355M

T = 96.0°C

## II Preliminary Investigation of the Rearrangement Reaction of $\alpha$ -Methylallyl Chloride in Acetonitrile

### (i) Introduction

A knowledge of the magnitude of possible unimolecular and solvent assisted rearrangement and elimination contributions to the behaviour of  $\alpha$ -methylallyl chloride in acetonitrile was a necessary precursor to a study of any chloride ion accelerated reactions.

To this end, a preliminary investigation of the rate of rearrangement of  $\alpha$ -methylallyl chloride to  $\gamma$ -methylallyl chloride, in both the absence and presence of chloride ions, was made. Analyses for chloride ion production were also carried out.

The temperature chosen for the investigation was 96.0°C. The compound chosen to provide chloride ions, i.e., the nucleophilic reagent, was tetraethylammonium chloride, henceforth to be referred to as  $\text{Et}_4\text{NCl}$ . This compound was known to be readily soluble and fairly stable in acetonitrile and to have a low association constant for ion-pair formation,<sup>107</sup> and, as any  $\text{S}_{\text{N}}2'$  reaction was expected to require fairly high temperatures and concentrations of nucleophile to produce a rate convenient for study,<sup>120</sup> it seemed a suitable choice.

### (ii) Procedure

Two runs were carried out at 96.0°C using the "ampoule or sealed tube" technique. One run (Run 17) contained no  $\text{Et}_4\text{NCl}$ , while the other (Run 18) contained  $\text{Et}_4\text{NCl}$  (ca. 0.05M).

The ampoules contained 2 ml. or 5 ml. of solution depending on their destination - analysis by gas chromatography for rearrangement, or for chloride ions - but those for the former were scaled down from the 5 ml. size and specially made. Analysis by gas chromatography was semi-quantitative at this stage, and as no pure sample of  $\gamma$ -methylallyl chloride was available for the preparation of standards by weight, mixtures of the two isomers were used and their compositions were determined by refractive index measurements. Analyses for chloride ion production were carried out as described in Section I except that only one extraction with 30 ml. of hexane and 25 ml. of water was carried out. Analysis for total chloride ions, after quantitative solvolysis of aliquots of the substrate, was by potentiometric titration with standard silver nitrate solution. (For details of the technique for preparing, carrying out and analysing the runs, see Section VII).

Before analysis, each ampoule was examined for discoloration of the reaction mixture.

#### (iii) Results and Discussion

The results for Runs 17 and 18 are shown in Table XVII.

In the presence of  $\text{Et}_4\text{NCl}$  rearrangement proceeds at a reasonable rate to produce 66% of the  $\gamma$ -isomer in 14 days. If the equilibrium percentage is taken to be 70%, this is approximately 94% reaction. On the other hand, in the absence of  $\text{Et}_4\text{NCl}$ , rearrangement proceeds at a very slow rate which tends to increase with time.

TABLE XVII

Run 17. Reactions of  $\alpha$ -Methylallyl Chloride in Acetonitrile ( $96^{\circ}\text{C}$ )Run 18. Reactions of  $\alpha$ -Methylallyl Chloride and  $\text{Et}_4\text{NCl}$  in Acetonitrile ( $96^{\circ}\text{C}$ )

Time (min.)	% $\delta$ -MAC (Run 17)	$[\text{Cl}^-]$ (Run 17)	% $\delta$ -MAC (Run 18)	$\Delta [\text{Cl}^-]$ (Run 18)	Colour of Sol'n
1339	< 1	-	14	-	Colourless
3125	< 1	-	30	-	"
4720	< 1	-	40	-	"
7058	< 1	-	50	-	"
11395	$\sim 3$	-	59	-	"
14400	-	$4.5 \times 10^{-3}$	-	$13.5 \times 10^{-3}$	"
20160	$\sim 9$	-	66	-	"
40000	26	$12.6 \times 10^{-3}$	68	-	-

 $[\alpha\text{-MAC}] = 0.1889\text{M}$  (Run 17)       $\alpha\text{-MAC} \equiv \alpha\text{-Methylallyl Chloride}$  $[\alpha\text{-MAC}] = 0.1682\text{M}$  (Run 18)      -       $\equiv$  no analysis $[\text{Et}_4\text{NCl}] = 0.0524\text{M}$  (Run 18)      T =  $96.00^{\circ}\text{C}$

The production of chloride ions, enhanced in the presence of  $\text{Et}_4\text{NCl}$ , and in both runs considerably greater in amount than would be expected from substrate-solvent interaction, as indicated by allyl chloride in Section I, suggested complications. The appearance of the gas chromatograms of the reaction mixtures verified this. These, for both runs, showed the presence of an extra peak, increasing in size with increasing reaction time and being considerably larger for Run 18 analyses than for Run 17, in the same reaction period. This peak had a low retention time of the order of 0.5 minutes, compared with that of about 5 minutes for the  $\alpha$ -isomer.

The production of chloride ions and the presence of the extra peak immediately suggested that an elimination reaction was occurring, rather than acetonitrilium salt formation.<sup>113</sup> i.e.



(The detector of the gas chromatograph does not respond to hydrogen chloride).

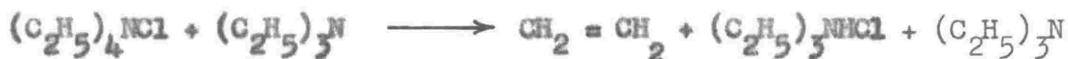
Butadiene, the product of the postulated elimination reaction, is a non-polar gas (b.p.  $= -4.51^\circ\text{C}$  at 757 mm)<sup>115</sup> which might be expected to have a low retention time on the polar GLC column used. This compound is known to form solid stereoisomeric tetrabromides with bromine (m.p.  $= 115-117^\circ\text{C}$ , m.p.  $= 37-39^\circ\text{C}$ )<sup>89,115</sup>, so the contents of a reaction tube were divided into two and one drop of liquid bromine (excess) was added to one portion, while the other was used as a reference. After 15 minutes a sample of each was analysed by gas chromatography and the

extra peak was missing from the gas chromatogram of the brominated sample.

A sample from a tube containing  $\alpha$ -methylallyl chloride in acetonitrile, to which excess sodium methoxide in methanol had been added before reacting it to "infinity", was also chromatographed and showed a peak in the position of that observed in Runs 17 and 18. Although this peak could have been produced by reaction of acetonitrile with methoxide/methanol - it was absent when the latter was chromatographed by itself - it could also be due to butadiene.

Vernon obtained a 10% yield of butadiene from the reaction of  $\alpha$ -methylallyl chloride with ethoxide ions in ethanol,<sup>92b</sup> so some butadiene might be expected to be produced with methoxide ions in methanol.

The possibility of the extra peak coming from the solvent or from decomposition of the  $\text{Et}_4\text{NCl}$ :<sup>121</sup>



was ruled out by the previous work on allyl chloride and by its presence in Run 17.

Examination of Table XVII reveals that the side reaction could be of the order of 10% of the total reaction. No discoloration of the reaction mixture was observed.

In general, although the magnitude of the catalytic effect of chloride ions on the rearrangement reaction augured well for the operation of the bimolecular mechanism, the possible effects of the products of the postulated elimination reaction had to be carefully considered.

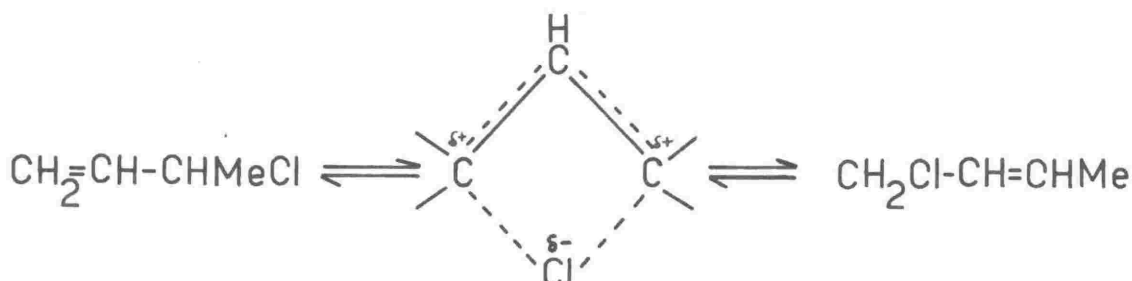
The products, butadiene and hydrogen chloride, were considered to introduce the possibility of two further mechanisms contributing to the rearrangement reaction. These were (a) an acid-catalysed  $S_N1'$  mechanism, and (b) an elimination-addition mechanism.

(a) The  $S_N1'$  mechanism of anionotropic rearrangement is known to be catalysed by strong acids, i.e., by the proton, and the effect is more pronounced the more basic the leaving group.<sup>122</sup> This is just one example of the general phenomenon of electrophilic catalysis, by ions such as  $Ag^+$ ,  $H^+$ ,  $Fe^{3+}$  and Lewis acids such as  $BF_3$ , which assist the rate-determining ionisation step of the  $S_N1'$  mechanism by bonding with the leaving group.

Hydrogen chloride in acetonitrile is a weak acid with respect to dissociation into hydrogen and chloride ions ( $K = 1.26 \times 10^{-9}$ ), (conversely the chloride ion is a strong base), but it has a much stronger tendency to associate with chloride ions to form the ion  $HCl_2^-$ ,



and therefore it might be expected to catalyse an  $S_N1'$  rearrangement reaction.<sup>124,170</sup>



Assuming rearrangement to occur before the dissociated carbonium ion stage,<sup>42a</sup> i.e., in some type of ion-pair intermediate, hydrogen chloride by hydrogen bonding to the departing chloride ion, could assist the bond-breaking step and increase the lifetime of the intermediate, thus reducing the chance of collapse to the same isomer and increasing the chance of the chloride ion being taken up in the isomeric position.

Electrophilic catalysis by hydrogen chloride occurs in the unimolecular racemisation of 1-mesitylethyl chloride in acetone and the exchange and racemisation reactions of 1-phenylethyl chloride with HCl<sup>36</sup> in nitromethane.<sup>125,126</sup> However, in the presence of excess Et<sub>4</sub>NCl the chloride ions involved in the formation of the HCl<sub>2</sub><sup>-</sup> ion should be supplied by this salt, thus eliminating the possibility of catalysis of an S<sub>N</sub>1' mechanism.

In the case of an S<sub>N</sub>2' mechanism, hydrogen chloride could not affect the concerted mechanism itself, except by competing as a nucleophile, but by combining with the chloride ions of the nucleophilic reagent it could decrease the effective concentration of the nucleophile. The effect on the reaction rate would then depend on the relative

nucleophilicity of the chloride and  $\text{HCl}_2^-$  ion, but the latter, with its larger size resulting in greater solvation stabilisation and its dispersed charge, might be expected to be somewhat less nucleophilic than the chloride ion.<sup>15</sup>

- (b) Butadiene can add hydrogen chloride to form either  $\alpha$ - or  $\delta$ -methylallyl chloride by 1,2 or 1,4 attack respectively.<sup>128</sup>

The kinetics and mechanism of hydrogen chloride addition to olefins in aprotic solvents is complex and has been studied in only a few cases. Some interpretations of the mechanism are as follows:<sup>129</sup>

- (1) The effective electrophile is the hydrogen chloride molecule which attacks the double bond to form a complex of undetermined structure. To carry addition further, it is necessary to break the hydrogen to chlorine bond and form the carbonium ion, for which a catalyst is necessary, one such being the hydrogen chloride molecule, which removes a chloride ion from the transition complex by forming a dihalide ion. This interpretation accounts for catalysis of both addition to, and polymerisation of, styrene by stannic chloride, in which the intermediate can be diverted by reaction with a second molecule of olefin.

- (2) The effective electrophile is the free proton produced by the dissociation process:



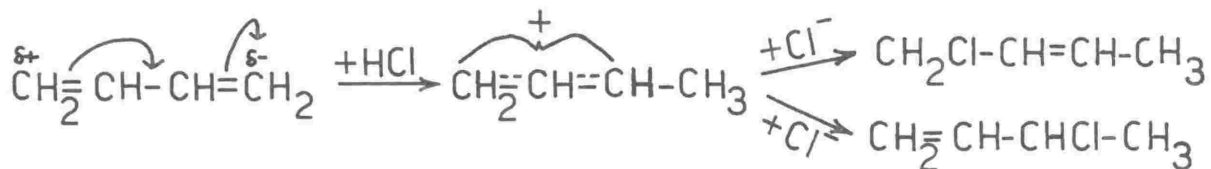
This mechanism results in the following rate equation:

$$v = k_3[\text{olefin}][\text{HCl}]^2$$

if deprotonation of the carbonium ion formed is faster than nucleophilic attack.<sup>130</sup>

(3) The nucleophile and electrophile trans attack the double bond simultaneously, either in a concerted process or by nucleophilic attack on a rapidly formed olefin-electrophile adduct, with simultaneous formation of the C-H and C-Cl bonds.

In the case of a conjugated diene, the position of electrophilic attack is, as with olefins, determined by the electronic orientating effects of substituents, but the nucleophilic fragment can be taken up in either of two positions. In the extreme case:



It is generally considered that reaction of carbonium ion-type intermediates with nucleophiles produces the less stable isomer more rapidly, but that if the products can easily reverse this step then the more stable isomer will eventually predominate in them, i.e., kinetic control of the products gives way to thermodynamic control.<sup>132,133</sup>

In the case of the methylallyl halides the primary halide is the more stable isomer due to methyl-hyperconjugation.<sup>132</sup>

The above interpretations of the mechanism of addition all require initial or simultaneous attack by an electrophile on the unsaturated compound and any reduction in the concentration or availability of this electrophile, whether it be the proton or the hydrogen chloride molecule, should reduce the rate. Therefore, dihalide ion formation when  $\text{Et}_4\text{NCl}$  is added to hydrogen chloride in acetonitrile, which produces a nucleophilic ion, should markedly lower the rate of the butadiene/hydrogen chloride reaction.

Hughes, Ingold and co-workers found that bromide and chloride ions retarded back addition to the olefin in the elimination-addition reactions of *t*-butyl bromide with  $\text{Et}_4\text{NCl}$  and  $\text{Et}_4\text{NBr}$  in nitromethane, while  $\text{Et}_4\text{NCl}$  completely suppressed back addition to *t*-butyl chloride in the same solvent.<sup>134,135</sup>

Elimination and back addition would need to occur at comparable rates for this mechanism to be an important contributor to the rearrangement of  $\alpha$ -methylallyl chloride.

Obviously it was necessary to have more experimental information on the relative rates of rearrangement and chloride ion production and on the effect of added hydrogen chloride on these, together with a substantiation of the elimination hypothesis and a determination of the rate of addition of hydrogen chloride to butadiene in acetonitrile, and the effect of  $\text{Et}_4\text{NCl}$  on this, before the preliminary observations could be elucidated.

### III Continuation of the Preliminary Investigation and the Effect of Hydrogen Chloride on the Rearrangement Reaction

#### (1) Introduction

Two runs were carried out at  $96.0^{\circ}\text{C}$ . The reaction mixture for one (Run 19) consisted of  $\alpha$ -methylallyl chloride and  $\text{Et}_4\text{NCl}$  in acetonitrile; for the other (Run 20) substrate,  $\text{Et}_4\text{NCl}$  and hydrogen chloride in acetonitrile, with  $[\text{Et}_4\text{NCl}] \sim 2[\text{HCl}]$  was used.

The rates of production of  $\gamma$ -methylallyl chloride, chloride ions and hydrogen ions were followed for each run and both runs were allowed to proceed for a time considered long enough for rearrangement to reach equilibrium, in order to investigate the behaviour of the chloride ions produced during the rearrangement reaction and that of the extra peak.

#### (11) Procedure

For details of the experimental technique, see Section VII. As in Section II, the v.p.c. analyses were semi-quantitative. The preparation of a solution of hydrogen chloride in acetonitrile is described on page 103.

A volume slightly greater than 5 ml. of reaction mixture was placed in each ampoule. After reaction and quenching, samples of the contents of each ampoule were put through the gas chromatograph, while a 5 ml. aliquot was added to 30 ml. of *n*-pentane and 25 ml. of water in a 100 ml. separating funnel and extracted. The extracted aqueous layer was run off into a 150 ml. conical flask and titrated with sodium

hydroxide solution (0.02182N) to determine the concentration of hydrogen ions. The solution was then evaporated down, while being flushed with nitrogen, before being analyzed for chloride ions by potentiometric titration with silver nitrate solution (0.01925N). The initial concentrations of  $\text{Et}_4\text{NCl}$  and hydrogen chloride were determined in an analogous way. The initial concentration of the substrate was determined by quantitative solvolysis and subsequent potentiometric titration for total chloride. The acid analyses of the aliquots used to determine the initial  $\text{Et}_4\text{NCl}$  concentration in Run 19 were "blanks", which were used to correct for solvolysis of the substrate during the extraction procedure and as an indicator blank.

Despite its being almost outside the pH range for use in titrations at this dilution, phenolphthalein gave more easily detectable and stable end-points than other indicators such as bromothymol blue. An extraction blank of 30 ml. of *n*-pentane and 30 ml. of water took 0.1 ml. of sodium hydroxide solution (0.01365N) to change the indicator and, as all acid analyses had to be corrected for hydrolysis of the substrate during extraction and the effect of acetonitrile, by the use of "blanks", deviation of the end-point from the true equivalence point was automatically corrected for, and thus its use in preliminary analyses was considered appropriate. Precautions were taken against carbon dioxide and the titrations were reproducible to 0.1 ml.

#### (iii) Results and Discussion

The results are shown in Table XVIII.

TABLE XVIII

Run 19. The  $\alpha$ -Methylallyl Chloride/ $\text{Et}_4\text{NCl}$  Reactions in Acetonitrile ( $96^\circ\text{C}$ )Run 20. The  $\alpha$ -Methylallyl Chloride/ $\text{Et}_4\text{NCl}/\text{HCl}$  Reactions in Acetonitrile ( $96^\circ\text{C}$ )

Time (min.)	% $\delta$ -MAC (Run 19)	% $\delta$ -MAC (Run 20)	$[\text{H}^+]$ (Run 19)	$\Delta[\text{H}^+]$ (Run 20)	$\Delta[\text{Cl}^-]$ (Run 19)	$\Delta[\text{Cl}^-]$ (Run 20)
0	6.7	1.3	$0.0 \times 10^{-3}$	$0.0 \times 10^{-3}$	$0.0 \times 10^{-3}$	$0.0 \times 10^{-3}$
476	11	5	0.7	0.7	0.0	0.5
1151	22	10	1.7	1.4	2.0	1.3
1671	26	14	2.8	2.0	2.0	1.4
3080	40	23	4.5	3.5	-	-
4508	46	30	5.9	4.3	5.7	3.9
7317	59	43	7.9	5.8	-	-
11445	66	53	10.0	7.2	10.3	8.0
(hr.)						
336.5	70	-	14.1	-	14.3	-
551.0	-	68	-	12.1	-	12.6
1055.0	73	71	26.0	-	26.7	16.5
1585.0	73	72	31.3	-	31.7	-

%

 $[\alpha\text{-MAC}] = 0.113\text{M}$  (Run 19)  $[\alpha\text{-MAC}] = 0.1082\text{M}$  (Run 20) $[\text{Et}_4\text{NCl}] = 0.0641\text{M}$  (Run 19)  $[\text{Et}_4\text{NCl}] = 0.0578\text{M}$  (Run 20)Acid blank =  $6 \times 10^{-4}\text{M}$  (Run 19)  $[\text{HCl}] = 0.0237\text{M}$  (Run 20)T =  $96.00^\circ\text{C}$

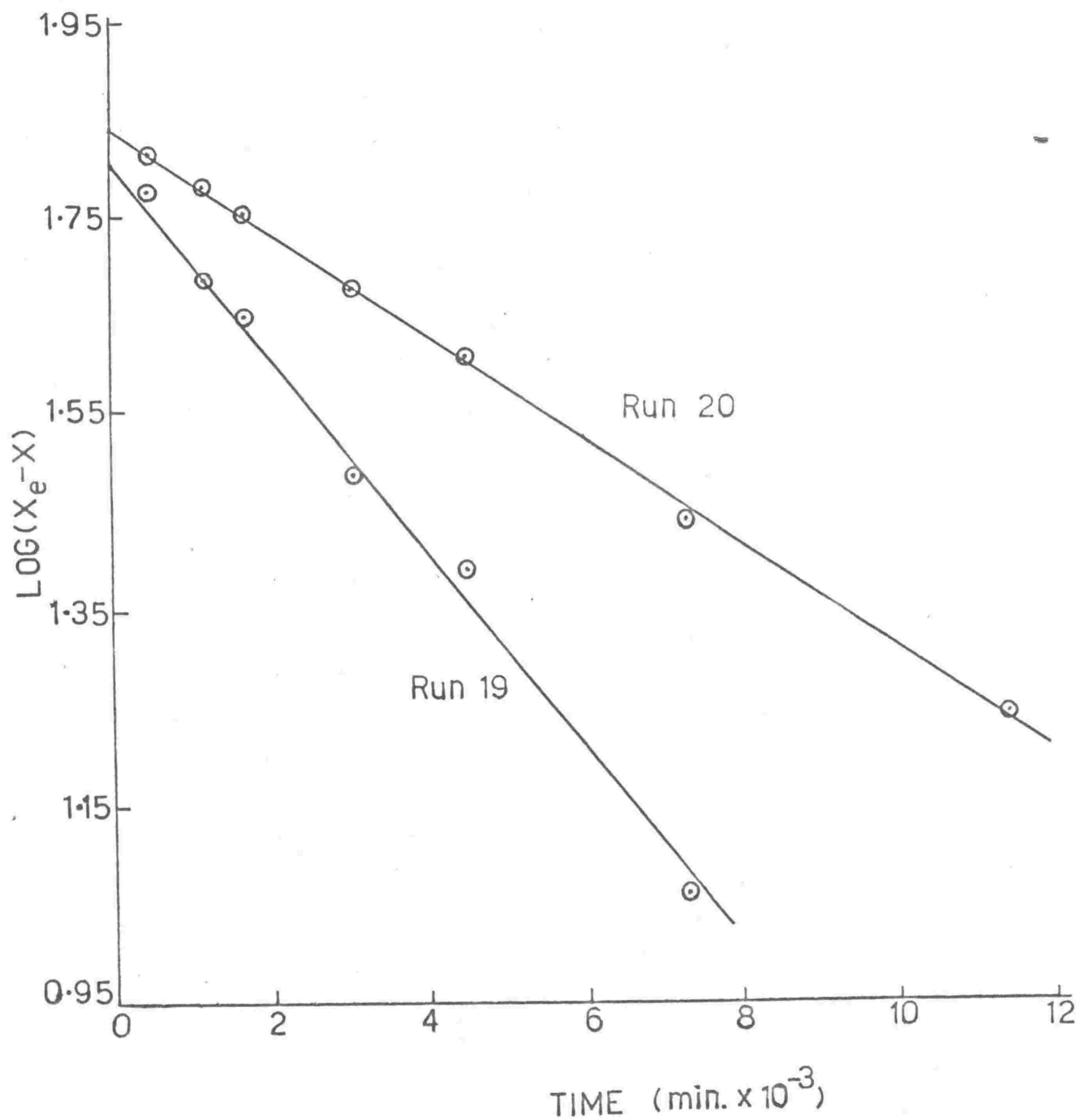
The  $[\alpha\text{-MAC}]$  values shown in the table give the actual concentrations of  $\alpha$ -methylallyl chloride at zero time, i.e., the initial substrate concentration corrected for rearrangement up to zero time.

Approximate pseudo-first-order rate constants for rearrangement were determined by the graphical method of plotting  $\log_{10}(X_0 - X)$  versus time. (See Appendix I). The effect of chloride ion production was neglected. These plots, in which the value for  $X_0$  determined as described in Section XI has been used, are shown in Fig. 3,  $X_0$  being the percentage of  $\delta$ -methylallyl chloride present at equilibrium and  $X$  the percentage present at time  $t$ . Division of the pseudo-first-order rate constant by the concentration of  $\text{Et}_4\text{NCl}$  gives a value for  $k_2'$ , the composite second-order rate constant (see Appendix I), of  $5.89 \times 10^{-5} \text{ M}^{-1}\text{sec.}^{-1}$  for Run 19 and  $3.53 \times 10^{-5} \text{ M}^{-1}\text{sec.}^{-1}$  for Run 20. The pseudo-first-order rate constant for Run 20, when divided by an effective concentration of  $\text{Et}_4\text{NCl}$  equated to  $[\text{Et}_4\text{NCl}]_{\text{eff}} = [\text{Et}_4\text{NCl}]_{\text{act.}} - [\text{HCl}]$ , gives a value for  $k_2'$  of  $5.97 \times 10^{-5} \text{ M}^{-1}\text{sec.}^{-1}$ .

The addition of hydrogen chloride to a reaction mixture therefore causes a decrease in the rate of rearrangement. The magnitude of the rate depression is, assuming a second-order reaction and within the limits of the semi-quantitative data, equivalent to a reduction in the effective concentration of  $\text{Et}_4\text{NCl}$  of the order of the concentration of hydrogen chloride added, i.e., it is what one would expect if the equilibrium constant for the formation of the  $\text{HCl}_2^-$  ion were large and if the ion were relatively inefficient as a nucleophile.

FIG. 3

The  $\alpha$ -MAC/ $\text{Et}_4\text{NCl}$  Rearrangement Reaction  
in AN



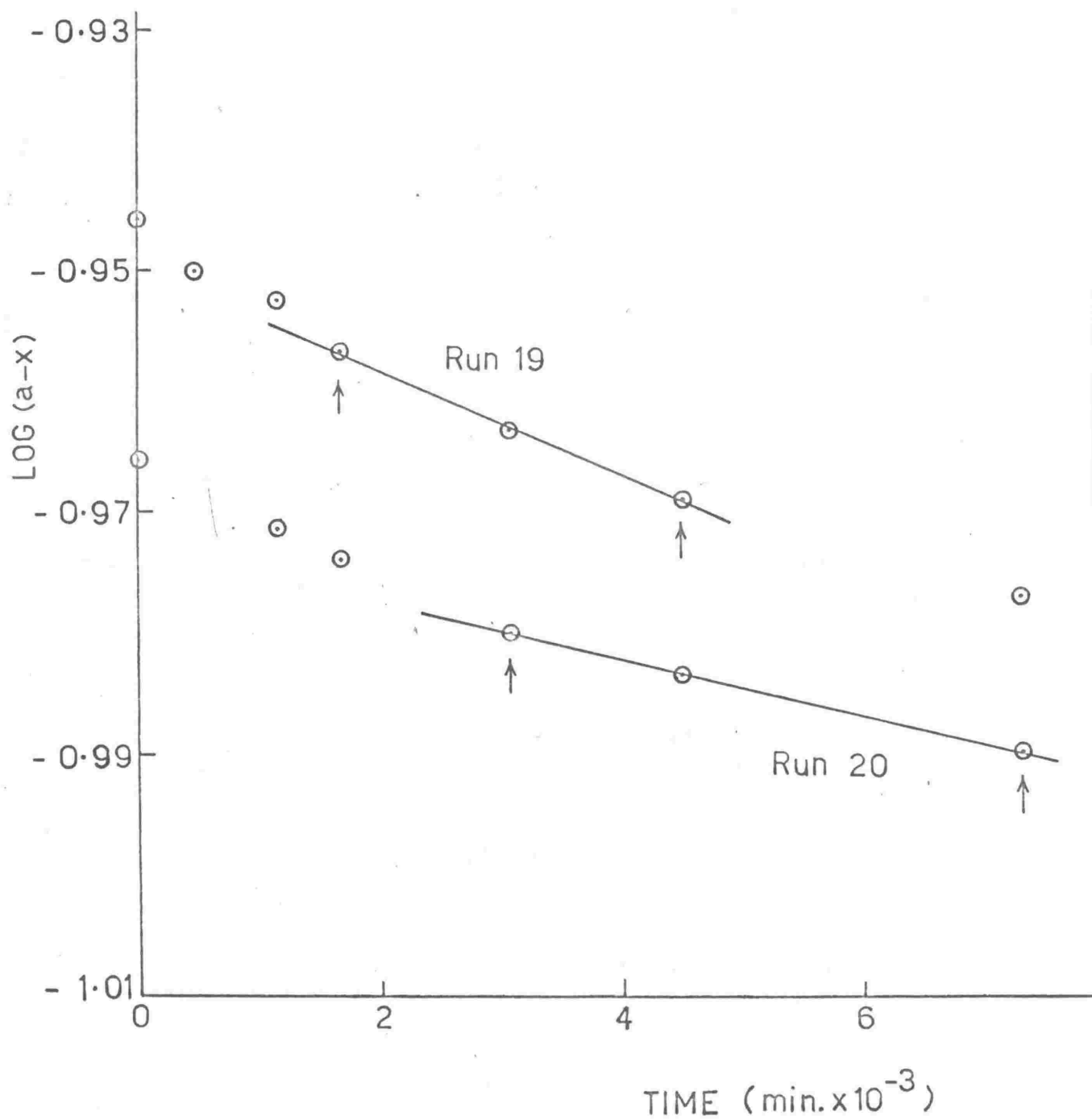
The effect of hydrogen chloride on chloride ion production was less clear. Rearrangement of the substrate to the  $\gamma$ -isomer, probable solvolytic production of chloride ions ( $\sim 1 \times 10^{-3}M$  as determined in Section I) and the comparatively large analysis errors in determining the low concentrations of hydrogen and chloride ions produced during the early stages of the rearrangement reaction, made comparison difficult. However, pseudo-first-order rate "constants" for "elimination" were evaluated by plotting  $\log_{10}(a-x)$  versus time, where  $a$  is the initial concentration of  $\alpha$ -methylallyl chloride and  $(a-x)$  that at time  $t$  assuming only "elimination" and no rearrangement takes place, and determining the slope over the time interval in which the formation of 20%-40% rearranged product does actually occur. Data from acid analyses was used for the plots which are shown in Fig. 4. Values for the rate constants of  $1.66 \times 10^{-7} \text{ sec.}^{-1}$  for Run 19 and  $8.95 \times 10^{-8} \text{ sec.}^{-1}$  for Run 20 were obtained. These values, when corrected for an approximate depression of 20% due to the method of analysis, gave values of 2.08 and  $1.12 \times 10^{-7} \text{ sec.}^{-1}$ . This method of analysing the "elimination" data is discussed in Appendix III.

One can conclude that the effect of hydrogen chloride is to depress, rather than accelerate, the rate of chloride ion production, but the data is not sufficiently accurate to estimate the magnitude of the effect.

The pseudo-first-order rate constants for Run 19, together with an examination of product ratios in the data of Table XVIII, enable an approximate estimate of the relative rates of rearrangement and chloride ion production to be made.

FIG. 4

The  $\alpha$ -MAC/Et<sub>4</sub>NCI Elimination Reaction  
in AN



$$\frac{5.89 \times 10^{-5} \times 0.0641 \times 0.705}{2.08 \times 10^{-7}} \sim 13, \text{ from product ratios } \sim 10.$$

In the time required for about 50% reaction with respect to rearrangement, approximately 4% of the substrate has decomposed as estimated from hydrogen ion production. It was therefore expected that the kinetics of the rearrangement reaction, over at least an initial fraction of the reaction, would be reasonably uncomplicated if the mechanism were bimolecular and if back addition of the products of the postulated elimination reaction were unimportant.

The production of chloride ions is maintained when the rearrangement reaction is near equilibrium and the extra peak on the gas chromatograms is large, suggesting that if the products are from an elimination reaction, back addition to the diene is relatively slow. If back addition were taking place at an appreciable rate, one would expect the rate of chloride ion production to fall off rapidly as the concentration of products builds up and addition takes place. The rate does fall, but this is probably due to removal of  $\alpha$ -methylallyl chloride by the rearrangement reaction.

As a check on the first bromination experiments, 1 ml. of the contents of an "equilibrium" reaction tube was placed in each of two 5 ml. stoppered flasks. To one was added one drop of liquid bromine (excess). After a reaction time of five minutes, samples of each were analysed by gas chromatography. As observed previously, the peak which was suspected to be due to butadiene was absent from the brominated samples.

The contents of the flasks were then mixed together, and after adding one drop of bromine, samples were analysed. The peak was again absent.

The rate of production of chloride ions as estimated by titration with silver nitrate, and the rate of production of hydrogen ions as estimated by titration with sodium hydroxide, are identical within the limits of experimental error. This indicates that the production of chloride ions is accompanied either by the production of hydrogen ions, or by an ion which reacts with water to form hydrogen ions. It also implies that either method of analysis may be used to follow the reaction.

#### IV Investigation of the Rate of Addition of Hydrogen Chloride to Butadiene in Acetonitrile

##### (i) Introduction

To test the validity of the hypothesis that elimination of hydrogen chloride from  $\alpha$ -methylallyl chloride to form butadiene was occurring and that the extra peak on the gas chromatograms was due to the latter, a sample of butadiene was prepared.

A study of the rate of addition of hydrogen chloride to butadiene, in the presence of  $\text{Et}_4\text{NCl}$  of concentrations 0-2 times the concentration of hydrogen chloride, was made at  $96.0^\circ\text{C}$  to see (a) if elimination followed by back addition could contribute significantly to the rate of rearrangement, and (b) the effect of  $\text{Et}_4\text{NCl}$  on the rate of addition. Analyses by gas chromatography, to determine which isomer was formed preferentially, were also carried out.

##### (ii) Experimental

###### (a) Preparation of a Solution of Butadiene in Acetonitrile

The preparation and purification of butadiene is described in Chapter VI.

Butadiene was regenerated from purified butadiene tetrabromide as follows: an appropriate weight of the tetrabromide was mixed thoroughly with zinc powder in the weight ratio 1.5:1, in a 100 ml., two-necked flask fitted with a Leibig condenser. Ethanol (25 ml. of 95%)

was added and the flask was heated so that the ethanol refluxed vigorously.<sup>169</sup> The regenerated butadiene passed through the condenser and a wash trap containing water into a trap cooled in liquid air.

Butadiene for kinetic runs was prepared as above, except that the weight of butadiene tetrabromide required to give a solution of approximately the desired concentration was used.

After heating for one hour, nitrogen was bubbled slowly through the apparatus to displace the butadiene filling it into the collection trap.

The trap containing the solid butadiene was then attached to a chain of apparatus consisting of:

- (a) a wash trap containing a 10% solution of sodium hydroxide, which was cooled in an ice-bath,
- (b) a drying tube containing potassium hydroxide pellets,
- (c) three drying tubes in series containing calcium chloride (fused, anhydrous, 8-16 mesh),
- (d) a 100 ml., B24 flask containing a suitable volume of acetonitrile, which was cooled in an ethanol-bath at  $-35^{\circ}\text{C}$ , and
- (e) a drying tube containing calcium chloride.<sup>169</sup>

All connections were made with dry polythene tubing and rubber bungs where glass joints were unsuitable. The receiver flask was prepared in the dry-box, i.e., the required volume of acetonitrile was added and then an adaptor fitted with drying tubes (calcium chloride) was inserted - the joint being well greased with silicone grease. The contents of the

flask were therefore protected from moisture during all subsequent operations outside the dry-box.

The frozen butadiene was allowed to warm up slowly and bubble through the chain into the acetonitrile. When the trap was at room temperature, a 100 ml. dropping funnel was connected to the previously sealed off inlet to the trap and water was run into it slowly to displace the remaining butadiene. When the water level reached the outlet of the second trap, the flow was stopped and the receiver was disconnected from the chain and allowed to warm up to room temperature, before being transferred to the dry-box.

The purity of these solutions of butadiene in acetonitrile was estimated by v.p.c. analysis for 1-2 hours. Only butadiene and acetonitrile peaks were present.

(b) Preparation of a Solution of Hydrogen Chloride in Acetonitrile

A suitable volume of acetonitrile was added to <sup>a</sup>/100 ml., B24 flask in the dry-box and an adaptor fitted with drying tubes (calcium chloride) was inserted. The flask was then removed and attached to the hydrogen chloride generator.

Hydrogen chloride was generated from "Analar" potassium chloride by slowly adding "Analar" sulphuric acid (conc.) from a dropping funnel. It was dried, by passing it through a trap containing "Analar" sulphuric acid (conc.), before being passed through the calcium chloride tube into the solvent.<sup>130</sup> When sufficient had been dissolved in the solvent, the receiver was disconnected and, while a stream of dry nitrogen was

directed across the mouth of the flask, the adaptor was quickly removed and replaced with a greased stopper. The flask was then transferred to the dry-box. Solutions were prepared the day before use to standardise the effects reported by Janz and Danyluk, Kolthoff and co-workers, and others.<sup>124,170,171</sup>

(c) Preparation of Kinetic Runs

Aliquots (ca. 5 ml.) of each solution were transferred to two small stoppered flasks under the anhydrous conditions of the dry-box, and these were removed for an analysis of the approximate concentrations of the solutions. This enabled the relative volumes of the reagents and acetonitrile, required for a kinetic run, to be calculated.

All the specially dried apparatus for a run was then placed in the dry-box and left for twelve hours. (Overnight).

For those runs in which  $\text{Et}_4\text{NCl}$  was also a reagent, solutions of it in acetonitrile were prepared as described in Section VII.

To the solution of  $\text{Et}_4\text{NCl}$  in a 100 ml. flask, or the flask itself, as appropriate, was added the bulk of the solvent required to give a solution of the desired concentrations of reagents, and to this, the required volume of each prepared solution was added. The mixture was shaken vigorously and then transferred to a 100 ml. dropping funnel fitted with an adaptor and a greased tap and stopper. This funnel was removed from the dry-box and attached to the reservoir of a calibrated automatic pipette, which was protected with drying tubes. A drying tube was substituted for the stopper and the outlet from the adaptor

of the dropping funnel was similarly protected. The reaction mixture was run into the reservoir of the pipette which, after removal of the funnel, was closed with a drying tube.

The reservoir was surrounded by a jacket through which ice water was pumped to reduce loss of butadiene from the solution.

The outlet of the pipette passed through a dried rubber bung which fitted into the mouths of the constricted test tubes used for the runs.

After allowing the reaction mixture to cool down to the jacket temperature (10 min.), aliquots (5.03 ml.) were placed in a series of constricted test tubes. Each one was quickly stoppered with a dried rubber bung and placed in an ice-bath after being filled. The tubes were then frozen in liquid air, sealed, and placed simultaneously in a thermostat at  $96.0^{\circ}\text{C}$  to react. Ampoules were quenched at various times by plunging them into an ice-water bath.

(d) Analysis of Kinetic Runs

(1) Acid Analyses and Chloride Ion Analyses

The ampoules were cooled in liquid air and cracked open with a hot, glass point. The contents of each ampoule were then added to 30 ml. of *n*-pentane and 15 ml. of water in a separating funnel and the ampoule was rinsed with water (<5 ml.). After vigorous shaking to extract the butadiene and addition products into the organic layer, the aqueous layer was run off into a 150 ml. conical flask and titrated

with sodium hydroxide solution (0.01365N) for hydrogen ions, using bromothymol blue as indicator.

The solution was then evaporated down, while being flushed with nitrogen, before being titrated with silver nitrate (0.01618N) by the potentiometric method, to determine the total concentration of chloride ions. Initial acid and chloride ion concentrations were determined in an identical way.

## (2) Butadiene Analyses

Each ampoule was cooled and shaken in liquid air until the contents were semi-frozen. It was then opened and the contents were poured quickly into 40 ml. of a bromine in methanol solution + 25 ml. of dry methanol in a 150 ml. stoppered flask. The ampoule was then rinsed with methanol and the flask was stoppered and gently shaken.

At the same time, 5 ml. of acetonitrile containing hydrogen chloride at the reaction mixture concentration, was added to a similar solution of bromine in methanol to act as a blank, i.e., to correct for any reaction of the bromine with methanol or acetonitrile during the bromination period and also for volatility losses.

Addition appeared to be rapid and from tests made by titrating successively blanks and reaction mixtures versus time, it was concluded that thirty minutes was adequate for complete reaction.

The excess bromine was estimated in both blanks and reaction mixtures by adding solid potassium iodide followed by water and titrating the liberated iodine with sodium thiosulphate (0.1001N).<sup>134</sup> The difference in titre between the blank and

the reaction mixture was judged to be proportional to the butadiene concentration. It was therefore not necessary to know the exact concentration of the solution of bromine in methanol used.

Analyses of ampoules filled at the beginning and end of the filling period agreed within experimental error, so volatility losses while filling the tubes were negligible.

In calculating the concentration of butadiene it was assumed that effectively four equivalents of bromine were removed by each butadiene molecule, i.e., that no addition of hydrogen chloride or bromide took place and that the reactions:



and possibly:



proceed to completion in the presence of excess bromine.

To test for reversibility of reaction (a), a solution of butadiene tetrabromide (ca. 0.03M) and hydrogen chloride in acetonitrile was prepared and a 5 ml. aliquot was added to 20 ml. of methanol. Solid potassium iodide (0.5 gm.) was added and the solution was left for 30 minutes before being titrated with sodium thiosulphate solution (0.1001N). The titre compared with that of a blank was 0.17 ml., and after a further 40 minutes the solution was still colourless, so that reversibility of tetrabromide formation appeared to be negligible over this reaction time.

The literature gave rather nebulous information on the above assumptions, but as a preliminary experiment had indicated that addition

of hydrogen chloride to butadiene in the presence of  $\text{Et}_4\text{NCl}$  was very slow, it was decided that, despite the assumptions and approximations of the method, it gave at least the lower limit of the butadiene concentration, and therefore further investigation and refinement of the butadiene analysis method was postponed until after some preliminary runs.

Because bromine can also add to the unsaturated products of the addition reaction, analyses for butadiene could only be carried out to confirm an absence of appreciable reaction as indicated by the other two methods.

### (3) V.P.C. Analyses

Analyses for the presence and relative amounts of  $\alpha$ - and  $\gamma$ -methylallyl chloride were carried out by removing two (2  $\mu\text{l.}$ ) samples from each tube destined for acid analysis and putting them through the gas chromatograph.

Three kinetic runs were carried out at  $96.0^\circ\text{C}$  with  $\text{Et}_4\text{NCl}$  concentrations:  $[\text{Et}_4\text{NCl}] = 0$ ,  $[\text{Et}_4\text{NCl}] \sim [\text{HCl}]$ ,  $[\text{Et}_4\text{NCl}] \sim 2[\text{HCl}]$ .

Acid analysis and chloride ion analysis were used to follow the addition reaction and estimate its rate. V.P.C. analysis was used to detect the formation of addition products and to estimate the isomer ratio and butadiene analysis was used to check that an absence of reaction as indicated by the other methods also meant an absence of reaction of the butadiene.

(e) Investigation of the Butadiene Analysis Method

Subsequent to the performance of the above runs the bromination method of analysing for butadiene was checked, by preparing a solution of butadiene in methanol of known concentration by weight and analysing aliquots by reacting them with bromine under various conditions.

Experimental

Butadiene was regenerated from the tetrabromide, washed with water and dried with calcium chloride, as described previously, before being collected in a small graduated tube cooled in a Dry Ice-ethanol mixture and protected with drying tubes from atmospheric moisture. The volume collected was 1-2 ml.

The adaptor of the tube was then connected to that of a 100 ml. flask of known weight containing a known weight of "Analaar" methanol (ca. 75 ml.), which was cooled in Dry Ice, and the butadiene was allowed to pass over into the flask and condense from the outlet of the adaptor (which was just above the surface of the solvent) into the solvent. The flask was then stoppered and shaken, and brought up to ambient temperature before being weighed. From the weights of butadiene and methanol the concentration of the solution was calculated.

Aliquots (5 ml.) of the solution were then added to an excess of bromine in methanol (20 ml. of bromine in methanol solution + 30 ml. of methanol), and allowed to react for various times. The solutions were then titrated with standard sodium thiosulphate solution

(0.0998N), after adding excess potassium iodide. In each case the titre was compared with that for a "blank", consisting of the reaction medium only. (A).

An aliquot of this "stock solution" of butadiene in methanol was then diluted (25 ml.  $\longrightarrow$  100 ml.) in a volumetric flask, to give a solution of approximately the same concentration as those used in the kinetic runs. Aliquots of this solution (5 ml.) were then analysed under various reaction conditions. The concentrations of the reagents in the bromination mixtures were kept similar to those used in analyses during the kinetic runs. Analyses of aliquots of butadiene solution with reaction media consisting of bromine in methanol ( $B_2$ ), bromine + acetonitrile + hydrogen chloride + chloride ions in methanol ( $B_1$ ), and bromine + acetonitrile + hydrogen chloride in methanol were carried out, the titres in all cases being compared with those of the appropriate "blanks".

Reversibility of the bromination reaction forming butadiene tetrabromide was tested for again, by adding 0.1 gm. of solid tetrabromide to 35 ml. of methanol in each of two stoppered flasks and adding 1.7 gm. of solid potassium iodide to one and 25 ml. of an aqueous solution (0.4M) to the other. The effect of hydrogen chloride on these mixtures was also examined.

Duplicate preparations of a stock solution of butadiene in methanol were carried out.

### Results and Discussion

The calculated and experimental concentrations of the "stock" and diluted solutions of butadiene in methanol are shown in Table XVIII. The experimental concentrations of the "stock" solutions, determined by bromination of the solutions, are 15-17% lower than the concentrations calculated from the known weights of butadiene and solvent, while the concentrations of the diluted solutions (i.e., the solutions with butadiene concentrations approximately equal to those used in the kinetic runs) are 18-22% lower than the calculated values. Therefore, concentration by weight  $\approx$  1.25 times concentration by bromination.

The addition of hydrogen chloride and acetonitrile or hydrogen chloride, acetonitrile and chloride ions had no effect on the analyses except to cause a marked deterioration in the sharpness of the end-point of the titrations, so that they had to be performed rapidly.

Butadiene tetrabromide was quite stable in the presence of potassium iodide in methanol and aqueous methanol over a period of 19 hours and, after adding hydrogen chloride, 1% decomposition had occurred after 27 hours. Therefore, any reversible reaction involved in this method of analysis must involve products other than the tetrabromide.

The discrepancy between the calculated and experimental concentrations appeared too large to be attributed entirely to volatility losses during the analyses and was probably due, at least partly, to reversible side-reactions. This view derived some support from the observation that the end-point of titrations faded quite rapidly and

TABLE XVIII

Analysis Type	Calculated Normality	Experimental Normality	$\frac{\Delta N}{N}$
A (Prep. I)	0.928	0.791	0.15
B <sub>1</sub>	0.232	0.192	0.18
B <sub>2</sub>	0.232	0.188	
A (Prep. II)	1.19	0.984	0.17
B <sub>1</sub>	0.297	0.233	0.22
B <sub>2</sub>	0.297	0.233	

A = data for the stock solutions

B<sub>1</sub> = analysed in the presence of acetonitrile, HCl and Cl<sup>-</sup> ions

B<sub>2</sub> = analysed as for A

continued doing so if the solutions were continuously titrated, whereas, if they were left standing for periods of up to a week, a volume of titre equivalent to only 5-10% of the butadiene concentration was required for the liberated bromine. The above titres were estimated relative to those of the "blanks".

Therefore, although the bromination method of analysis used for the runs would not be satisfactory for a precise kinetic study, it was adequate for the demonstration, by the runs carried out above, of the slow rate of addition of hydrogen chloride to butadiene, which is discussed next in this section. The possibility of the values for the initial concentration of butadiene being 20% low affects neither the validity of the demonstration nor of the conclusions reached. Further work on either the kinetics of the reaction or the method of diene analysis was therefore terminated at this stage.

#### (iii) Results and Discussion

Analysis by gas chromatography of solutions of butadiene in acetonitrile, prepared by regenerating butadiene from pure butadiene tetrabromide, showed that butadiene has a retention time identical with that of the unknown peak observed in the rearrangement runs with  $\alpha$ -methylallyl chloride. The addition of excess bromine resulted in the disappearance of the butadiene peak from the chromatogram. The unknown peak was therefore considered to be identified as being due to butadiene.

V.P.C. analysis for 1-2 hr. showed no other peaks, which was taken to be proof of the purity of the regenerated butadiene (retention time ca. 0.5 min.).

The kinetic and v.p.c. results for Runs 21, 22 and 23 are shown in Tables XIX, XX and XXI.

In the absence of  $\text{Et}_4\text{NCl}$  (Run 21) addition occurs slowly, accompanied by the production of a brown decomposition product, as the reaction mixture turns from colourless to brown and finally deposits a black solid on the walls of the ampoules. In the presence of  $\text{Et}_4\text{NCl}$ ,  $[\text{Et}_4\text{NCl}] \sim [\text{HCl}]$  (Run 22), the rate of addition is greatly reduced and much less decomposition occurs as the reaction mixture only turns a pale yellowish brown. In Run 23, where  $[\text{Et}_4\text{NCl}] \sim 2[\text{HCl}]$ , the rate of addition is reduced still further and here no decomposition, as indicated by the development of colour in the reaction mixture, was observed.

These observations suggest that the development of colour in the reaction mixture is due to acid-catalysed polymerisation of the unsaturated compounds present. It is also possibly evidence for the presence of protonated intermediates, which can initiate polymerisation as well as add a chloride ion.<sup>129,136a,136b</sup>

The gas chromatograms for all three runs showed the appearance of a small peak as the reaction proceeded, which was identified as  $\alpha$ -methylallyl chloride by running an authentic sample; another small peak, which was identified as  $\gamma$ -methylallyl chloride by the method above, appeared as the reaction proceeded still further. Percentages

TABLE XIX

Run 24. The Butadiene/HCl Reaction in Acetonitrile (96°C)

Time (hr.)	ml. AgNO <sub>3</sub> (0.01618N)	ml. NaOH (0.01365N)	$\Delta[H^+]$ (10 <sup>3</sup> M)	$\Delta[Cl^-]$ (10 <sup>3</sup> M)	V.P.C.
0.0	6.35	7.53	0.0	0.0	-
1.17	6.37	7.40	0.3	0.0	-
5.55	-	7.23	0.8	-	$\alpha$ (sm.)
17.4	6.10	7.05	1.3	0.8	( $\alpha + \gamma$ )(sm.)
44.0	5.70	6.69	2.3	2.1	$\alpha + \gamma$ (sm.)
92.3	5.24	6.31	3.3	3.6	$\alpha + \gamma$
149.6	4.69	5.60	5.2	5.3	$\alpha + \gamma$
238.0	4.23	5.06	6.7	6.8	$\sim 40\% \gamma$
333.0	3.78	4.52	8.2	8.3	$\sim 50\% \gamma$
548.8	3.19	3.99	9.6	10.2	$\sim 50\% \gamma$

115.

[Butadiene] = 0.0385M

 $\alpha$  =  $\alpha$ -Methylallyl Chloride

[HCl] = 0.0204M

 $\gamma$  =  $\gamma$ -Methylallyl Chloride

T = 95.97°C

sm. = small

TABLE XX

Run 22. The Butadiene/HCl/Et<sub>4</sub>NCl Reaction in Acetonitrile (96°C.)

Time (hr.)	ml. AgNO <sub>3</sub> (0.01618N)	ml. NaOH (0.01365N)	$\Delta[H^+]$ (10 <sup>-3</sup> M)	$\Delta[Cl^-]$ (10 <sup>-3</sup> M)	V.P.C.
0.0	28.80	17.21	0.0	0.0	-
21.6	28.82	17.20	0.0	0.0	-
73.7	28.63	17.07	0.4	0.5	$\alpha$
148.3	28.47	16.78	1.2	1.1	$\alpha + \gamma$ (sm.)
217.6	28.08	16.63	1.6	2.3	$\alpha + \gamma$
359.1	27.70	16.08	3.1	3.5	$\sim 40\% \gamma$

116.

 $\Delta[\text{Butadiene}] = 2.0 \times 10^{-3} \text{M}$  $[\text{Butadiene}] = 0.0421 \text{M}$  $[\text{HCl}] = 0.0467 \text{M}$  $[\text{Et}_4\text{NCl}] = 0.0459 \text{M}$  $T = 95.97^\circ\text{C}$

TABLE XXI

Run 23. The Butadiene/HCl/Et<sub>4</sub>NCl Reaction in Acetonitrile (96°C)

Time (hr.)	ml. AgNO <sub>3</sub> (0.01618N)	ml. NaOH (0.01365N)	$\Delta[H^+]$ (10 <sup>-3</sup> M)	$\Delta[Cl^-]$ (10 <sup>-3</sup> M)	ml. "Thio." (0.1001N)	V.P.C.
0.0	29.75	13.44	0.0	0.0	6.32	-
42.2	29.64	13.50	0.0	0.3	6.18	-
138.3	29.64	13.25	0.5	0.3	6.22	-
234.7	29.46	13.10	0.9	0.9	6.09	$\alpha$
357.7	-	12.90	1.5	-	6.28	$\alpha$
403.3	-	-	-	-	6.20	-
478.1	29.28	12.79	1.8	1.5	-	$\alpha + \gamma$
598.5	29.12	12.63	2.2	2.0	-	$\alpha + \gamma$
744.8	28.93	12.58	2.3	2.6	-	$\sim 60\% \gamma$

117.

[Butadiene] = 0.0314M

[HCl] = 0.0365M

[Et<sub>4</sub>NCl] = 0.0592M

T = 95.96°C

of the  $\gamma$ -isomer present were estimated when the peak sizes became large enough for reasonable accuracy and these are shown in the Tables. Thus, even in the rearranging medium of Run 23 the equilibrium value of about 70%  $\gamma$ -isomer was not reached. Kinetic control of the products of the addition reaction is not unexpected in acetonitrile as this solvent does not particularly favour ionisation reactions, by comparison with protic solvents.<sup>8,15</sup>

The "thiosulphate" titre in Run 23 remains practically constant indicating little reaction has occurred to form either methylallyl chlorides or polymer. A small decrease of about 0.3 ml. would be expected from comparison with the other analyses, but addition of bromine to the chlorides and errors involved in the unsophisticated analysis method must have masked this.

Considering the kinetic data in more detail, in the time required for approximately 70% of the theoretical rearrangement of  $\alpha$ -methylallyl chloride at 96.0°C to occur (with substrate/nucleophile concentrations of 0.1/0.06M), i.e., 120 hr., only about 11%, 2% and 1% of the butadiene (of concentration 0.03-0.04M) in Runs 21, 22 and 23 respectively, has reacted and the addition product is predominantly the  $\alpha$ -isomer. It is therefore obvious that back addition of the products of the elimination reaction can make no significant contribution to the mechanism of rearrangement in the presence of  $\text{Et}_4\text{NCl}$ , the latter evidently combining with hydrogen chloride to form the dihalide ion, which reduces the availability of the electrophile for addition to butadiene to a very low level. This conclusive evidence against the

elimination-addition mechanism resulted in the termination, at this stage, of work on the addition of hydrogen chloride to butadiene in acetonitrile - an interesting study in itself.

The elimination-addition mechanism tends to operate when both elimination and back addition are faster than direct substitution, due for example to steric hindrance to nucleophilic attack or facile removal of a proton.<sup>134,137</sup>

The preceding work has shown that neither an acid-catalysed, nor an elimination-addition mechanism can contribute significantly to the rate of rearrangement of  $\alpha$ -methylallyl chloride in the presence of  $\text{Et}_4\text{NCl}$ .

The character of the side-reaction is considered to be established as being due to elimination of hydrogen chloride to form butadiene, by (a) chloride ion analysis, (b) hydrogen ion analysis, (c) bromination of the compound responsible for the unknown peak and (d) confirmation by v.p.c. analysis of the identical retention times of the unknown compound and an authentic sample of butadiene.

A precise study of the rates of the rearrangement and elimination reactions of  $\alpha$ -methylallyl chloride in acetonitrile and the effect of  $\text{Et}_4\text{NClO}_4$  on these was planned, prior to a precise study of the kinetics of rearrangement in the presence of  $\text{Et}_4\text{NCl}$ .

V The Rearrangement and Elimination Reactions of  $\alpha$ -Methylallyl Chloride in Acetonitrile

(i) Introduction

A study of the rearrangement and elimination reactions of  $\alpha$ -methylallyl chloride in acetonitrile and the effect of an inert electrolyte on both of these was made at 96.0°C.

Tetraethylammonium perchlorate ( $\text{Et}_4\text{NClO}_4$ ) was chosen as the inert electrolyte, because it is highly dissociated in acetonitrile,<sup>138</sup> and as perchloric acid is a strong acid,<sup>124</sup> while the perchlorate ion is a very weak nucleophile,<sup>113</sup> it could not have any specific effect on either reaction.

The  $\text{S}_\text{N}1$  mechanism of rearrangement had not been excluded and although the catalytic effect of chloride ions appeared too large to be a salt effect of the "ionic-strength" type, i.e., causing an increase in the rate of ionisation of the substrate,<sup>125,140,141</sup> a knowledge of the effect of an inert electrolyte was important to clarify this.

Some idea of the magnitude of the salt effect of  $\text{Et}_4\text{NClO}_4$  on an  $\text{S}_\text{N}1$  or E1 reaction in acetonitrile may be derived from the work of Pocker and Kevill, who obtained a 64% increase in  $k_1$  for the solvolysis of 2-octyl bromide on adding 0.0620M  $\text{Et}_4\text{NClO}_4$ .<sup>113</sup>

The effect of added hydrogen chloride on the rate of rearrangement in the presence of  $\text{Et}_4\text{NCl}$  is effectively a test of whether catalysis by chloride ions is specific, or a general salt effect,

because, if the former were true, dihalide ion formation should affect the rate, while if the latter were true, the rate should be unaffected as the ionic strength remains essentially constant.

A knowledge of the effect of an inert electrolyte on the rate of elimination was also important, to enable an estimation of the specific effect of chloride ions on this reaction to be made.

#### (11) Procedure

Two reaction mixtures were prepared. That for Run 24 consisted of  $\alpha$ -methylallyl chloride in acetonitrile and that for Run 25 consisted of the above and  $\text{Et}_4\text{NClO}_4$  (ca. 0.05M). (See Section VII for the preparation of reaction mixtures and Chapter VI for the preparation and purification of  $\text{Et}_4\text{NClO}_4$ ). The method of drying the  $\text{Et}_4\text{NClO}_4$  was the same as that for  $\text{Et}_4\text{NCl}$ , except that the drying pistol was charged with potassium hydroxide pellets instead of phosphorus pentoxide.

A solution of  $\text{Et}_4\text{NClO}_4$  of known concentration in acetonitrile was prepared as follows: a stoppered flask containing the boat in which the  $\text{Et}_4\text{NClO}_4$  was to be dried, was weighed and placed in the dry-box, after removing the boat. A sample of  $\text{Et}_4\text{NClO}_4$  of approximately the weight required was placed in the boat and dried. After drying, the boat containing the  $\text{Et}_4\text{NClO}_4$  was transferred in the dry-box to the weighed flask, which was then reweighed to give the weight of dry  $\text{Et}_4\text{NClO}_4$ . The flask was returned to the dry-box and the required volume of solvent was added. Reweighing of the flask enabled the

concentration of the solution to be calculated from the known weights of electrolyte and solvent.

The runs were carried out in sealed tubes of 5 ml. capacity. After quenching, duplicate samples of the contents of each tube were put through the gas chromatograph, which was calibrated with a 10% and a 15% gravimetric standard, (see Section VII) and the percentage of  $\gamma$ -methylallyl chloride present was determined. A 5 ml. aliquot was then extracted with 30 ml. of *n*-pentane and 25 ml. of water to remove the allylic halides. The aqueous layer, after separation, was titrated with sodium hydroxide (0.01365N) to the phenolphthalein endpoint. "Blanks" corrected for acid production at zero time.

The concentration of hydrogen ions produced in any reaction period was taken to be equal to the concentration of chloride ions produced.

### (iii) Results and Discussion

The results are shown in Tables XXII and XXIII and the rate constants in Table XXIV.

Rate constants were calculated from the equation:

$$k_1' = \frac{2.303}{t} \log_{10} \frac{X_e - X_0}{X_e - X_t}$$

for rearrangement and:

$$k_1 = \frac{2.303}{t} \log_{10} \frac{a}{a-x}$$

TABLE XXII

Run 24. Reactions of  $\alpha$ -Methylallyl Chloride in Acetonitrile ( $96^{\circ}\text{C}$ )

Time (hr.)	ml. NaOH (0.01365N)	$[\text{H}^+]$ ( $10^{-3}\text{M}$ )	$\left(\frac{\alpha}{\delta}\right)_{\text{std.}}$	$\left(\frac{\alpha}{\delta}\right)_{\text{R.M.}}$	$K_{(\text{cal.})}$	% $\delta$ -MAC	Colour of Sol'n
0.0	0.30	0.0	-	-	-	-	colourless
45.4	0.46	0.5	-	-	-	< 0.5	"
97.2	0.82	1.4	-	-	-	< 1.0	"
165.7	1.37	2.9	1.70	14.6	4.74	1.42	"
267.0	1.60	3.6	1.71	8.80	4.71	2.36	v.p. yellow
411.1	1.77	4.0	1.81	4.25	4.45	5.02	"
529.8	2.48	6.0	1.57	2.02	5.13	8.80	p. yellow
601.0	3.28	8.1	1.89	1.82	4.88	10.12	"
885.3	4.57	11.7	0.997	0.715	5.49	20.3	"

[ $\alpha$ -MAC] = 0.1085M $K_{(\text{cal.})}$  = the calibration constant of the GLC detectorT =  $95.93^{\circ}\text{C}$  $\left(\frac{\alpha}{\delta}\right)$  = the peak area ratio of the isomers

v. = very

p. = pale

std. = standard

R.M. = reaction mixture

TABLE XXIII

Run 25. Reactions of  $\alpha$ -Methylallyl Chloride/ $\text{Et}_4\text{NClO}_4$  in Acetonitrile ( $96^\circ\text{C}$ )

Time (hr.)	ml. NaOH (0.01365N)	$[\text{H}^+]$ ( $10^{-3}\text{M}$ )	$\left(\frac{\alpha}{\delta}\right)_{\text{std.}}$	$\left(\frac{\alpha}{\delta}\right)_{\text{R.M.}}$	$K_{\text{(cal.)}}$	% $\alpha$ -MAC	Colour of Sol'n
0.0	0.25	0.0	-	-	-	-	Colourless
45.4	0.39	0.4	-	-	-	< 0.5	"
97.2	0.79	1.5	-	-	-	< 1.0	"
165.7	1.27	2.8	1.70	12.7	4.74	1.63	"
267.0	1.38	3.1	1.71	7.35	4.71	2.81	v.p. yellow
411.1	1.86	4.4	1.81	3.58	4.45	5.91	"
529.8	2.13	5.1	1.57	1.90	5.13	9.30	p. yellow
601.0	2.90	7.2	1.89	1.61	4.88	11.29	"
885.3	3.94	10.1	0.997	0.697	5.49	20.7	"

$$[\alpha\text{-MAC}] = 0.0977\text{M}$$

$$[\text{Et}_4\text{NClO}_4] = 0.0507\text{M}$$

$$T = 95.93^\circ\text{C}$$

TABLE XXIV

Rate Constants for Runs 24 and 25

Time (hr.)	$10^8 k_1^E$ (sec. <sup>-1</sup> ) (Run 24)	$10^8 k_1^E$ (sec. <sup>-1</sup> ) (Run 25)	$10^8 k_1'$ (sec. <sup>-1</sup> ) (Run 24)	$10^8 k_1'$ (sec. <sup>-1</sup> ) (Run 25)
45.4	2.96	2.54	-	-
97.2	3.75	4.41	-	-
165.7	4.56	4.86	3.44	3.94
267.0	3.55	3.35	3.55	4.24
411.1	2.55	3.11	5.00	5.91
529.8	2.99	2.81	6.99	7.41
601.0	3.60	3.54	7.16	8.07
885.3	3.58	3.43	10.66	10.91

 $k_1^E$  = the rate constant for elimination $k_1'$  = the composite rate constant for rearrangement

for elimination,  $k_1'$  and  $k_1$  being the first-order rate constants for rearrangement and elimination respectively. (See Appendices I and III for definitions of the other symbols). The effect of the rearrangement reaction on the calculations for the elimination reaction and vice versa were neglected.

The addition of  $\text{Et}_4\text{NClO}_4$  to a reaction mixture appears to cause a small increase of approximately 10% in the rate of rearrangement, while the rate of elimination is, within the limits of experimental error, independent of the presence of  $\text{Et}_4\text{NClO}_4$ . The rate of rearrangement in the presence of  $\text{Et}_4\text{NCl}$  (0.0641M) is some  $10^2$  times faster than the rates of these reactions (cf. Run 19). The rate constant for rearrangement increases markedly with time in both runs, increasing by a factor of three in the time interval during which the concentration of hydrogen chloride increases by a factor of four. It seems reasonable, therefore, to correlate the catalysis of the rearrangement reaction with the production of hydrogen chloride by the elimination reaction.

Electrophilic catalysis, by specific interaction of hydrogen chloride with the rate-determining ionisation step of an  $\text{S}_{\text{N}}1'$  reaction, contradicts the observed results of the relative effects of  $\text{Et}_4\text{NCl}$  and  $\text{Et}_4\text{NClO}_4$  on the rate of rearrangement (cf. Run 19). There remains the possibility that hydrogen chloride is such a powerful promoter of ionisation, that it has the effect observed, on an otherwise negligibly slow ionisation rate.

Bimolecular attack by chloride ions from the dissociation of hydrogen chloride is a possible mechanism, while bimolecular attack by the hydrogen chloride molecule itself is another possibility. The latter mechanism could involve hydrogen-bonding facilitation of leaving group departure accompanying nucleophilic attack by the chlorine end of the dipole. This mechanism is analogous to that suggested for the reaction of allylic halides with secondary amines.<sup>69,75</sup>

Using the expression:  $\frac{2\Delta k_1'}{\Delta[\text{HCl}]}$  to calculate values for  $k_2'$

from the effect of acid production on  $k_1'$ , and taking time intervals between the 165.7 hr. analysis and the three final analyses, values of  $1-2 \times 10^{-5} \text{ M}^{-1} \text{ sec.}^{-1}$  are obtained, which are of the same order of magnitude as those for the  $\text{Et}_4\text{NCl}$  catalysed rearrangement reaction. (Run 19). This suggests that "free" chloride ion attack is incapable of accounting for the rate increases observed, as the concentration of such ions should be only a small fraction of the total acid concentration. Using the dissociation constant data for hydrogen chloride in acetonitrile, of Kolthoff and co-workers,<sup>124</sup> the degree of dissociation of hydrogen chloride by either of the processes:



is only of the order of  $5 \times 10^{-4}$  at  $25^\circ\text{C}$ , with  $0.01\text{M}$  hydrogen chloride and assuming activity coefficients to be unity. This implies a negligible contribution from "free" chloride ions to catalysis of the rearrangement reaction at  $96.0^\circ\text{C}$ .

No significant autocatalysis of the elimination reaction was observed, which is not unexpected as the catalytic effect of chloride ions on this reaction is much smaller than that on rearrangement (see Run 19), while the nucleophilicity of hydrogen chloride towards hydrogen would be expected to be negligible. The mechanism of the solvolytic elimination reaction is not clear. The present experiment has ruled out a unimolecular, or solvent-assisted E2 mechanism, unless the salt effect is very small, i.e., the results are not in accord with the charge separation required to form either of the transition states for the above mechanisms. Moreover, electrophilic catalysis of a unimolecular mechanism would be expected, with a similar effect for both the rearrangement and the elimination reaction.

The elimination rate constants for both runs show a minimum and, although small trends are of doubtful significance due to the large errors in determining rate constants over the first 10% of a reaction, this trend is somewhat greater than experimental error and may be due to solvolysis and elimination changing over to elimination and hydrogen chloride assisted elimination, by a mechanism other than the conventional ones mentioned above. An extension of the data on elimination in the presence of  $\text{Et}_4\text{NCl}$  was needed to provide more information about the effect of nucleophiles on the rate of elimination.

Some discoloration of the reaction mixtures occurred after prolonged heating at  $96^\circ\text{C}$ , due probably, to polymerisation of the isomers and butadiene.

No evidence so far contravenes the assignment of an  $S_N2'$  mechanism to the chloride ion catalysed rearrangement reaction, as it is obvious that a general salt effect on an  $S_N1'$  mechanism cannot account for the specific effect of chloride ions. The mechanism of catalysis by hydrogen chloride is not relevant to the situation in the presence of excess  $Et_4NCl$ , as the hydrogen chloride should be largely in the form of dihalide ions.

A precise study of the kinetics of the rearrangement reaction was therefore planned.

VI A Precise Study of the Et<sub>4</sub>NCl Catalysed Rearrangement Reaction of  $\alpha$ -Methylallyl Chloride in Acetonitrile

(i) Introduction

A precise study of the rate of chloride ion catalysed rearrangement was made at 96.0°C. The rate of elimination was also determined. Duplicate runs were carried out to test the reproducibility of the results.

(ii) Procedure

The technique used was the same as that used for all subsequent rearrangement runs and it is described in detail in Section VII.

Quantitative v.p.c. analyses were carried out to determine the isomer ratios, the detector being calibrated with gravimetric standards as described in Section VII. Derivation of the rate equation for a reversible first-order or pseudo-first-order reaction and definitions of the symbols used are given in Appendix I. Values for  $k_1'$ , the pseudo-first-order rate constant for rearrangement, were calculated by substituting the experimental data in the rate equation. Possible perturbations due to the concurrent minor elimination reaction were neglected. The value for the equilibrium constant determined as described in Section XI, has been used in the calculations of the rate constants.

Acid analyses were performed as described in Section V. These were checked in some cases by chloride ion analyses.

TABLE XXV

Run 26. The  $\alpha$ -Methylallyl Chloride/Et<sub>4</sub>NCl Reactions in Acetonitrile (96°C)

Time (min.)	% $\alpha$ -MAC	$\log_{10}(X_{\infty}-X)$ ( $X_{\infty} = 70.5$ )	$10^6 k_1'$ (sec. <sup>-1</sup> )	ml. NaOH (0.01365N)	[H <sup>+</sup> ] (10 <sup>-3</sup> M)	$10^7 k_1^E$ (obs.) (sec. <sup>-1</sup> )
0	1.57	1.8384	-	0.18	0.0	-
225	4.09	1.8223	2.75	0.29	0.3	-
500	6.59	1.8056	2.52	0.42	0.6	1.69
1034	12.11	1.7664	2.67	0.70	1.4	1.86
1855	20.3	1.7007	2.85	-	-	-
1935	-	-	-	1.08	2.4	1.73
3111	29.3	1.6149	2.76	1.42	3.4	1.52
4727	39.3	1.4942	2.79	2.00	5.0	1.48
6955	47.4	1.3636	2.62	2.50	6.3	1.27
11678	57.4	1.1173	2.37	2.60	9.3	1.14

13.

$$\begin{aligned}
 [\alpha\text{-MAC}] &= 0.123M \\
 [\text{Et}_4\text{NCl}] &= 0.0485M \\
 T &= 95.83^\circ\text{C} \\
 \text{Mean (6) } k_1' &= 2.72 \pm 0.12 \times 10^{-6} \text{ sec.}^{-1} \\
 k_2' &= 5.61 \times 10^{-5} \text{ M}^{-1} \text{ sec.}^{-1} \\
 k_2'^{\alpha} &= 3.95 \times 10^{-5} \text{ M}^{-1} \text{ sec.}^{-1}
 \end{aligned}$$

TABLE XXVI

Run 27. The  $\alpha$ -Methylallyl Chloride/Et<sub>4</sub>NCl Reactions in Acetonitrile (95°C)

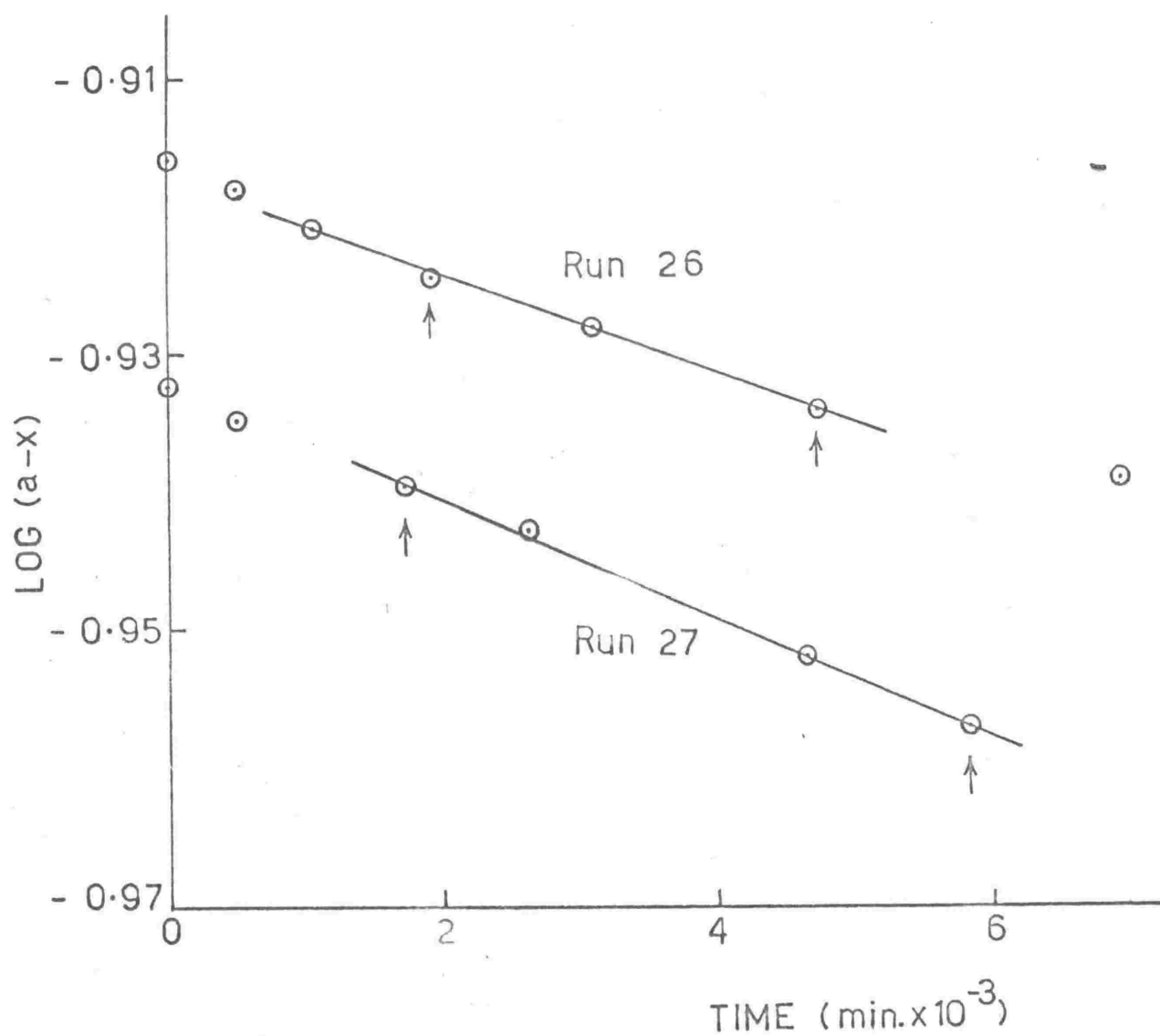
Time (min.)	% $\alpha$ -MAC	$\log_{10}(X_{\infty}-X)$ ( $X_{\infty} = 70.5$ )	$10^6 k_1'$ (sec. <sup>-1</sup> )	ml. NaOH (0.0136N)	[H <sup>+</sup> ] (10 <sup>-3</sup> M)	$10^7 k_1^E$ (obs.) (sec. <sup>-1</sup> )
0	0.55	1.8448	-	0.27	0.0	-
244	3.23	1.8279	2.66	0.36	0.3	1.73
496	5.60	1.8122	2.52	0.51	0.7	2.02
999	10.53	1.7779	2.57	-	-	-
1727	18.0	1.7202	2.77	0.97	1.9	1.60
2622	23.8	1.6693	2.57	1.23	2.7	1.49
4650	37.6	1.5172	2.70	2.10	5.0	1.58
5852	42.3	1.4502	2.59	2.60	6.4	1.61
8287	49.3	1.3263	2.40	2.69	6.6	1.17

Mean (6)  $k_1' = 2.63 \pm 0.09 \times 10^{-6} \text{ sec.}^{-1}$  $k_2' = 5.42 \times 10^{-5} \text{ M}^{-1} \text{ sec.}^{-1}$  $k_2^{\alpha} = 3.82 \times 10^{-5} \text{ M}^{-1} \text{ sec.}^{-1}$ [ $\alpha$ -MAC] = 0.1774M[Et<sub>4</sub>NCl] = 0.0485M

T = 95.85°C

FIG. 5

The  $\alpha$ -MAC/ $\text{Et}_4\text{NCl}$  Elimination Reaction  
in AN



(iii) Results and Discussion

The results of the duplicate runs (Runs 26 and 27) are shown in Tables XXV and XXVI.

For all runs except Runs 19 and 20 the  $[\alpha\text{-MAC}]$  (or  $[\gamma\text{-MAC}]$ ) values recorded in the tables give the initial substrate concentration, uncorrected for the small amount of rearrangement at zero time. The mean value of  $k_1'$  is the mean of values for the formation of up to 30-40% of the  $\gamma$ -isomer, the actual number of values averaged being given in brackets. The error quoted is the standard deviation of these values from the mean.

The data for the rearrangement reaction fits the assumed rate equation for a pseudo-first-order reversible reaction well, the first-order rate constants being constant for the production of at least 40% of the primary isomer. The mean first and second-order rate constants for the two runs agree within experimental error. The rate constants show some tendency to fall off during the formation of between 45-55% of the  $\gamma$ -isomer, which is not unexpected considering the accompanying elimination reaction, which is disregarded in the calculations.

Rate "constants" for the elimination reaction, calculated from the first-order rate equation (see Appendix III) are also included in the tables, while the plots of  $\log_{10}(a-x)$  versus time for graphical estimations, as described in Section III and Appendix III, are shown in Fig. 5. Values of  $1.36 \times 10^{-7} \text{ sec.}^{-1}$  for Run 26 and  $1.63 \times 10^{-7} \text{ sec.}^{-1}$  for Run 27 were obtained by the latter method and these may be compared with values of  $1.58 \times 10^{-7}$  and  $1.57 \times 10^{-7} \text{ sec.}^{-1}$  respectively,

obtained by taking the mean of the calculated rate constants for the time interval during which 20% to 40% of the  $\gamma$ -isomer was formed. These values are of course lower than the real rate constant for elimination, because they have been estimated during the production of 20%-40% of the  $\gamma$ -isomer while assuming no rearrangement occurs, and a correction for an assumed depression of 20% is made to allow for this. (Methods of estimating  $k_1^E(\text{obs.})$  are discussed in Appendix III).

Comparing the data in Tables XXV, XXVI and XXIV, it can be seen that the uncatalysed rearrangement reaction makes a negligible contribution to the rate of rearrangement in the presence of  $\text{Et}_4\text{NCl}$  (ca. 0.05M), while the uncatalysed elimination reaction makes a considerable contribution to the chloride ion catalysed rate of elimination. Taking the mean of the five rate constants over the time interval 165.7-601.0 hours inclusive for the uncatalysed elimination reaction (Run 24, Table XXIV), a value of  $3.45 \times 10^{-8} \text{ sec.}^{-1}$  is obtained, which may be used to correct the pseudo-first-order rate constants of Runs 26 and 27. Thus:

$$k_1^E(\text{obs.}) = k_1^E + k_2^E b \quad b = [\text{Et}_4\text{NCl}]$$

(see page 152).

Taking  $k_1^E(\text{obs.}) = 1.87 \times 10^{-7} \text{ sec.}^{-1}$  (the mean of the graphical estimates for Runs 26 and 27 multiplied by 1.25) and  $k_1^E$  as  $3.45 \times 10^{-8} \text{ sec.}^{-1}$ ,  $k_2^E b$  has the value  $1.53 \times 10^{-7} \text{ sec.}^{-1}$  and  $k_2$  is  $3.15 \times 10^{-6} \text{ M}^{-1} \text{ sec.}^{-1}$ . From the graphical estimates of  $k_1^E(\text{obs.})$  for Runs 19, 26 and 27, values of  $k_2^E$  of 2.71, 2.80 and  $3.51 \times 10^{-6} \text{ M}^{-1}$

sec.<sup>-1</sup> are obtained which indicate the reproducibility of the elimination data for the catalysed reaction. (See Appendix III).

It may be noted here, that the chloride ion catalysed component of the total elimination reaction cannot be due to a normal salt effect of the "ionic-strength" type on an E1 mechanism, as the rate of elimination in the absence of Et<sub>4</sub>NCl was not affected by adding Et<sub>4</sub>NClO<sub>4</sub>. (Section V).

A more accurate estimation of the relative rates of catalysed rearrangement and elimination can now be made, using mean values for Runs 26 and 27. e.g.

$$\frac{k_2'}{k_2^E} = \frac{5.52 \times 10^{-5}}{3.15 \times 10^{-6}} \sim 18 \qquad \frac{k_1'}{k_1^E(\text{obs.})} = \frac{2.67 \times 10^{-6}}{1.87 \times 10^{-7}} \sim 14$$

Therefore, with a concentration of Et<sub>4</sub>NCl of about 0.05M the rate of rearrangement is about 14 times that of elimination, so that it appeared that the rearrangement reaction could be studied over at least a fraction of the reaction, with negligible distortion of rate constants calculated on the assumption of a pure rearrangement reaction.

Further discussion of these results is postponed until Section XII.

Work on the elimination reaction was suspended at this stage as sufficient information on its magnitude had been obtained and the present method of analysis was not considered to be capable of making any useful extension to the data.

The next requirement was a determination of the order of the rearrangement reaction.

## VII General Technique for the Preparation, Performance and Analysis of Kinetic Runs

### (a) Use of the Dry-box

Small amounts of water in dipolar aprotic solvents have quite large effects on the rates of ion-molecule reactions, (e.g., a three-fold increase in rate was obtained by Parker for the reaction of methyl iodide with chloride ions in dimethylacetamide, on going from the anhydrous solvent + 1.0M water to the anhydrous solvent)<sup>146</sup>. For this reason, and the fact that anhydrous dipolar aprotic solvents are extremely hygroscopic, preparation of reaction mixtures and runs must be carried out without exposure to atmospheric moisture.<sup>221</sup>

To this end, the solvent - acetonitrile - was stored in a dry-box in 500 ml. flasks closed with well greased stoppers and the preparation of reaction mixtures and runs was also carried out in this box. The box was of conventional design and was equipped with rubber gauntlets. It was kept dry with silica gel which was frequently regenerated. When required, traces of acid vapour etc. (e.g., from the preparation of reaction mixtures containing hydrogen chloride), were removed by absorption with potassium hydroxide pellets and flushing with dry nitrogen.

All the kinetic runs were carried out by the "sealed tube" technique, which enabled them to be done with complete exclusion from contact with atmospheric moisture, from preparation of the reactants to quenching of the reaction tubes.

(b) Preparation of the Apparatus

All the glassware required for preparing the reaction mixture and filling the reaction tubes, together with the tubes themselves, was thoroughly cleaned and washed, rinsed with dilute ammonia solution followed by water and distilled water to ensure the absence of traces of acid, and baked in an oven at  $120^{\circ}\text{C}$  for 2-3 days, before being transferred to a desiccator or the dry-box.

The reaction tubes were 125 x 15 mm. Pyrex test tubes, constricted in the middle for sealing off, when 5 ml. aliquots of reaction mixture were used and specially made, scaled-down tubes similarly constricted when 2 ml. aliquots were used. Some constricted tubes of 10 ml. capacity were also required and these were made by constricting Pyrex test tubes near the top.

The remainder of the apparatus required for preparing a run - rubber bungs for stoppering the tubes, two small sheets of filter paper and the short length of capillary rubber tubing required for connecting the 10 ml. syringe, used for filling a pipette in the dry-box, to the pipette - was placed in a desiccator over silica gel. This was continuously evacuated with a "Hyvac" pump at 0.01 mm. of Hg for 2-3 hours and then left under vacuum until required, (2-3 days).

The rubber bungs were washed, rinsed with dilute ammonia solution, water and distilled water and allowed to dry before being placed in the desiccator.

(c) Preparation of  $\text{Et}_4\text{NCl}$

Approximately the required amount of recrystallised  $\text{Et}_4\text{NCl}$  was weighed out into a small glass boat, which was then placed in a desiccator over anhydrous calcium chloride for preliminary drying.

The boat was then transferred to a clean, dry drying pistol charged with phosphorus pentoxide suspended on glass wool. All joints were greased with silicone "Hyvac" grease. The pistol was then evacuated continuously, using a "Hyvac" pump, at 0.01 mm. of Hg for 8 hours, at a temperature of  $60^\circ\text{C}$ , achieved by refluxing chloroform.<sup>107</sup> The pistol, after being cooled and brought back to atmospheric pressure with precautions against the uptake of atmospheric moisture, was rapidly disconnected, stoppered and placed in the dry-box.

Analyses to test the purity and dryness of samples prepared as described above, are described in Chapter VI. ( $\text{Et}_4\text{NCl}$  is very hygroscopic).

(d) Preparation of Runs

All the apparatus for a run was placed in the dry-box, together with the pistol containing the dry  $\text{Et}_4\text{NCl}$  and a 5 ml. flask containing the substrate. These were left about 15 hours (overnight) to attain equilibrium.

The boat containing the  $\text{Et}_4\text{NCl}$  was then transferred to the flask to be used for preparing the reaction mixture.

The required volume of acetonitrile minus about 20 ml., was then added to the flask and shaken up. The substrate was dissolved in acetonitrile and transferred to the flask, which was then stoppered and vigorously shaken to ensure homogeneity of the reaction mixture. (As the reaction is very slow at room temperature, negligible rearrangement occurred between preparing the reaction mixture and placing the ampoules in the thermostat).

A series of reaction tubes were filled by sucking the reaction mixture up a pipette of the required capacity, by means of a 10 ml. syringe attached to the pipette by a short length of capillary rubber tubing, and delivering the aliquot to a reaction tube. It was difficult to deliver an exact volume by this method, but as this was not required in tubes destined for v.p.c. analysis, it did not matter. A volume slightly greater than 5 ml., from which an exact aliquot could be taken later, was delivered to tubes destined for (a) analysis for initial reactant concentrations, (b) chloride ion analysis, or (c) acid analysis.

Care was taken not to produce large pressure differences while using the pipette in view of the volatility of the compounds used, but tubes filled at both ends of the filling period showed no change in the concentrations of the reactants.

The tubes were firmly stoppered with rubber bungs before removal from the box for sealing. They were then placed in an ice-water bath and each tube, before it was sealed, was cooled in liquid air. This enabled the sealing off to be done without removing the bung, as a sufficiently large reduction in pressure occurred inside the tubes to more than

compensate for the heating effect of the flame at the constriction. Each tube (or ampoule) was returned to the ice-water bath after sealing.

The ampoules were then placed simultaneously in a thermostat at the required temperature. After a period sufficient for them to have attained thermal equilibrium, one ampoule was quenched for analysis as the zero-time ampoule. Further ampoules were removed at various times and quenched in ice water before being transferred to liquid air to await analysis.

(e) Thermostats

These were of conventional design with temperature control to  $0.02^{\circ}\text{C}$  by means of a mercury-toluene or diethylphthalate switch. The thermostats contained water with a layer of oil on top for temperatures up to and including  $96^{\circ}\text{C}$ , and a high-temperature resistant oil for reaction temperatures higher than this. Temperatures were measured with N.P.L. standard thermometers.

(f) Timing of Runs

An electric clock was suitable for rearrangement runs at and below  $96^{\circ}\text{C}$ . Above this temperature, a stopclock checked against an electric clock was used.

(g) Analysis by Gas-Liquid Chromatography for Isomer Ratios

Note: Data from References 164, 165 and 166 is used in this discussion.

The gas chromatograph available was a FFE Argon model (No. 12000) with a  $\beta$ -ray/argon-ionisation detector using strontium-90 as the radioactive source. The column used was a 4 foot x 4 mm. glass one packed with 15% tritolyl phosphate on 90-110 mesh celite, prepared from a slurry of celite and the liquid phase dissolved in diethyl ether. It was run at ambient temperature with an argon flow-rate set at a value within the range of 90-120 ml. per minute as measured by a soap-film flowmeter. A needle-valve control on the cylinder gauge head ensured a steady and easily adjusted flow-rate. The  $\beta$ -ray/argon detector is not very sensitive to changes in temperature, pressure or flow-rate, so that the heating jacket surrounding the column was sufficient to prevent short term fluctuations in the ambient temperature affecting the performance of the instrument, while long term effects were corrected for in the standardisation procedure. The location of the instrument made control of the ambient temperature difficult. However, it was controlled at one stage, to test the effect on the instrument's performance and found to have none. The recorder was of the conventional potentiometric type and it was run at top chart speed (24"/hr.).

The sample was injected with a 10  $\mu$ l. "Hamilton" syringe, through a rubber septum into a plug of glass wool on top of a short precolumn. Injection was facilitated by a guide tube attached to the top of the precolumn. (See Fig. 10). p. 233

The components of a sample emerged in the order butadiene,  $\alpha$ -methylallyl chloride, acetonitrile,  $\gamma$ -methylallyl chloride, i.e.,

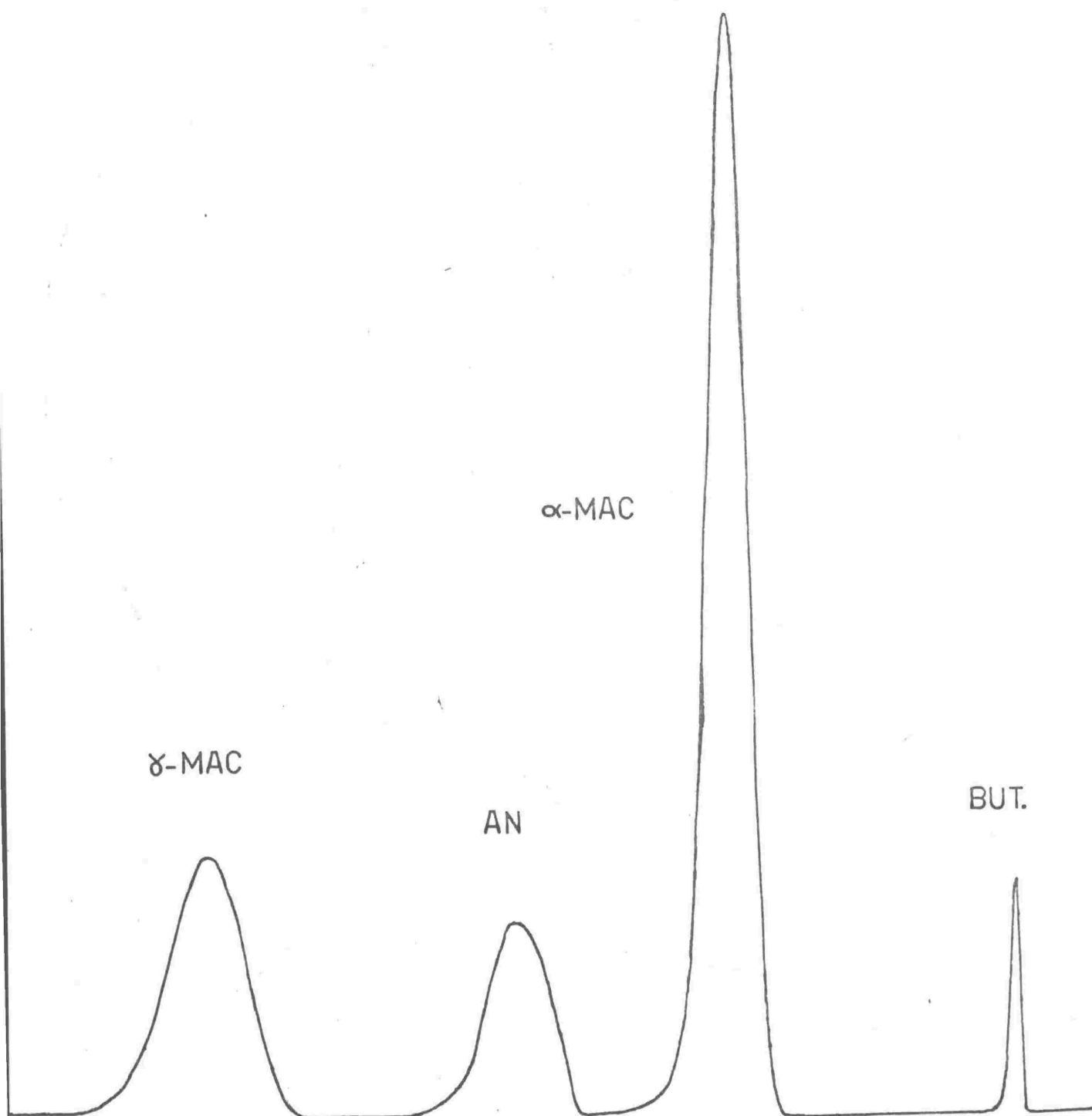
in the order of their boiling-points. Both isomeric chlorides were shown to be stable on the column under the above operating conditions. The isomeric chlorides gave symmetrical peaks and the resolution of the components of a sample was adequate for an analysis of peak areas, the retention times being  $\sim 0.5, 6, 11$  and  $18$  minutes, or in the ratio of  $1, 12, 22, 36$ . The acetonitrile peak for a  $0.1M$  solution of substrate, with this component near full scale deflection on the recorder, was small and did not interfere with peak area analysis. The butadiene peak was very sharp. (See Fig. 6).

#### Calibration of the Detector

The  $\beta$ -ray/argon-ionisation detector utilised by this chromatograph is very sensitive to the presence of traces of water in the carrier gas, which greatly impair its performance causing baseline instability and decreased sensitivity to emerging components of a sample. At column temperatures below  $100^{\circ}C$  water vapour introduced into the column collects in the detector.

Consequently, standards to be used for calibrating the detector were made up as follows: a sample bottle of  $10$  ml. capacity with a plastic cap, in which there was a small pinhole closed with a small pin, was filled in the dry-box with a suitable volume (ca.  $5$  ml.) of dry acetonitrile. It was then removed and weighed on a balance to  $0.0001$  gm. The required weight of the minor isomer component (smallest weight used was  $0.020$  gm.) was then added, by injecting the isomer through the pinhole into the solvent using a  $10$   $\mu$ l. syringe and the bottle was

FIG. 6  
Chromatogram



reweighed to give the weight of this component. The required weight of the major isomer component was then added in the same way, followed by reweighing of the bottle to give the weight of this isomer. The relative concentrations of the isomers in each standard were obtained from these weights.

Standards containing 5%, 10%, 20%, 30%, 40% and 50% of the  $\delta$ -isomer and standards containing 10%, 20% and 30% of the  $\alpha$ -isomer were prepared in this way. These standards were stored in a refrigerator when not in use.

This method of preparation was considered to minimize errors due to the volatility of the compounds. Fresh sets of standards were prepared at intervals to eliminate errors due to deterioration on storage and use over lengthy periods of time.

#### Quantitative Analysis

The response of the detector to a given compound is proportional to the concentration of the compound in the carrier gas. If the relative response to two compounds, as measured by the ratio of their peak areas on the recorder chart, is measured for a mixture of known concentration ratio, then the ratio of the concentration ratio and the peak area ratio is a constant called the "calibration constant of the detector" ( $K(\text{cal.})$ ), for a range of concentration ratios of which the above is the central value. If the response of the detector is linear over a wide concentration range, then irrespective of the concentration ratio of a sample, the calibration constant as defined above should be

constant. Most detectors are linear over a restricted range (e.g. 1000 to 1).

To determine the concentration ratio of an unknown mixture, samples of it are run, together with samples of standards in the same concentration ratio range as the unknown and the calibration constant for this range is calculated. The concentration ratio of the unknown is then simply the product of its peak area ratio and the calibration constant.

$$\frac{[A]_s}{[B]_s} \times \frac{\text{P.A. } B(s)}{\text{P.A. } A(s)} = K_{(\text{cal.})} \quad \frac{[A]_u}{[B]_u} = K_{(\text{cal.})} \frac{\text{P.A. } A(u)}{\text{P.A. } B(u)}$$

To determine the concentration ratio of the methylallyl chlorides in a reaction tube, at least three samples were run, together with at least two samples of each of two standards having concentration ratios one on either side of that of the unknown. The mean of the calibration constants for the two standards was used to calculate the composition of the unknown. Thus if:

$[\alpha]$  = the concentration of  $\alpha$ -methylallyl chloride

$[\gamma]$  = " " "  $\gamma$ -methylallyl "

$A_\alpha$  = " peak area of  $\alpha$ -methylallyl chloride

$A_\gamma$  = " " " "  $\gamma$ -methylallyl "

then for each standard:

$$\frac{[\alpha]_s}{[\gamma]_s} \times \left( \frac{A\gamma}{A\alpha} \right)_{av.}^{(s)} = K_{(cal.)}$$

and taking the mean of the two constants to determine the concentration ratio of the unknown:

$$\frac{[\alpha]_u}{[\gamma]_u} = \frac{K_{(cal.)} + K_{(cal.)}}{2} \times \left( \frac{A\alpha}{A\gamma} \right)_{av.}^{(u)}$$

Now, the percentage of  $\gamma$ -isomer present in each reaction tube was required for calculations of the rate constants for runs starting from the  $\alpha$ -isomer.

$$\frac{[\alpha]_u}{[\gamma]_u} + 1 = \frac{[\alpha]_u + [\gamma]_u}{[\gamma]_u}$$

and

$$\frac{100}{\frac{[\alpha]_u}{[\gamma]_u} + 1} = \frac{100 [\gamma]_u}{[\alpha]_u + [\gamma]_u} = \% \gamma\text{-isomer}$$

Substitution of the percentages in the equation:

$$k_1' = \frac{2.303}{t} \log_{10} \frac{X_e - X_o}{X - X_o}$$

which is derived in Appendix I, enabled the rate constant  $k_1'$  to be calculated. It may be noted here that it was unnecessary to calculate the concentration of the product. An analogous treatment was used for runs starting from the  $\gamma$ -isomer.

Each reaction tube was removed from liquid air for analysis and, after it was partially melted, shaken up and refrozen, a small hole was made at the tip, which was then closed with a rubber cap. The tube was placed in a small glass stand, immersed in an ice-salt mixture to prevent volatility losses. Samples were withdrawn through the hole and placed on the GLC column using a 10  $\mu$ l. syringe. The normal sample size was 1-2  $\mu$ l.

For percentages of up to twenty of the minor component of an isomer mixture, the "sensitivity" was increased by a factor of three while this component came off the column. This procedure enabled a peak of reasonable area to be obtained with a peak height for the major component of the order of 80% full scale deflection. Above this percentage the sensitivity was not changed. The detector voltage normally used was 1500 volts.

#### Measurement of Peak Areas

There are several methods of measuring peak areas, three of these being the exact methods of using a planimeter, or cutting out the peaks and weighing them, and the approximate method of multiplying the peak height by the width at half the height. Because of the extensive calibration and considerable number of samples used in the present work, and the nature of the peaks obtained, the latter method was suitable. To confirm this, checks by the other two methods were made, and these gave results which were identical within the limits of the error in the methods. e.g.

Sample	Peak Area Ratio (A)	Peak Area Ratio (B)	K <sub>(cal.)</sub> (A)	K <sub>(cal.)</sub> (B)	% $\alpha$ -MAC (A)	% $\alpha$ -MAC (B)
standard	3.09	3.21	0.715	0.688		
standard	1.43	1.49	0.720	0.691		
unknown	3.42	3.57			29.0	28.9

A = the approximate method

B = the weighing method

Sample	Peak Area Ratio (A)	Peak Area Ratio (B)	K <sub>(cal.)</sub> (A)	K <sub>(cal.)</sub> (B)	% $\delta$ -MAC (A)	% $\delta$ -MAC (B)
standard	1.95	1.93	4.64	4.69		
unknown	1.16	1.14			15.7	15.8
unknown	5.80	5.54			3.58	3.70

A = the approximate method

B = the planimeter method

The extensive calibration procedure not only corrected for fluctuations in performance and possible deviations from linearity (negligible in this case), but would also have corrected for any consistent errors in the method of determining the peak area ratios, which were proportional to the peak area ratio.

The estimated average error in peak area ratio determinations was  $\sim 2\%$ , as it may be seen from the analysis data (see Appendix V) that a spread of 4% in the values obtained for two or three analyses was normal. This means that an error of 3-4% in concentration ratio determinations would be normal, and therefore an error of 2-4% in the calculated percentage of minor component in an unknown sample may be

taken as the average analysis error.

The complete v.p.c. analysis data for some representative kinetic runs is shown in Appendix V.

#### Maintenance of the Instrument's Performance

The stability of the instrument's detector deteriorated after the injection of about fifty samples, resulting in a decrease in the reproducibility of peak area ratios. This may have been due, at least partially, to the introduction of traces of water with the samples, these being absorbed during the removal of other samples from the standards and reaction tubes. The low operating temperature would allow these to collect in the detector and impair its performance. Heating the column to 100°C and allowing it to cool in a stream of argon always improved the reproducibility.

The reproducibility of the instrument's performance also improved when it was not being used by other workers, especially those using high temperatures, i.e., when it was left running continuously under operating conditions. After shut-down or use by others, it required about 8 hours stabilisation.

A further increase in stability and reproducibility was obtained by protecting the detector leads from atmospheric moisture. To this end, bags of silica gel were placed in the analysing unit's cabinet, close to the detector, and the cabinet was sealed up as well as possible.

The detector was periodically removed and shaken out and flushed out with argon to remove dirt, and the column-detector seal was

replaced. Flushing with argon through an empty column at 200°C was also carried out to remove stationary phase bled from columns. Both of these treatments improved performance.

The rubber septum of the injection system was frequently replaced to eliminate errors due to leaks and the short precolumn was frequently cleaned out by replacing the glass wool plug and top layer of packing, on which  $\text{Et}_4\text{NCl}$  would accumulate. The use of this precolumn meant that this procedure could be carried out without disturbing the main analytical column. Its joints were greased with a little silicone grease to prevent leaks.

#### Comparison of V.P.C. and Kinetic Analysis Techniques

The technique described above for following the rearrangement reactions may be compared with that used by England and Hughes for the corresponding reactions of the isomeric bromides.<sup>76b,79</sup> (See Chapter I, page 43 ).

Their kinetic analysis method determined accurately small percentages of the  $\delta$ -isomer, but as the percentage rose to about 50% the accuracy fell, and the method could not be used for small percentages of the  $\alpha$ -isomer, which precluded a study of rearrangement starting with the  $\delta$ -isomer.

The method of analysis used in this project is, on the other hand, accurate at low percentages of either isomer and also at higher percentages, i.e., over the whole range of isomer ratios, so that the range available for study is much extended. This technique also has the advantage of being experimentally less complicated and onerous.

(h) Determination of Initial Reactant Concentrations(1) Et<sub>3</sub>NC1

A 5 ml. aliquot of the reaction mixture was added to an extraction mixture of 30 ml. of n-pentane and 25 ml. of water in a separating funnel and vigorously shaken. The aqueous layer was run off into a 150 ml. conical flask, and, after titration with standard sodium hydroxide solution (when this was required) and being made alkaline with ca. 0.05 gm. of "Analar" sodium hydroxide, it was evaporated down on a water-bath while being flushed with nitrogen. The resultant solution was then transferred to a beaker and, after acidification with dilute nitric acid, it was titrated with standard silver nitrate by the potentiometric method.<sup>168</sup> An electrode consisting of silver wire was used, the reference being a saturated calomel electrode. The two half-cells were joined by a potassium nitrate-agar salt bridge.

Analyses were carried out in duplicate and agreed to 0.5%.

Volhard titration "blanks" on the aqueous extracts of allylic chloride solutions treated as above, and also potentiometric titration of these after adding an aliquot of standard chloride solution, indicated that not more than 1% solvolysis of a 0.1M solution occurred during the extraction and evaporation procedure.

(2) Allylic Chloride

Aliquots of reaction mixture (5 ml.) were placed in constricted test tubes of 10 ml. capacity and approximately 5 ml. of sodium methoxide in methanol (ca. 1M) was added. The tubes were stoppered, frozen and

sealed and then placed in a water-bath at  $100^{\circ}\text{C}$  to react to "infinity". The ampoules were cracked open using a hot, glass point, after cooling the contents, which were then poured into a 25 ml. standard flask and made up to volume. Aliquots (10 ml.) were then analysed by titration with standard silver nitrate by the potentiometric method. The analysis data gave the total chlorine concentration of the reaction mixture, from which the substrate concentration could be determined, by subtracting the concentration of  $\text{Et}_4\text{NCl}$ . The analysis error was 0.5%.

The end-points of all the potentiometric titrations were determined from a plot of E.M.F. versus titre.

(1) Solvent Purity and Water Content

The criterion of purity for the solvent used for kinetic runs was analysis by gas chromatography as described in Chapter VI.

Proof that the drying procedure was adequate was deduced from the stability of allyl chloride in the solvent and from the identical rate constants obtained for runs using acetonitrile dried by three distillations from phosphorus pentoxide compared with five distillations from phosphorus pentoxide. (See Chapter VI).

VIII The Dependence of the Rate Constant on Nucleophile Concentration(i) Introduction

To establish the order of the rearrangement reaction, the effect on the first-order rate constant of varying the concentration of the nucleophilic reagent was studied. Runs 28, 29, 30 and 31 were carried out at 96.0°C, using concentrations of  $\text{Et}_4\text{NCl}$  of approximately 0.025, 0.05 and 0.1M. Duplicate runs with  $\text{Et}_4\text{NCl} \sim 0.025\text{M}$  were carried out. The effect of added water on the rate constant was tested in Run 31 and the precise effect of added hydrogen chloride was determined in Run 32 with  $[\text{Et}_4\text{NCl}] \sim 2[\text{HCl}]$ .

(ii) Results and Discussion

The results for Runs 28-32 are shown in Tables XXVII-XXXI.

Obviously  $k_1'$  does depend on the concentration of  $\text{Et}_4\text{NCl}$ .

Now, for a pseudo-first-order reaction which could be truly first-order, second-order or concurrent first- and second-order, i.e., for a reaction in which the concentration of the nucleophilic reagent remains constant throughout the reaction:<sup>142</sup>

$$v = k_1 a + k_2 a \alpha b$$

(assuming  $k_1$  is independent of ionic strength at low concentrations) where  $v$  is the reaction rate,  $k_1$  and  $k_2$  are the first- and second-order rate constants respectively,  $a$  is the substrate concentration,  $b$  is the nucleophile concentration and  $(\alpha)$  is the degree of dissociation of the nucleophile.

TABLE XXVII

Run 28. The  $\alpha$ -Methylallyl Chloride/Et<sub>4</sub>NCl Reaction in Acetonitrile  
(96°C)

Time (min.)	% $\alpha$ -MAC	$\log_{10}(X_e - X)$ ( $X_e = 70.5$ )	$10^6 k_1'$ (sec. <sup>-1</sup> )
0	0.41	1.8457	-
468	3.29	1.8275	1.49
1017	6.62	1.8053	1.52
1923	11.82	1.7685	1.54
3357	18.4	1.7168	1.47
5447	26.2	1.6464	1.40
7252	32.2	1.5832	1.39
9071	37.1	1.5237	1.36
9075	36.6	1.5302	1.33
13267	45.8	1.3927	1.31

$$[\alpha\text{-MAC}] = 0.1246M$$

$$[\text{Et}_4\text{NCl}] = 0.0259M$$

$$T = 95.88^\circ\text{C}$$

$$\text{Mean (5)} \quad k_1' = 1.48 \pm 0.05 \times 10^{-6} \text{ sec.}^{-1}$$

$$k_2' = 5.72 \times 10^{-5} M^{-1} \text{ sec.}^{-1}$$

$$k_2' \alpha = 4.03 \times 10^{-5} M^{-1} \text{ sec.}^{-1}$$

TABLE XXVIII

Run 29. The  $\alpha$ -Methylallyl Chloride/ $\text{Et}_4\text{NCl}$  Reaction in Acetonitrile  
(96°C)

Time (min.)	% $\delta$ -MAC	$\log_{10}(X_e - X)$ ( $X_e = 70.5$ )	$10^6 k_1'$ ( $\text{sec.}^{-1}$ )
0	0.32	1.8462	-
480	3.13	1.8285	1.41
1015	6.07	1.8091	1.40
1800	10.12	1.7809	1.39
2705	14.5	1.7482	1.39
4177	20.9	1.6955	1.38
5805	27.2	1.6365	1.39
7550	31.4	1.5922	1.29
11372	39.8	1.4871	1.21
17610	48.9	1.3345	1.12

$$[\alpha\text{-MAC}] = 0.1187\text{M}$$

$$[\text{Et}_4\text{NCl}] = 0.0249\text{M}$$

$$T = 95.92^\circ\text{C}$$

$$\text{Mean (6) } k_1' = 1.39 \pm 0.01 \times 10^{-6} \text{ sec.}^{-1}$$

$$k_2' = 5.59 \times 10^{-5} \text{ M}^{-1} \text{ sec.}^{-1}$$

$$k_2'^{\alpha} = 3.94 \times 10^{-5} \text{ M}^{-1} \text{ sec.}^{-1}$$

TABLE XXIX

Run 30. The  $\alpha$ -Methylallyl Chloride/ $\text{Et}_4\text{NCl}$  Reaction in Acetonitrile

(96°C)

Time (min.)	% $\alpha$ -MAC	$\log_{10}(X_e - X)$ ( $X_e = 70.5$ )	$10^6 k_1'$ ( $\text{sec.}^{-1}$ )
0	0.60	1.8445	-
295	3.85	1.8238	2.69
522	6.11	1.8088	2.62
990	10.64	1.7771	2.61
1542	15.7	1.7388	2.63
2050	19.6	1.7067	2.58
2945	26.0	1.6484	2.56
2974	26.3	1.6454	2.57
4165	34.2	1.5599	2.62
5710	41.3	1.4654	2.55
7601	48.2	1.3483	2.51

$$[\alpha\text{-MAC}] = 0.1176\text{M}$$

$$[\text{Et}_4\text{NCl}] = 0.0470\text{M}$$

$$T = 95.88^\circ\text{C}$$

$$\text{Mean (8) } k_1' = 2.61 \pm 0.04 \times 10^{-6} \text{ sec.}^{-1}$$

$$k_2' = 5.55 \times 10^{-5} \text{ M}^{-1} \text{ sec.}^{-1}$$

$$k_2'^\alpha = 3.91 \times 10^{-5} \text{ M}^{-1} \text{ sec.}^{-1}$$

TABLE XXX

Run 31. The  $\alpha$ -Methylallyl Chloride/ $\text{Et}_4\text{NCl}$  Reaction in Acetonitrile  
(96°C)

Time (min.)	% $\alpha$ -MAC	$\log_{10}(X_e - X)$ ( $X_e = 70.5$ )	$10^6 k_1'$ (sec. <sup>-1</sup> )
0	0.52	1.8450	-
130	3.36	1.8270	5.31
252	6.01	1.8095	5.41
490	10.69	1.7768	5.34
732	14.8	1.7459	5.20
1022	19.9	1.7402	5.29
1501	26.8	1.6405	5.23
2159	34.6	1.5551	5.15
2904	42.7	1.4440	5.30
3605	48.8	1.3365	5.41
4165	51.6	1.2765	5.24
1501	25.0	1.6580	4.78 $[\text{H}_2\text{O}] \sim 0.05\text{M}$

$[\alpha\text{-MAC}] = 0.0981\text{M}$

$[\text{Et}_4\text{NCl}] = 0.0970\text{M}$

$T = 95.86^\circ\text{C}$

Mean (8)  $k_1' = 5.28 \pm 0.08 \times 10^{-6} \text{ sec.}^{-1}$

$k_2' = 5.45 \times 10^{-5} \text{ M}^{-1} \text{ sec.}^{-1}$

$k_2'^\alpha = 3.85 \times 10^{-5} \text{ M}^{-1} \text{ sec.}^{-1}$

TABLE XXXI

Run 32. The  $\alpha$ -Methylallyl Chloride/ $\text{Et}_4\text{NCl}$ / $\text{HCl}$  Reaction in Aceto-  
nitrile ( $96^\circ\text{C}$ )

Time (min.)	% $\alpha$ -MAC	$\log_{10}(X_e - X)$ ( $X_e = 70.5$ )	$10^6 k_1'$ ( $\text{sec.}^{-1}$ )
0	0.38	1.8458	-
471	2.92	1.8298	1.30
1012	5.43	1.8134	1.23
1918	10.96	1.7748	(1.42)
3352	15.9	1.7372	1.24
5442	23.4	1.6730	1.22
7247	28.4	1.6243	1.17
9066	33.5	1.5682	1.17
9075	33.4	1.5694	1.17
13262	42.0	1.4548	1.13

$$[\alpha\text{-MAC}] = 0.1124\text{M}$$

$$[\text{Et}_4\text{NCl}] = 0.0470\text{M}$$

$$[\text{HCl}] = 0.0263\text{M}$$

$$[\text{Et}_4\text{NCl}] - [\text{HCl}] = 0.0207\text{M}$$

$$\text{Mean (4) } k_1' = 1.25 \pm 0.04 \times 10^{-6} \text{ sec.}^{-1}$$

$$\text{Apparent } k_2' = 2.66 \times 10^{-5} \text{ M}^{-1} \text{ sec.}^{-1}$$

$$\text{Real } k_2' = 6.04 \times 10^{-5} \text{ M}^{-1} \text{ sec.}^{-1}$$

$$T = 95.88^\circ\text{C}$$

$$\begin{aligned}\text{Therefore, } v &= (k_1 + k_2 \alpha b)a \\ &= k_1(\text{obs.}) a\end{aligned}$$

$$\text{i.e., } k_1(\text{obs.}) = k_1 + k_2 \alpha b.$$

If the reaction is pure second-order, then  $k_1=0$  and a plot of  $k_1(\text{obs.})$  versus  $\alpha b$  should be a straight line of slope  $k_2$  passing through the origin. If the reaction is concurrent first- and second-order, then a plot of  $k_1(\text{obs.})$  versus  $\alpha b$  should be a straight line of slope  $k_2$  and intercept  $k_1$ . (This treatment assumes ion-pairs have negligible reactivity.)

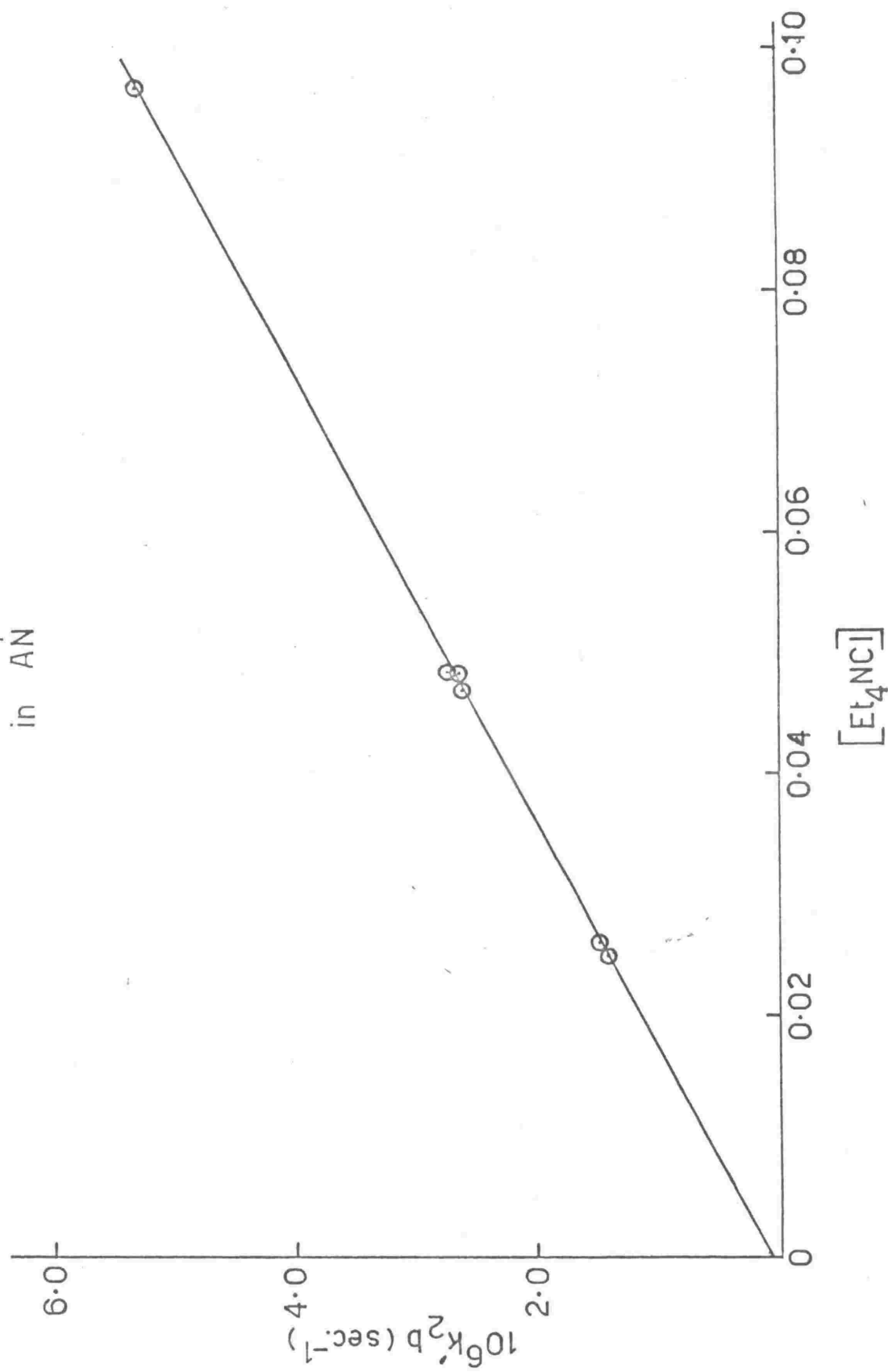
Considering the data in the tables, mean values of  $k_1'$ , derived from the rate constants over the initial fraction of the reaction during which they remain constant, have been divided by the concentration of the nucleophile to give values of  $k_2'$  which agree very closely for Runs 26-31 inclusive. The mean values of  $k_1'$  ( $k_1(\text{obs.})$ ) for these runs, plotted against  $\text{Et}_4\text{NCl}$  concentration, are shown in Fig. 7. The plot is linear and passes, within the limits of experimental error, through the origin, the intercept being  $5 \times 10^{-8} \text{ sec.}^{-1}$ .

This means that the kinetics, over the initial fraction of the reaction during which values of  $k_1'$  are constant, are pure second-order. The constancy of the  $k_2'$  values over a fourfold change in nucleophile concentration and the zero intercept justify ( $\alpha$ ) being neglected in the  $k_1(\text{obs.})$  versus  $b$  plot.

It appears therefore, that either (a) ion-pairs are as effective as "free ions" in catalysing the rearrangement reaction, or (b)  $\text{Et}_4\text{NCl}$  is highly dissociated in acetonitrile at the concentrations used. If

FIG. 7

Kinetic Order of the  $\alpha$ -MAC|Et<sub>4</sub>NCl Rearrangement Reaction  
in AN



ion-pairing were appreciable and the effective nucleophilicity of the ion-pair greatly reduced compared with that of the "free" chloride ion, then a decrease in  $k_2'$  with increasing  $\text{Et}_4\text{NCl}$  concentration would be observed.<sup>143</sup>

Miller and Parker<sup>32</sup> consider that the effect on  $k_2$ , of incomplete dissociation of tetraethylammonium salts in solvents of dielectric constant greater than 33, is to cause a depression of not more than 10%, with salt concentrations of  $< 0.04\text{M}$ . Acetonitrile has a dielectric constant of 36.7.<sup>16</sup>

The dissociation constant for  $\text{Et}_4\text{NCl}$  in acetonitrile has the value  $2.88 \times 10^{-2}$  at  $25^\circ\text{C}$ .<sup>131</sup> Calculations of  $(\alpha)$  - the degree of dissociation - for  $0.1\text{M}$  and  $0.025\text{M}$   $\text{Et}_4\text{NCl}$  at this temperature, give values of 0.56 and 0.75 respectively. Values for  $(\alpha)$  were obtained from the following equations:

$$\frac{\alpha^2 \gamma^2 c}{(1-\alpha)} = K \quad -\log f = \frac{A \sqrt{\alpha c}}{1+Bq \sqrt{\alpha c}}$$

using the method of successive approximations.<sup>91</sup> Therefore, although  $\text{Et}_4\text{NCl}$  is highly dissociated in acetonitrile at  $25^\circ\text{C}$ , a detectable salt effect would be expected and this should also be observable at  $96^\circ\text{C}$ .

Despite the considerable body of evidence for the low nucleophilic reactivity of ion-pairs,<sup>13,142,144</sup> especially for lithium salts in acetone (e.g., in the work of Winstein and co-workers and Hughes, Ingold and co-workers)<sup>13</sup> there is evidence that in some cases their reactivity is not negligible compared with that of the free ion.<sup>144,145</sup>

Ugelstad, Ellingsen and Berge postulate a highly active ion-pair of tetra-n-butylammonium phenoxide to account for the reactivity of this compound towards butyl halides in various solvents and suggest this may be due to a low interaction energy in the ion-pair resulting from the large size of the cation.<sup>145</sup>

Fara and co-workers<sup>48</sup> have attacked the assumption of negligible reactivity for ion-pairs and are suspicious of kinetic evaluations of ion-pair dissociation constants such as those of Casapieri and Swart<sup>142</sup> and Weaver and Hutchison.<sup>21</sup> They consider that the assumption may be justified in the extreme case, where bond-making is the predominant factor in the transition state of the reaction, but for transition states in which heterolysis is well advanced they consider that the reactivity of the ion-pair may approach that of the free ion.

The concentration of  $\text{Et}_4\text{NCl}$  which gives a pseudo-first-order rate constant equal to that observed in Run 32 was found from Fig. 7 to be 0.0220M. Therefore a decrease of 0.0250M in the effective  $\text{Et}_4\text{NCl}$  concentration must have occurred. Assuming (a) that hydrogen chloride combines with chloride ions to form the dihalide ion, and (b) that this reaction does not affect the reactivity of the remaining  $\text{Et}_4\text{NCl}$ , then the results are in accord with the assumption that the acid removes 95% of an equivalent concentration of chloride ions to form an ion of negligible nucleophilicity. Calculations of  $k_2'$  (apparent) and  $k_2'$  (real), assuming the hydrogen chloride to be 100% efficient, are shown in Table XXXI. These results agree with those obtained by Lesnini, for the effect of hydrogen chloride on the isomerisation reaction of

5-methyl-2-cyclohexenyl chloride catalysed by  $\text{Et}_4\text{NCl}$  in acetonitrile, for which deactivation was 100% efficient.<sup>107</sup>

A calculation (assuming activity coefficients to be unity) of the concentration of  $\text{HCl}_2^-$  ions in a solution of 0.05M  $\text{Et}_4\text{NCl}$  and 0.025M hydrogen chloride in acetonitrile at 25°C, gives a value of 0.0213M.<sup>124</sup>

The dependence of the constancy of the pseudo-first-order rate constant on the concentration of  $\text{Et}_4\text{NCl}$  is of considerable interest. The fraction of the reaction over which the rate constant  $k_1'$  is constant, decreases markedly with decrease in  $\text{Et}_4\text{NCl}$  concentration and the deviation from the mean initial value for  $k_1'$  increases correspondingly for any given percentage of  $\gamma$ -isomer formed. For example, with 0.1M  $\text{Et}_4\text{NCl}$   $k_1'$  is constant for the formation of 50% of the  $\gamma$ -isomer, with 0.05M  $\text{Et}_4\text{NCl}$  it is constant for the formation of approximately 35% and with 0.025M  $\text{Et}_4\text{NCl}$  it is constant for the formation of only about 25%. The run with added hydrogen chloride (Run 32) behaves similarly to the runs with 0.025M  $\text{Et}_4\text{NCl}$ .

If it is postulated that the downward drift in the rate constants is caused by hydrogen chloride, produced by the elimination reaction, combining with chloride ions to form  $\text{HCl}_2^-$  ions, which have been shown to be ineffective in catalysing the rearrangement reaction, then, neglecting any other effects of the elimination reaction, the observed depressions of the rate constants for given percentages of  $\gamma$ -isomer formation can be compared with calculated depressions. The latter were

derived from the data on the elimination reaction, by plotting hydrogen ion concentration versus percentage of  $\gamma$ -isomer for Runs 26 and 27 and interpolating the hydrogen ion or acid concentration for any desired percentage of  $\gamma$ -isomer formation. (See Fig. 8). The difference in substrate concentration of the runs was neglected. After subtracting  $1 \times 10^{-3}M$  from the values for the acid concentration, to allow for the solvolytic production of chloride ions which is of ambiguous origin and effect, division by the experimental concentrations of  $Et_4NCl$  gave the calculated depressions. The observed depressions were obtained from plots of  $k_2'$  versus percentage of  $\gamma$ -isomer, using data from Runs 26, 27, 30, 28, 29 and 32. (See Fig. 9). The labelling of the Y-axis was varied to make the mean initial values of  $k_2'$  for the runs coincide. The observed and calculated effects are shown in Table XXXII.

The observed rate constant depressions are 6-7% less than the calculated ones. However, irrespective of the magnitude of the drift, i.e., the total effect of the elimination reaction on the rate constants for rearrangement, the variation in  $\Delta\Delta k_2'$  as the chloride ion concentration is varied at an approximately constant substrate concentration (i.e., an approximately constant initial concentration of  $\alpha$ -methylallyl chloride), should reflect the effect of hydrogen chloride produced by the elimination reaction. Assuming pure second-order kinetics for both rearrangement and elimination, which is an approximation for the latter, then, for any given percentage of  $\gamma$ -isomer formation, the ratio of the concentrations of  $\gamma$ -isomer and

FIG. 8

Product Data for the  $\alpha$ -MAC/ $\text{Et}_4\text{NCl}$   
Reactions in AN

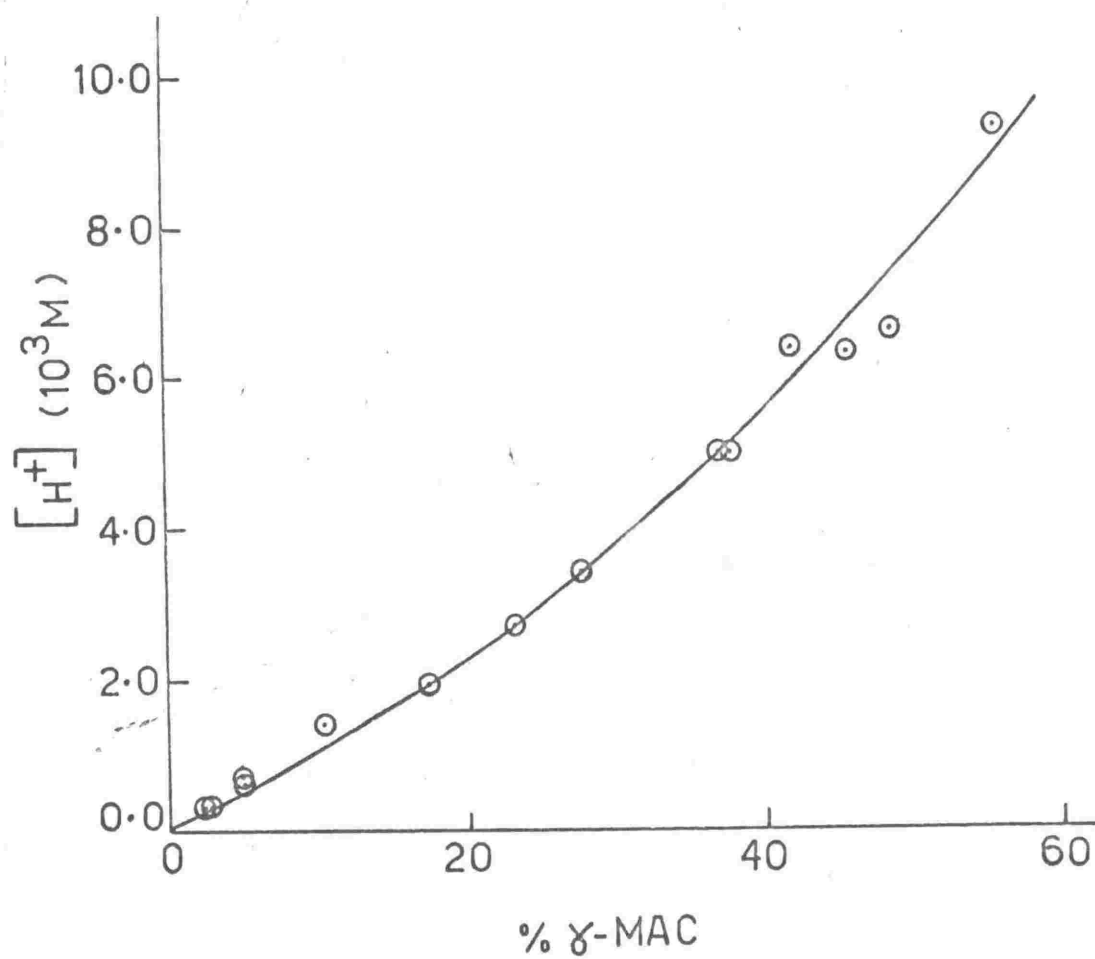


FIG. 9

Dependence of the Fall-Off in  $k'_2$  on  $\text{Et}_4\text{NCl}$  Concentration

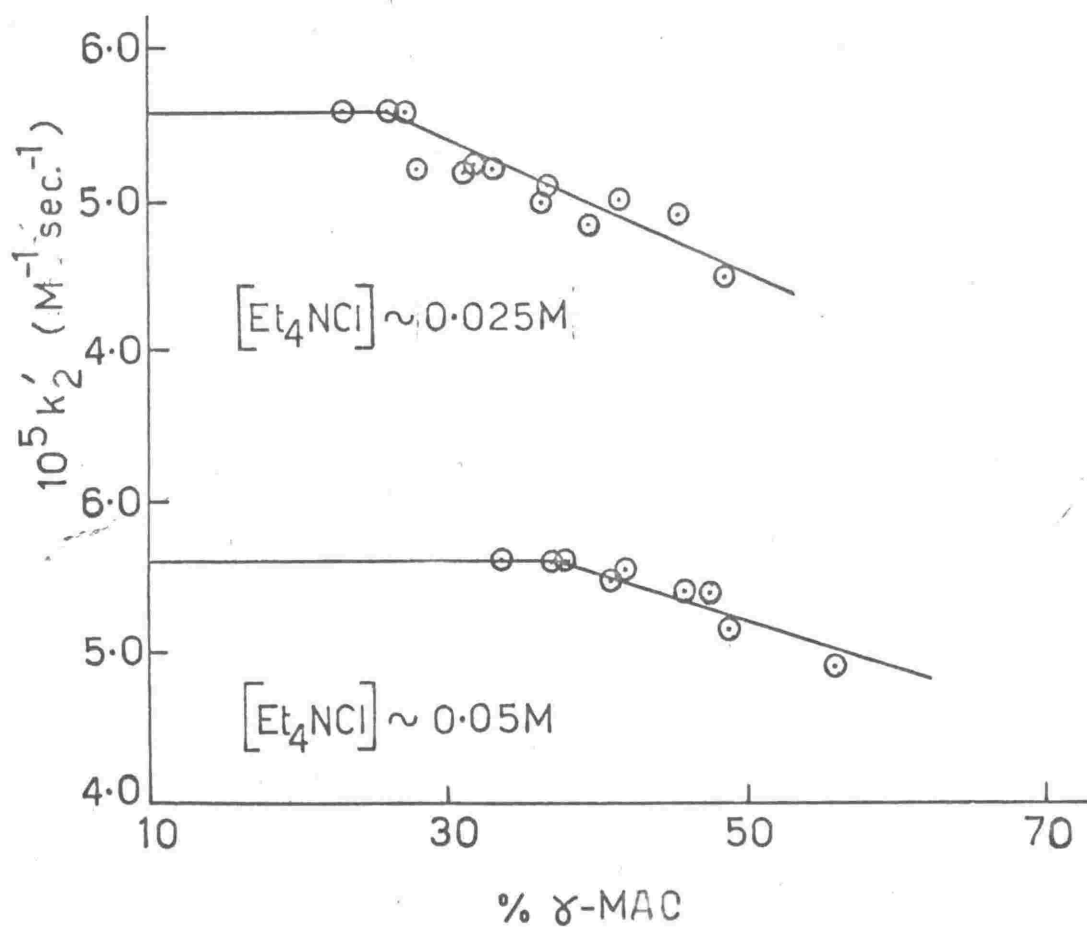


TABLE XXII

% $\gamma$ -MAC	$\Delta k_2^*$ (obs.) ( $b \sim 0.1M$ )	$\Delta k_2^*$ (calc.) ( $b \sim 0.1M$ )	$\Delta k_2^*$ (obs.) ( $b \sim 0.05M$ )	$\Delta k_2^*$ (calc.) ( $b \sim 0.05M$ )	$\Delta k_2^*$ (obs.) ( $b \sim 0.025M$ )	$\Delta k_2^*$ (calc.) ( $b \sim 0.025M$ )	$[HCl]_{tot.}$ ( $10^3 M$ )
35	$\sim 0$	$\sim 3.5$	$\sim 0$	$\sim 7$	$\sim 7$	$\sim 14$	$\sim 4.6$
45	$\sim 0$	$\sim 5.5$	$\sim 4.5$	$\sim 11$	$\sim 15$	$\sim 22$	$\sim 6.5$
50	$\sim 1$	$\sim 6.5$	$\sim 7$	$\sim 13$	$\sim 19$	$\sim 26$	$\sim 7.5$
	$\Delta(\Delta k_2^*)$	$\Delta(\Delta k_2^*)$	$\Delta(\Delta k_2^*)$	$\Delta(\Delta k_2^*)$	$\Delta(\Delta k_2^*)$	$\Delta(\Delta k_2^*)$	
35-45	0	2	4.5	4	8	8	163.
35-50	1	3	7	6	12	12	

 $b = [Et_4NCl]$ 
 $\Delta k_2^* = \% \text{ depression of } k_2^*$

hydrogen chloride will be constant irrespective of the concentration of  $\text{Et}_4\text{NCl}$ . Therefore, if the substrate concentration is kept constant in a series of runs, the concentration of hydrogen chloride at a given percentage of  $\gamma$ -isomer formation will be the same in all the runs. Thus  $\Delta\Delta k_2'$ , which is the difference between  $\Delta k_2'$  values for any two percentages of  $\gamma$ -isomer formation in the same run, should equal the percentage by which the  $\text{Et}_4\text{NCl}$  concentration decreases due to  $\text{HCl}_2^-$  formation, so these values of  $\Delta\Delta k_2'$  should be equal to the increase in hydrogen chloride concentration divided by the  $\text{Et}_4\text{NCl}$  concentration. Calculated and observed values of  $\Delta\Delta k_2'$  are shown in Table XXXII and they are in accord with the above predictions.

To turn to the total observed depression, percentages of the  $\gamma$ -isomer were obtained from the ratios of the areas of the peaks for the two isomers on gas chromatograms and these percentages were substituted into the expression:  $\frac{\% \gamma (\text{eq.})}{\% \gamma (\text{eq.}) - \% \gamma (t)}$  which is derived from:

$$\frac{x_e}{x_e - x} = \frac{\% \gamma (\text{eq.}) \times \frac{a}{100}}{\frac{a}{100} \times \% \gamma (\text{eq.}) - \% \gamma (t) \times \frac{a}{100}} \quad \text{where } a = [\alpha\text{-MAC}] \text{ at}$$

time  $t = 0$ . Therefore the assumption is made that the concentration of allylic chlorides remains constant throughout the reaction, i.e., that the only reaction is rearrangement. Consequently, at 20%  $\gamma$ -isomer formation we assume that  $[\gamma\text{-MAC}] = 0.2a$ , whereas if elimination is considered  $[\gamma\text{-MAC}] = 0.2(a - 0.0012)$  and if  $a = 0.1M$ ,

$$\frac{\Delta\gamma}{\gamma} = \frac{0.024 \times 10^{-2}}{0.02} = 1.2\% \quad \text{i.e., there is a 1.2\% compensation error in}$$

the determination of the concentration of the  $\gamma$ -isomer.

At 50%  $\gamma$ -isomer formation, the assumed concentration is 0.5a, while the real concentration is 0.5 ( $a = 0.0065$ ), so that  $\frac{\Delta\gamma}{\gamma} = \frac{0.325 \times 10^{-2}}{0.05} = 6.5\%$ . Calculations of  $k_2'$  using the corrected  $\gamma$ -isomer concentrations give values 1.7% lower for 20%  $\gamma$ -isomer formation and 13.6% lower for 50%  $\gamma$ -isomer formation, than the assumed concentrations do. Therefore, not only does the method of analysis compensate for the elimination reaction destroying substrate, it also compensates to the extent of 7.1% at 50%  $\gamma$ -isomer formation, for the depression in  $k_2'$  due to  $\text{HCl}_2^-$  ion formation. However, as this compensation is only 1.4% at 35%  $\gamma$ -isomer formation, it does not explain the apparently constant 6-7% discrepancy between observed and calculated  $\Delta k_2'$  values for from 35%-50%  $\gamma$ -isomer formation.

As the average error in determining the percentage of  $\gamma$ -methylallyl chloride is 2-4% (of the percentage), an overall spread of the order of that obtained for the depressed values of  $k_2'$  shown in Fig. 9, is within experimental error.

It is clear therefore, that after the formation of 35% of the  $\gamma$ -isomer, when the  $\text{Et}_4\text{NCl}$  concentration is approximately 0.05M, the constancy of values for  $k_1'$  or  $k_2'$  is an experimental artifact and the values do not reflect, nor are they simply related to, the true rate constant for the reaction. Consequently attention was focussed upon the determination of  $k_2'$  values over the region of the reaction involving 0-35%  $\gamma$ -isomer formation. Over this region, the effects of the concurrent elimination reaction on rate constants for rearrangement

calculated from the simple rate equation of Appendix I, are small enough to be neglected and the use of more complex equations in an attempt to take this side-reaction into account was not warranted.

The effect of added water on the rate constant was tested by adding approximately 0.05M water to one reaction tube in Run 31. The result is shown in Table XXX. A rate constant depression of 9.5% was obtained. This is similar to the depression obtained by Parker<sup>146</sup> for the reaction of methyl iodide with chloride ions in dimethylacetamide. He reports a three-fold increase in rate on going from dimethylacetamide containing 1M water to pure dimethylacetamide.

The behaviour of  $k_2'$  in the presence of hydrogen chloride added initially, the mean initial value for which is correlated with an  $\text{Et}_4\text{NCl}$  concentration approximately equal to that in excess of the requirements for dihalide ion formation, rather than its added concentration, shows that the character of  $k_2'$  depends only on the concentration of non-specifically bonded halide ions.

Despite the complexity of the rearrangement reaction when it is approaching equilibrium, the formation of at least 25% of the  $\gamma$ -isomer can be studied under conditions of negligible ambiguity and the second-order kinetics obtained are indicative of the operation of the  $\text{S}_{\text{N}}2'$  mechanism.

Considering the complications involved in the approach to equilibrium starting from  $\alpha$ -methylallyl chloride, the approach starting from  $\gamma$ -methylallyl chloride was of considerable interest and an investigation of this was accordingly planned.

TABLE XXXIII

Run 33. Reactions of  $\gamma$ -Methylallyl Chloride in Acetonitrile (96°C)

Time (hr.)	ml. NaOH (0.01365N)	$[H^+]$ ( $10^{-3}M$ )	$(\bar{\alpha})_{std.}$	$(\bar{\alpha})_{R.M.}$	$K_{(cal.)}$	% $\alpha$ -MAC	$10^8 k_1$ ( $sec.^{-1}$ )
0.0	0.21	0.0	3.87	79.6	2.46	0.51	-
94.9	0.69	1.3	4.22	49.8	2.26	0.88	(3.77)
191.2	0.67	1.2	3.88	41.2	2.46	0.98	2.41
320.5	0.69	1.3	4.13	36.0	2.31	1.19	2.06
505.5	0.85	1.7	3.97	25.2	2.40	1.63	2.18

168.

 $[\gamma\text{-MAC}] = 0.1032M$  $T = 95.89^\circ C$  $K_{(cal.)}$  = the calibration constant of the GLC detector $(\bar{\alpha})$  = the peak area ratio of the isomers

the two reactions, reveals that the composite rate constant for rearrangement starting from the  $\gamma$ -isomer is approximately 0.65 times that of the first estimated value for starting from the  $\alpha$ -isomer.

As acid catalysis of the rearrangement reaction is at a minimum for the  $\gamma$ -isomer, the rate constant observed is the upper limit of the uncatalysed reaction.

$\gamma$ -Methylallyl chloride is obviously much more stable in acetonitrile than the  $\alpha$ -isomer and this is attributed to its inability to undergo elimination of hydrogen chloride to form butadiene at a significant rate, as has been shown by acid analyses and v.p.c. analyses. As only a small amount of decomposition of the substrate occurs, catalysis of the rearrangement reaction through the formation of hydrogen chloride cannot operate.

The amount of "acid" produced ( $\sim 1.3 \times 10^{-3}M$ ) is similar to that obtained from allyl chloride in acetonitrile in Section I and is a confirmation of the absence of substrate-solvent interactions, other than elimination, of any magnitude in this solvent.<sup>113</sup> These other interactions could either be acetonitrilium salt formation, or hydrolysis of the substrate by traces of water in the solvent.

The assumption that the concentrations of chloride ions produced in reactions of  $\alpha$ -methylallyl chloride, except for  $1 \times 10^{-3}M$ , are due to elimination, is therefore justified.

Despite the small percentage of  $\alpha$ -isomer formed at equilibrium (29.5%) and the accompanying difficulties in determining the small percentages en route to equilibrium, a fairly precise study of the

approach to equilibrium starting from the  $\gamma$ -isomer and catalysed by  $\text{Et}_4\text{NCl}$  appeared to be feasible.

X The Et<sub>4</sub>NCl Catalysed Rearrangement Reaction of  $\gamma$ -Methylallyl Chloride in Acetonitrile

(i) Introduction

Duplicate runs at 96.0°C were carried out to study the chloride ion catalysed reactions of  $\gamma$ -methylallyl chloride in acetonitrile. Et<sub>4</sub>NCl (ca. 0.1M) provided the nucleophile, the higher concentration being chosen to minimize the effect of any hydrogen chloride produced during the rearrangement reaction.

Analyses for both hydrogen and chloride ions were carried out for one run.

(ii) Results and Discussion

The results for Runs 34 and 35 are shown in Tables XXXIV and XXXV.

The composite pseudo-first-order rate constant is constant for approximately 50% of the theoretical rearrangement, i.e., for the formation of about 15% of the  $\alpha$ -isomer and then it falls off as the reaction proceeds. Production of hydrogen chloride is slow, with only  $1 \times 10^{-3} M$  at the most being attributable to an elimination reaction rather than solvolysis. A small butadiene peak was present on the gas chromatograms for the latter part of the runs. This peak was considerably larger than that observed for the run in the absence of Et<sub>4</sub>NCl (Run 33).

TABLE XXXIV

Run 3. The  $\gamma$ -Methylallyl Chloride/Et<sub>4</sub>NCl Reaction in Acetonitrile(96°C)

Time (min.)	% $\alpha$ -MAC	$\log_{10}(X_e - X)$ ( $X_e = 29.5$ )	$10^6 k_1'$ (sec. <sup>-1</sup> )
0	0.58	1.4612	-
390	4.27	1.4019	5.84
833	7.94	1.3336	5.88
1351	11.62	1.2524	5.93
1860	14.2	1.1847	5.71
2759	18.4	1.0453	5.79
3707	20.8	0.9395	5.40
5855	24.6	0.6902	5.05

$$[\gamma\text{-MAC}] = 0.1136M$$

$$[\text{Et}_4\text{NCl}] = 0.1080M$$

$$T = 95.85^\circ\text{C}$$

$$\text{Mean (5) } k_1' = 5.85 \pm 0.08 \times 10^{-6} \text{ sec.}^{-1}$$

$$k_2' = 5.40 \times 10^{-5} M^{-1} \text{ sec.}^{-1}$$

$$k_2'' = 1.59 \times 10^{-5} M^{-1} \text{ sec.}^{-1}$$

TABLE XXV

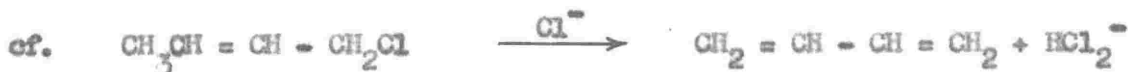
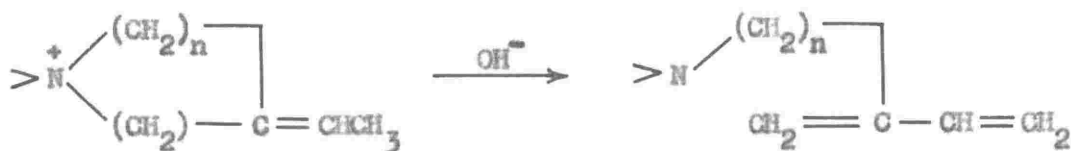
Run 35. The  $\delta$ -Methylallyl Chloride/ $\text{Et}_4\text{NCl}$  Reaction in Acetonitrile ( $96^\circ\text{C}$ )

Time (min.)	% $\alpha$ -MAC	$\log_{10}(X_\infty - X)$ ( $X_\infty = 29.5$ )	$10^6 k_1$ ( $\text{sec.}^{-1}$ )	ml. NaOH (0.01365N)	$[\text{H}^+]$ ( $10^{-3}\text{M}$ )	ml. $\text{AgNO}_3$ (0.01518N)	$\Delta[\text{Cl}^-]$ ( $10^{-3}\text{M}$ )
0	0.62	1.4606	-	0.34	0.0	32.71	0.0
375	3.86	1.4089	5.29	0.36	0.1	32.88	0.5
826	7.35	1.3454	5.35	0.44	0.3	-	-
1335	10.82	1.2714	5.44	0.63	0.8	-	-
2025	14.2	1.1847	5.23	0.51	0.5	32.85	0.4
2837	17.5	1.0792	5.16	0.63	0.8	-	-
4215	20.6	0.9494	4.66	0.86	1.4	33.00	0.9
5612	23.4	0.7853	4.62	1.16	2.3	33.20	1.5

173.

$$\begin{aligned}
 [\delta\text{-MAC}] &= 0.1124\text{M} \\
 [\text{Et}_4\text{NCl}] &= 0.0993\text{M} \\
 T &= 95.89^\circ\text{C} \\
 \text{Mean (5) } k_1' &= 5.29 \pm 0.11 \times 10^{-6} \text{ sec.}^{-1} \\
 k_2' &= 5.33 \times 10^{-5} \text{ M}^{-1} \text{ sec.}^{-1} \\
 k_2'' &= 1.57 \times 10^{-5} \text{ M}^{-1} \text{ sec.}^{-1}
 \end{aligned}$$

Elimination of hydrogen chloride from  $\gamma$ -methylallyl chloride to form butadiene by a bimolecular mechanism, would involve attack on a hydrogen atom attached to the  $\delta$ -carbon atom, i.e., 1,4 elimination. This mechanism is rare, occurring in special structures, but it can involve the rearrangement of a double bond.<sup>147</sup> e.g.



It tends to occur in highly activated systems or under vigorous conditions. For example, in the reaction above, the hydrogen atoms of the methyl group are activated by the strongly electron-withdrawing, positively-charged nitrogen atom, while unsaturated 1,4-dibromo-compounds undergo 1,4 elimination with metals.<sup>59,74,84</sup>

There is little activation of the protons of the  $\gamma$ -methyl group for removal in  $\gamma$ -methylallyl chloride and the inductive effect of the  $\alpha$ -chlorine atom should aid the approach of the nucleophile and the breaking of the carbon-hydrogen bond more for an  $\alpha$ -methyl group, than for a more remote  $\gamma$ -methyl group. Therefore, if elimination from  $\alpha$ -methylallyl chloride is slow, elimination from the  $\gamma$ -isomer could be expected to be even slower, which is in accord with the results observed.

The small amount of elimination product formed is attributed to elimination from the  $\alpha$ -isomer produced by the rearrangement reaction.

The values of  $k_2'$  for the two runs were plotted against the percentage of  $\alpha$ -isomer formed, to estimate the percentage depression of the rate constant for given percentages of  $\alpha$ -isomer formation. These estimations were 5% at 20%, 12% at 22.5%, 14% at 23.5% and 18.5% at 25%.

A satisfactory explanation for the fall-off in the rate constant is not easily found, but it is postulated that elimination of hydrogen chloride from the product -  $\alpha$ -methylallyl chloride - is partially responsible. Using the data for Run 35 and the rate constants for the elimination reactions, both catalysed and uncatalysed, of the  $\alpha$ -isomer (Section VI), the concentration of elimination products produced during the time interval 4215-5612 minutes was calculated. The value obtained,  $6.5 \times 10^{-4} M$ , was in accord with the hydrogen and chloride ion analysis data for Run 35, and the destruction of this concentration of product isomer, reduces the value for  $k_1'$  at 5612 minutes from 4.95 to 4.62, i.e., by 6.5%.

An experimental error of 3-4% in estimating the fraction of  $\alpha$ -isomer would change the rate constant by 7.5-10.5% at 23.4%  $\alpha$ -isomer formation, but there is no reason to assume consistently low values were being obtained. Errors in the compositions of the standards used for calibrating the gas chromatograph could contribute no more than 2% to the depression of the final rate constant, while an error of 0.5% in the

equilibrium percentage, i.e., 29.5%  $\alpha$ -isomer instead of 29.0%, would depress  $k_1'$  from 4.81 to 4.62, i.e., by 4%, but it would also depress the initial value. Dihalide ion formation could contribute only about 1% to the observed depression. Further discussion of the drift is postponed until Section XIII, when more information is available.

Considering the first 50% of the rearrangement reaction where the rate constants are constant, the mean value for  $k_1'$ , when divided by the concentration of  $\text{Et}_4\text{NCl}$ , gives a value for  $k_2'$  - the composite second-order rate constant - in good agreement for both runs, while the mean of these values is in good agreement with the mean of values obtained starting from the  $\alpha$ -isomer. (See Table LXIII).

The composite rate constant for the approach to equilibrium starting from the  $\alpha$ -isomer is not very sensitive to a small error in the equilibrium percentage of  $\gamma$ -methylallyl chloride; however, the rate constant for the approach starting from the  $\gamma$ -isomer is quite sensitive to a small error in the equilibrium percentage of the  $\alpha$ -isomer, so that a kinetic estimation of the equilibrium constant can be made by determining which value gives agreement of the composite  $k_2'$  values for the approach to equilibrium starting from either isomer. This will be discussed further in Section XIV.

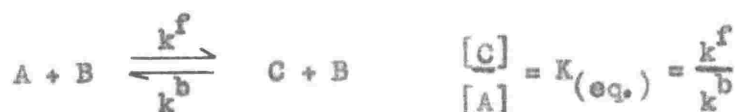
Having demonstrated the linear dependence of  $k_1'$  on the concentration of  $\text{Et}_4\text{NCl}$  (over the range 0.025-0.1M) for the rearrangement reaction of the  $\alpha$ -isomer, it was not considered necessary to repeat this for the  $\gamma$ -isomer. The rate of rearrangement

is obviously greatly accelerated by chloride ions and the primary chloride is less likely than the secondary to react by an  $S_N1'$  mechanism.<sup>148</sup> Moreover, by the principle of microscopic reversibility,<sup>149</sup> if the forward reaction is second-order then the back reaction must be second-order.

# XI Determination of the Equilibrium Constant at 96.0°C

## (1) Introduction

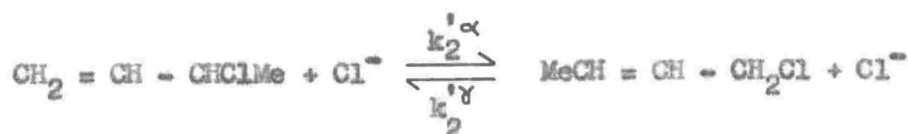
There are two methods of evaluating the equilibrium constant for a reversible first-order or pseudo-first-order reaction as the kinetics are simply related to the stoichiometry:<sup>53</sup>



(a) The relative concentrations of the compounds C and A, when the reaction is at equilibrium, may be determined, or (b) the rate of approach to equilibrium from both directions, i.e., starting from both A and C, may be studied and the composite first-order rate constants for pairs of runs, (runs carried out using approximately the same concentrations of reactants and adjusted to the same nucleophile concentration), are then calculated using various values of  $K_{(eq.)}$  to find the value for which both coincide.

If both methods are used they serve as a check on one another.

In this section seven determinations of  $K_{(eq.)}$  using method (a) are described.



$$\frac{[\gamma\text{-MAC}]}{[\alpha\text{-MAC}]} = K_{(eq.)} = \frac{k_2^{\alpha}}{k_2^{\gamma}}$$

Five of them were carried out using the  $\alpha$ -isomer as the substrate and two using the  $\gamma$ -isomer as the substrate.

(ii) Procedure

Reaction mixtures were prepared and reaction tubes were filled and sealed as for a kinetic run. In all the tubes, except one, the concentration of each reagent was 0.1M. In this tube the concentration of  $\text{Et}_4\text{NCl}$  was 0.05M. The tubes were placed in a thermostat at  $96.0^\circ\text{C}$ , for the times specified in the tabulated results, to react to "infinity". Analyses by gas chromatography to determine the isomer ratio were performed as for a kinetic run.

(iii) Results and Discussion

The results are shown in Table XXXVI.

The seven estimations give an average value of 2.39 for  $K_{(\text{eq.})}$  at  $96.0^\circ\text{C}$ , or an equilibrium percentage of the  $\alpha$ -isomer of 29.5%, with a spread of 0.9% over the seven values. The standard deviation of the values from the mean is shown in the Table.

It is interesting to compare this value for  $K_{(\text{eq.})}$  with that obtained by Dittmer and Marcantonio in the low polarity aprotic solvent toluene at  $80^\circ\text{C}$ , which was 2.35.<sup>150</sup>

The half-life of the rearrangement reaction at  $96.0^\circ\text{C}$  with reactant concentrations of approximately 0.1M, is approximately 36 hours, so that ten half-lives amount to about 15 days. The reaction times used were considerably longer than this, to allow for the fall-off in the rate constants for the rearrangement reactions of both isomers, which has been discussed in Sections VIII and X.

TABLE XXXVI

The Equilibrium Constant at 96.0°C (Method (a))

Reaction Time (day)	K <sub>(cal.)</sub> (GLC detector)	( $\frac{\gamma}{\alpha}$ ) <sub>R.M.</sub>	% $\alpha$ -MAC	Reactant Isomer	K <sub>(eq.)</sub>
29	0.711	3.39	29.3	$\alpha$ -MAC	2.41
52	0.710	3.36	29.5	$\alpha$ -MAC	2.39
86	0.716	3.35	29.4	$\alpha$ -MAC	2.40
* 90	0.735	3.20	29.8	$\alpha$ -MAC	2.36
100	0.713	3.26	30.1	$\alpha$ -MAC	2.32
59	0.716	3.33	29.5	$\gamma$ -MAC	2.39
71	0.752	3.23	29.2	$\gamma$ -MAC	2.42

188.

[MAC] = 0.1M

Mean K<sub>(eq.)</sub> = 2.39  $\pm$  0.03[Et<sub>4</sub>NCl] = 0.1M except for \* (0.05M) $\Delta G^\circ = -639 \pm 9 \text{ cal.mole}^{-1}$

The equilibrium constant does not vary with time over a period equal to three times the shortest reaction time, which indicates that equilibrium had been attained. Values obtained starting from either isomer are identical, within experimental error, again signifying the attainment of equilibrium. Therefore it appears that despite the complications of side reactions, a constant value for  $K_{(eq.)}$  can be determined by this method.

The fact that the composite rate constants for the approach to equilibrium starting from either isomer are in good agreement, when calculated using the value of  $K_{(eq.)}$  determined above, suggests that side reactions do not significantly alter the value of  $K_{(eq.)}$  from that which would obtain in their absence. As  $k_2'$  values have been shown to be almost independent of the concentration of  $Et_4NCl$  over the concentration range 0.025-0.1M, the different concentrations of  $Et_4NCl$  in the runs for the two isomers may be neglected.

The effect of side reactions on the value for  $K_{(eq.)}$  will be discussed further in Section XIV.

XII Mechanistic Conclusions

Extraction of the rate constants for the first- and second-order rearrangement and elimination reactions, from the data previously recorded, allows the following rate ratios to be determined for 96.0°C.

TABLE XXVII

$\frac{k_2' b}{k_1}$	$\sim$	125	$\frac{k_2^E b}{k_1}$	$\sim$	4.5	$\frac{k_1'}{k_1^E}$	$\sim$	0.65
$\frac{k_2' b}{k_1^E + k_2^E b}$	$\sim$	10	$\frac{k_2' b}{k_1^E + k_2^E b}$	$\sim$	14	$\frac{k_2^E b}{k_1^E + k_2^E b}$	$\sim$	4.0

These ratios have been determined using the rate expressions:

$$v = k_1 a$$

$$v = k_2 a b = k_1(\text{obs.})a \quad (b = 0.05M)$$

so that the rates of the first- and second-order reactions can be compared. Values for the rate constants used are as follows:

$$k_1' = 2.22 \times 10^{-8} \text{ sec.}^{-1} \quad (\text{Run 33})$$

$$k_1^E = 3.45 \times 10^{-8} \text{ sec.}^{-1} \quad (\text{Run 24})$$

$$k_2' = 5.55 \times 10^{-5} \text{ M}^{-1} \text{ sec.}^{-1} \quad (\text{Run 30})$$

$$k_2^E = 3.15 \times 10^{-6} \text{ M}^{-1} \text{ sec.}^{-1} \quad (\text{Runs 26 + 27})$$

$$k_2^{\alpha} = 3.91 \times 10^{-5} \text{ M}^{-1} \text{ sec.}^{-1} \quad (\text{Run 30})$$

$$k_2^{\gamma} = 1.59 \times 10^{-5} \text{ M}^{-1} \text{ sec.}^{-1} \quad (\text{Run 34})$$

(Note: The accuracy of the rate constants for elimination does not really warrant three figure representation. The variation in temperature between the runs is negligible).

### The Chloride Ion Catalysed Rearrangement Reaction

The catalytic effect of chloride ions on the rate of rearrangement is very large. It is not a salt effect of the "ionic-strength" type on an  $S_N1$  mechanism, as it has been shown to be specific by substituting  $\text{Et}_4\text{NClO}_4$  for  $\text{Et}_4\text{NCl}$  and by partially converting  $\text{Et}_4\text{NCl}$  into  $\text{Et}_4\text{NHCl}_2$ . (See Runs 25 and 32).

An ion-pair mechanism similar to that proposed by Rawlinson and Noyes<sup>141</sup> and Shandala, Waight and Weinstock,<sup>140</sup> for the rearrangement of 1-phenylallyl chloride in dimethylformamide, is also ruled out by the magnitude and specificity of the catalysis. Their mechanism involves stabilisation of rearrangement via an ion-pair, by interaction of the anion, or an ion-pair of the added electrolyte, with the positive centre.

An intramolecular mechanism involving little charge separation is of course, also not possible.

Both an acid-catalysed  $S_N1$  mechanism and an elimination-addition mechanism have also been shown to be incapable of contributing significantly to the catalysed rearrangement reaction. (See Sections III and IV and Run 32).

The ionising and dissociating ability of acetonitrile is (as for other dipolar aprotic solvents) low, when compared with that for protic solvents of comparable dielectric constant,<sup>8</sup> so that promotion of an ion-pair mechanism at the expense of a concerted mechanism is not particularly favoured, especially in a compound not containing good carbonium ion-stabilising substituents.

Dittmer and Marcantonio observed a pseudo-zero-order rearrangement reaction for  $\alpha$ - and  $\delta$ -methylallyl chloride, catalysed by glass wool and diethylammonium chloride, in toluene at 80°C.<sup>150</sup> They interpreted their results as being due to rearrangement through an ion-pair mechanism, with the reaction occurring on the glass surface saturated with reactant and being electrophilically catalysed by the boron atoms in the glass and by the diethylammonium ion. The rate observed was great enough for the mechanism to merit consideration in the present project.

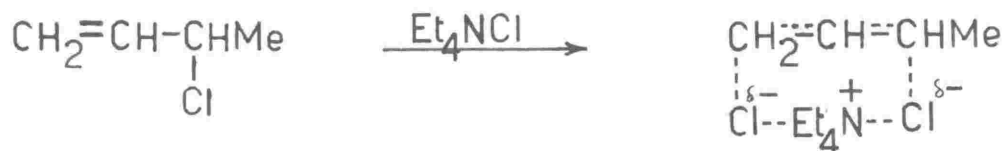
However, although not specifically tested for at this stage by varying the surface area of the reaction tubes by means of adding packing, this mechanism was considered unimportant, because of (a) the magnitude and specificity of the catalysis by  $\text{Et}_4\text{NCl}$ , (b) the absence of any significant catalysis by  $\text{Et}_4\text{NClO}_4$  or  $\text{Et}_4\text{NHCl}_2$ , both containing the tetraethylammonium ion which could presumably act as an electrophilic catalyst, (c) the slow rate of rearrangement in the absence of  $\text{Et}_4\text{NCl}$ , and (d) the nature of the solvent, acetonitrile, which, by donating the lone pair of electrons on the nitrogen atom to electron-deficient boron atoms in the glass, should effectively compete with the methylallyl

chloride molecules for these centres. Acetonitrile forms adducts with Lewis acids such as boron trifluoride.<sup>151</sup>

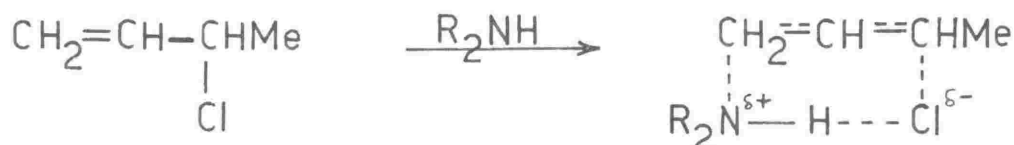
Young, Clement and Shih established the homogeneity of the reaction of  $\alpha$ -methylallyl chloride with trimethylamine in acetone at 75°C.<sup>81b</sup> This reaction is however faster than the rearrangement reaction in acetonitrile and so would be better able to compete with a surface reaction. Both acetone and acetonitrile are electron-pair donors whereas toluene has only the  $\pi$ -bond electrons for interaction with a surface.

The concept of electrophilic catalysis by the cation of the nucleophilic reagent must be considered. Obviously, cation catalysis of an  $S_N1$  mechanism for the rearrangement reaction is ruled out by the salt effects observed. (See Runs 25 and 32).  $Et_4NClO_4$  has a dissociation constant for the ion-pair similar to that for  $Et_4NCl$ ,  $5.6 \times 10^{-2}$  compared with  $2.88 \times 10^{-2}$ .<sup>131,138</sup>

However, cation catalysis could aid an  $S_N2$  mechanism. Nucleophilic attack on the  $\gamma$ -carbon atom of the substrate could involve either the "free" chloride ion or an ion-pair of  $Et_4NCl$ , with the cation facilitating the departure of the leaving group in a similar way to that postulated for the hydrogen atom of secondary amines in amine catalysed rearrangement.<sup>75</sup> e.g.



cf.



This could mean an efficiency for the ion-pair comparable with that of the free ion. However, the tetraethylammonium ion is large and it has a well shielded charge,<sup>40</sup> so that its interaction with a negative ion, or end of a dipole is weak, as shown by the high ion-pair dissociation constants for various salts, e.g., those quoted above and other halides.<sup>153</sup> It would not therefore be expected to facilitate leaving group departure to a significant extent. Moreover, it is probably extending the concept of electrophilic catalysis a little too far, to compare ion-dipole interactions of cations with hydrogen bonding, in polar solvents, except perhaps for the lithium cation.<sup>42b</sup>

The pure second-order kinetics obtained for the rearrangement reaction, together with the stability of the methylallyl chlorides in acetonitrile in the absence of  $\text{Et}_4\text{NCl}$ , when the catalysis due to hydrogen chloride produced by the concomitant elimination reaction is allowed for in the case of the  $\alpha$ -isomer, are considered to favour assignation of a straight forward  $\text{S}_{\text{N}}2'$  mechanism to the reaction.

### The Chloride Ion Catalysed Elimination Reaction

The catalytic effect of  $\text{Et}_4\text{NCl}$  on the elimination reaction is much smaller, but it is attributed to the addition of a second-order, bimolecular component to the existing first-order reaction, on the basis of salt effects.

$\text{Et}_4\text{NClO}_4$  has no effect on the first-order reaction, (Run 24), so that the catalysis by  $\text{Et}_4\text{NCl}$  cannot be a normal salt effect on an  $\text{E1}$  mechanism. Also the rate of the reaction is dependent on the concentration of  $\text{Et}_4\text{NCl}$ , while  $\text{Et}_4\text{NHCl}_2$  is ineffective as a nucleophile.

This information was derived from the gas chromatograms for Runs 28, 29, 31 and 32, by determining the peak area ratios of  $\gamma$ -methylallyl chloride to butadiene for various percentages of  $\gamma$ -isomer formation. (See Table XXXVIII). If both rearrangement and elimination were pure second-order reactions then the ratio of the products should be constant, independent of the concentration of the nucleophile, for any given percentage of rearranged product formed. For a four-fold change in  $\text{Et}_4\text{NCl}$  concentration, the ratios are in accord with second-order kinetics and when the first-order component of elimination is taken into account, the ratio of butadiene to  $\gamma$ -methylallyl chloride falls in between that expected assuming pure second-order kinetics and that expected allowing for the first-order component, using Run 29 as a standard. The ratios are also constant for a given percentage of  $\gamma$ -isomer formation, for the two runs containing approximately the same concentration of  $\text{Et}_4\text{NCl}$ , but with one also containing  $\text{Et}_4\text{NHCl}_2$ . (See Table XXXVIII).

TABLE XXXVIII

## The Dependence of the Rate of Elimination on Nucleophile Concentration

	Run 29. $[\text{Et}_4\text{NCl}] = 0.0249M$		Run 31. $[\text{Et}_4\text{NCl}] = 0.0970M$	
% $\gamma$ -MAC	14.5	27.2	48.9	14.8
P.A. $\left(\frac{\gamma}{\text{But.}}\right)$	7.11	6.75	4.01	8.36
P.A. $\left(\frac{\text{But.}}{\gamma}\right)$	0.141	0.148	0.249	0.120
P.A. $\left(\frac{\text{But.}}{\gamma}\right)_{\text{calc.}}$	0.141	0.148	0.249	0.109
				0.114
				0.192

188.

	Run 28. $[\text{Et NCl}] = 0.0259M$		Run 32. $[\text{Et NCl}] = 0.0470M, [\text{HCl}] = 0.0263M$	
% $\gamma$ -MAC	32.2		33.5	
P.A. $\left(\frac{\gamma}{\text{But.}}\right)$	4.78		4.98	

P.A. = peak area      But. = Butadiene       $\gamma$  =  $\gamma$ -Methylallyl Chloride

P.A. (calc.) means allowance has been made for the first-order component of elimination for one run relative to the other.

A bimolecular mechanism involving rate-determining nucleophilic attack on an ion-pair is a possibility which can be ruled out, as this would mean that ion-pair collapse, or first-order rearrangement, would have to be much faster than second-order elimination which is not observed. This mechanism, designated E2C+, has never been observed, presumably because the activation energy for proton loss is too small.<sup>147</sup>

### The Hydrogen Chloride Catalysed Rearrangement Reaction

The mechanism of catalysis of the first-order rearrangement reaction of the  $\alpha$ -isomer, by hydrogen chloride produced by the first-order elimination reaction, could either be  $S_N2'$  with or without hydrogen-bonding assistance to leaving group departure, or specific electrophilic catalysis of an ion-pair mechanism. In the former case, the hydrogen chloride molecule would be assigned a nucleophilicity of the order of that of the chloride ion, which would be in accord with the behaviour of neutral nucleophiles discussed in Chapter I. This would mean a nucleophilicity order of  $Cl^- \sim HCl \gg HCl_2^-$  for the  $S_N2'$  reaction of this substrate.

Rearrangement via electrophilic catalysis of ion-pair formation cannot be ruled out, but the magnitude of the catalytic effect appears to be somewhat larger than is observed for similar reactions, (See Sections V and IX). For example, the unimolecular racemisation reaction of 1-mesitylethyl chloride in acetone is only ten times faster in the presence of 0.1M hydrogen chloride than in that of lithium perchlorate of the same concentration.<sup>125</sup> However, the rate

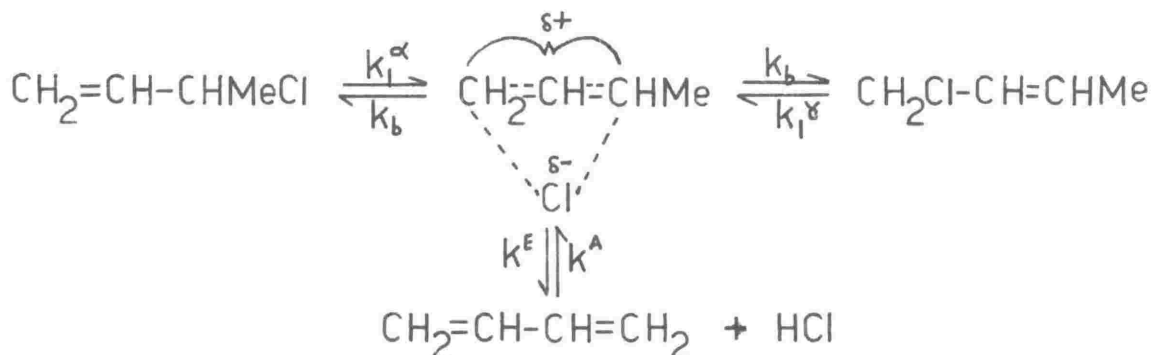
enhancement is  $10^2$  times that for the reaction in the absence of added electrolytes, and as lithium salts can be particularly effective in promoting ionisation,<sup>154</sup> this may be a bad example for comparison. For example, in the chloride ion and hydrogen chloride catalysed reactions of 1-phenylethyl chloride in nitromethane the catalytic effects of the acid and  $\text{Et}_4\text{NCl}$  are of somewhat similar magnitude to those of the acid and  $\text{Et}_4\text{NClO}_4$  in the present work.<sup>126</sup>

The absence of significant catalysis of the first-order elimination reaction by hydrogen chloride is difficult to explain with this mechanism. (See Section V). The similar reaction of 2-octyl bromide in acetonitrile was catalysed by the hydrogen bromide formed.

### Mechanisms of the Uncatalysed Reactions

The mechanisms of the first-order (or uncatalysed) rearrangement and elimination reactions are obscure.

If we assume that the first-order reactions proceed through an ion-pair intermediate, then the reactions could be represented as follows:



with the ion-pair being partitioned between collapse to either isomer and elimination, while the elimination products could recombine to form either isomer in the absence of a hydrogen chloride scavenger.

The following data from Runs 24, 27, 33 and 35 on (a) the first-order and (b) the  $\text{Et}_4\text{NCl}$  catalysed elimination reactions, is also required for the discussion.

(a)	In	$\sim 95$ hr.	the $\alpha$ -isomer	has formed	$1.4 \times 10^{-3} \text{ M}$	chloride ions.
	In	$\sim 95$ hr.	" $\gamma$ -isomer "	"	$1.3 \times 10^{-3} \text{ M}$	" "
	In	$\sim 520$ hr.	" $\alpha$ -isomer "	"	$6.0 \times 10^{-3} \text{ M}$	" "
	In	$\sim 520$ hr.	" $\gamma$ -isomer "	"	$1.7 \times 10^{-3} \text{ M}$	" "
(b)	In	$\sim 95$ hr.	" $\alpha$ -isomer "	"	$6.4 \times 10^{-3} \text{ M}$	excess chloride ions.
	In	$\sim 95$ hr.	" $\gamma$ -isomer "	"	$2.3 \times 10^{-3} \text{ M}$	" " "

Now  $k_1^\alpha \sim 2.4 k_1^\gamma$  would be expected from the value of the equilibrium constant for the rearrangement reaction, as  $K_{(\text{eq.})} = \frac{k_1^\alpha}{k_1^\gamma}$ . Similarly, the rates of elimination from the two isomers should be in the same ratio  $k_1^\alpha(\text{E}) \sim 2.4 k_1^\gamma(\text{E})$ , if the probability of ion-pair collapse to either isomer is the same. However, considering the data above for the first-order reaction, in the time interval 95-520 hr. the  $\alpha$ -isomer forms  $4.6 \times 10^{-3} \text{ M}$  chloride ions, while the  $\gamma$ -isomer forms  $0.4 \times 10^{-3} \text{ M}$  chloride ions. i.e.,  $k_1^\alpha(\text{E}) \sim 11 k_1^\gamma(\text{E})$  and this is a lower limit. Therefore, elimination is eleven times faster from the  $\alpha$ -isomer than from the  $\gamma$ -isomer, and this cannot be reconciled with the above discussion.

Again, and assuming (a) below to hold, in 95 hr., the chloride ion catalysed reaction of the  $\alpha$ -isomer has produced  $5.0 \times 10^{-3} M$  excess chloride ions over the concentration for the uncatalysed reaction, while for the  $\gamma$ -isomer the value is  $1 \times 10^{-3} M$  of which  $6.5 \times 10^{-4} M$  may be attributed to elimination from the  $\alpha$ -isomer, i.e., the product. Therefore once again  $k_1^\alpha(E) \sim 14 k_1^\gamma(E)$ . However, if elimination occurred from an intermediate with the positive charge localised on the  $\alpha$ -carbon atom, i.e., from an intermediate reached before the one in which rearrangement takes place, then  $k_1^\alpha(E) \sim 11 k_1^\gamma(E)$  would be possible.

Now, if an ion-pair mechanism is operative, the degree of charge formation and separation in the intermediates would appear to be low, judging from the low sensitivity of the rearrangement and elimination reactions to the ionic strength of the medium. No effect was observed for the latter reaction, when  $Et_4NClO_4$  was added, while the small increase in the rate of the former ( $\sim 10\%$ ) could be equally well explained as being due to stabilisation of the  $S_N2'$  transition state of a reaction in which the hydrogen chloride molecule is the nucleophile. Moreover, assuming that catalysis of rearrangement by hydrogen chloride is due to electrophilic catalysis of an ion-pair mechanism, catalysis of only one reaction can only be explained (see (b) below) by assuming a considerable difference in the degree of charge formation and separation in the intermediates for the two reactions. i.e., the intermediate from which elimination takes place would involve less development of charge separation than that in which rearrangement takes place.

However, if the normal stereochemical requirements for elimination are operative, i.e., trans elimination, then the intermediate for elimination would appear to need to involve a greater development of charge separation than that for rearrangement, and therefore the elimination reaction should be the more sensitive to the ionic strength of the medium and electrophilic catalysis. This is in direct opposition to the observed results, so that unless an intermediate can be envisaged in which the reverse holds, a homogeneous ion-pair mechanism will not explain the results.

Assuming an ion-pair mechanism for the first-order reactions two further possible effects may be considered.

(a) Catalysis of the elimination reaction by  $\text{Et}_4\text{NCl}$  could be due to its combining with the hydrogen chloride produced, to form the dihalide ion ( $\text{HCl}_2^-$ ), thus preventing the back addition of hydrogen chloride to butadiene. If this were true and, as there is no enhancement of the elimination reaction due to a normal salt effect,  $k_1^E(\text{true}) \sim 5.5 k_1^E$ , i.e., the first-order rate constant would be that determined in Runs 26 and 27, which was assigned to a mixed-order reaction. (See Table XXXVII).

However, using data from Run 24, in a reaction time of approximately 530 hr., the concentration of each elimination product is  $6 \times 10^{-3} \text{M}$  in the absence of  $\text{Et}_4\text{NCl}$ . Therefore, if back addition were prevented the concentration of products would be about  $5.5 \times 6 \times 10^{-3} = 33 \times 10^{-3} \text{M}$ , so that about  $27 \times 10^{-3} \text{M}$  of the products would have back added.

Now, using data from Run 21, in approximately 550 hr. with butadiene and hydrogen chloride concentrations of about  $4 \times 10^{-2} \text{M}$  and  $2 \times 10^{-2} \text{M}$  respectively, only about  $1 \times 10^{-2} \text{M}$  of each has reacted, so that even with an initial concentration of elimination products of  $2 \times 10^{-2} \text{M}$ , only about  $5 \times 10^{-3} \text{M}$  would back add in 530 hr., compared with the value of  $27 \times 10^{-3} \text{M}$  required by the hypothesis. Therefore back addition is too slow for the assumption to be justified. The assumption is also not in accord with the second-order kinetics observed for the chloride ion catalysed elimination reaction.

(b) Catalysis of the first-order rearrangement reaction could also be due to back addition of the products of the first-order elimination reaction. (See Runs 24 and 25). Again using data from Runs 21 and 24, in approximately 530 hr.,  $6 \times 10^{-3} \text{M}$  of each elimination product is produced, while in the same time the addition reaction produces  $1 \times 10^{-2} \text{M}$  of product, with reactant concentrations of  $4 \times 10^{-2}$  and  $2 \times 10^{-2} \text{M}$  as given in (a) above. Therefore, assuming the rate expression:<sup>130</sup>

$$v = k_3 [\text{Butadiene}][\text{HCl}]^2$$

the concentration of addition products from reactant concentrations of  $6 \times 10^{-3} \text{M}$  would be  $\frac{(6 \times 10^{-3})^3 (1 \times 10^{-2})}{(2 \times 10^{-2})^2 (4 \times 10^{-2})} \sim 1 \times 10^{-4}$ .

Comparison with the concentration of the  $\gamma$ -isomer produced during this reaction time,  $\sim 9 \times 10^{-3} \text{M}$ , shows that this explanation is untenable. The rate constants for the elimination reaction would be expected to be high initially and to fall off as back addition occurs, if the rate of the latter were appreciable.

It should also be noted that the addition reaction forms predominantly the  $\alpha$ -isomer. (Decomposition of the unsaturated compounds (Run 21) has been neglected in this discussion).

Nucleophilic Reactivity of the Chloride Ion

The considerable difference in reactivity towards even a  $\pi$ -bonded carbon atom, and hydrogen, exhibited by the chloride ion, suggests that the carbon nucleophilicity of the chloride ion is much greater than its hydrogen nucleophilicity, for this substrate.

XIII Surface Effects and the Effect of a Hydrogen Chloride  
Scavenger on the Rearrangement and Elimination Reactions  
of  $\alpha$ -Methylallyl Chloride

(i) Introduction

To further investigate and confirm some of the mechanistic conclusions of Section XII, the following work was carried out.

- (a) An investigation of the effect of adding 2,6-lutidine, to act as a scavenger for hydrogen chloride,<sup>102b,193,222</sup> on the rearrangement and elimination reactions of  $\alpha$ -methylallyl chloride in acetonitrile in the presence of  $\text{Et}_4\text{NCl}$  at  $100.0^\circ\text{C}$ .
- (b) An investigation of the effect of varying the surface area of the reaction tubes, by adding Pyrex glass wool, on the above reactions.
- (c) An investigation of the effect of varying the substrate concentration by a factor of three, on the above reactions.
- (d) An investigation of the effect of using soda glass and silicone grease-coated soda glass reaction tubes on the above reactions.
- (e) An investigation of the effect of Pyrex glass wool on the rearrangement and elimination reactions of  $\alpha$ -methylallyl chloride in acetonitrile, at  $100^\circ\text{C}$  in the absence of  $\text{Et}_4\text{NCl}$ .

(ii) Procedure

Reaction mixtures were prepared and reaction tubes were filled and sealed as described in Section VII. The concentrations of substrate and  $\text{Et}_4\text{NCl}$  were 0.1M and 0.05M respectively in all the runs except that

for (c) above, in which the substrate concentration was 0.3M.

2,6-Lutidine was dried and purified as described in Chapter VI.

Pyrex glass wool was washed thoroughly, dried in an oven, and finally cooled and stored in an evacuated desiccator. Silicone grease was dried in an oven. The reaction tubes to be coated were washed and dried, and then coated with grease to a height slightly greater than the proposed liquid height, before being constricted. They were then rebaked in the oven. All analyses were by gas chromatography. For Run 36, a suitable volume of reaction mixture was prepared and aliquots of a portion of it were added to a series of constricted Pyrex test tubes, as for normal procedure. 2,6-Lutidine was added to another portion and a series of tubes were again filled, while the final portion was added to a series of tubes containing Pyrex glass wool. Sets of three tubes, consisting of one from each series, were reacted for various suitable times at 100.0°C. By comparing the v.p.c. analysis data for the tubes containing 2,6-lutidine, or Pyrex glass wool, with that for the tube run under normal conditions, the effect of each variable could be estimated. Therefore the series of tubes prepared and reacted by the normal procedure constituted a "reference run", with which the series of tubes treated differently, i.e., the runs testing variables, could be compared. Three to four reaction tubes were used to test each variable and these were reacted for selected times.

A similar procedure was used for Runs 37 and 38.

The analysis data therefore involves comparison of the results for three or four tubes - one reference and two or three testing

variables - all run for the same reaction time and these are labelled A-D in the tables. Another set of results for another set of tubes, run for a different time is also labelled A-D, and so on. There are three runs each having a reference run.

The tables show the percentage of  $\gamma$ -isomer formed, the percentage change in the pseudo-first-order rate constant relative to that of the reference run, the ratio of the peak areas of the isomers and of the products (which is proportional to their concentration ratio) and, in the run where the percentages of rearranged product are not closely similar (Run 38), the peak area ratio of elimination product to total substrate, with the peak area of the  $\gamma$ -isomer being reduced to the value it would be if it were  $\alpha$ -isomer. The error in the  $(\frac{\alpha}{\gamma})$  ratios is the same as that estimated in Section VII, while that in the  $(\frac{\gamma}{\text{But.}})$  ratios is about 10%, due presumably to the volatility of butadiene and the very sharp peak obtained which makes peak width determinations difficult.

The runs were carried out at 100.0°C. Reaction times are not included in the tables, as the percentage of  $\gamma$ -isomer indicates when the set of reaction tubes was analysed and which sets were run for similar times.

#### (iii) Results and Discussion

The results for Runs 36, 37 and 38 are shown in Tables XXXIX-XLI.

TABLE XXXIX

Run 36. The Effect of Glass Wool and 2,6-Lutidine on the  $\text{Et}_4\text{NCl}$  Catalysed Reactions (100.0°C)

Run	$\left(\frac{\alpha}{\gamma}\right)$	% $\alpha$ -MAC	$\frac{10^2 \Delta k_1}{k_1 \cdot (A)}$	$\left(\frac{\alpha}{\text{But.}}\right)$
A	-	-	-	-
B	2.44	21.4	-	7.21
C	2.49	21.2	-	7.39
A	2.67	20.8	0	6.30
B	2.53	21.6	4.4	5.95
C	2.61	21.1	1.6	5.87
A	1.49	33.4	0	5.12
B	1.43	34.4	4.3	5.36
C	1.35	35.6	9.6	5.40
A	1.46	34.2	0	4.72
B	1.38	35.4	5.0	4.76
C	1.37	35.6	5.9	4.71

Run A.  $[\alpha\text{-MAC}] = 0.1M$   $[\text{Et}_4\text{NCl}] = 0.05M$  (reference run)

Run B.  $[\alpha\text{-MAC}] = 0.1M$   $[\text{Et}_4\text{NCl}] = 0.05M$  (glass wool  $\sim 0.2$  gm. per 2 ml.)

Run C.  $[\alpha\text{-MAC}] = 0.1M$   $[\text{Et}_4\text{NCl}] = 0.05M$  ( $[2,6\text{-Lutidine}] = 0.045M$ )

TABLE XL

Run 37. The Effect on the  $\text{Et}_4\text{NCl}$  Catalysed Reactions of Varying the Concentration of the Substrate and the Nature of the Surface of the Reaction Vessel ( $100.0^\circ\text{C}$ )

Run	( $\frac{\alpha}{\gamma}$ )	% $\alpha$ -MAC	$\frac{10^2 \Delta k_1}{k_1} (\text{\AA})$	$\left(\frac{\alpha}{\text{But.}}\right)$
A	3.29	19.8	0	6.25
B	3.27	19.9	+0.4	7.21
C	3.13	20.6	+4.8	7.07
D	3.41	19.3	-3.1	7.23
A	3.23	19.0	0	5.56
B	3.27	18.8	-1.4	5.93
C	3.22	19.1	+0.9	5.69
D	3.59	17.4	-9.9	5.89
A	1.66	32.2	0	4.82
B	1.75	31.0	-5.4	5.50
C	1.73	31.2	-4.1	4.89
D	1.79	30.6	-6.8	5.62
A	1.56	33.4	0	5.04
B	1.67	31.8	-6.8	5.54
C	1.69	32.8	-2.3	4.83
D	1.83	31.1	-9.6	4.98

Run A = reference run  $[\alpha\text{-MAC}] = 0.1M$   $[\text{Et}_4\text{NCl}] = 0.05M$

Run B = substrate concentration  $\frac{1}{2}$  that of reference run

Run C = soda glass tubes

Run D = tubes coated with silicone grease

TABLE XII

Run 38. The Effect of Glass Wool on the Uncatalysed Reactions (100.0°C)

Run	$\left(\frac{\alpha}{\gamma}\right)$	% $\alpha$ -MAC	$\left(\frac{\alpha}{\text{But.}}\right)$	$\left(\frac{\text{But.}}{\text{MAC}}\right)$
A	8.55	2.52	1.86	0.062
B	1.56	12.4	3.73	0.151
A	6.09	3.42	1.49 (5.04)*	0.098 (0.033)*
B	1.14	15.9	3.41 (12.2)*	0.214 (0.060)*
A	7.42	2.78	1.91	0.068
B	1.55	12.1	3.71	0.152

[  $\alpha$ -MAC ] = 0.1M

Run A = reference run

Run B = glass wool  $\sim 0.2$  gm. per 2 ml.

\* = sensitivity of GIC recorder changed.

The addition of 2,6-lutidine to a reaction mixture (Run 36C) has no effect, (within the limits of experimental error), on the relative rates of the rearrangement and elimination reactions, while a slight increase in the pseudo-first-order rate constant for rearrangement, of about 2% at 21%  $\gamma$ -isomer formation and about 8% at 35%  $\gamma$ -isomer formation, may be due to the 2,6-lutidine competing with chloride ions for the hydrogen chloride produced, thus eliminating the fall-off in the rate constant, due to  $\text{HCl}_2^+$  ion formation reducing the effective concentration of the nucleophile, which is observed in the absence of 2,6-lutidine.

There is obviously no enhanced rate of elimination and depressed rate of rearrangement due to the scavenger preventing hydrogen chloride from back adding to butadiene. Thus, the results are in accord with the conclusion reached in Section IV, that  $\text{Et}_4\text{NCl}$  effectively inhibits back addition so that an elimination-addition contribution to the mechanism of rearrangement is negligible. Bases such as 2,6-lutidine and collidine are frequently used as acid scavengers in reactions in aprotic or dipolar aprotic solvents, because they are weak nucleophiles and therefore do not interfere with the reaction to be studied.<sup>102b,193,222</sup>

Pyrex glass wool causes at the most a 5% increase in the rate constant for rearrangement (Run 36B), while the relative rates of rearrangement and elimination are unaffected.

Assuming that the adsorption isotherm of Freundlich<sup>39</sup> applies to  $\alpha$ -methylallyl chloride in acetonitrile, then:

$$\frac{x}{m} = kc^{1/n}$$

where  $x$  and  $m$  are the mass of adsorbed compound and adsorbent respectively,  $c$  is the concentration of the solution in equilibrium with the adsorbent, and  $n \geq 1$ . Now, rearrangement taking place on the surface of the reaction tubes has been shown to be unimportant, as has cation catalysis by the tetraethylammonium ion, by determining the rate of rearrangement in the absence of  $\text{Et}_4\text{NCl}$  and in the presence of  $\text{Et}_4\text{NClO}_4$ . (Runs 24 and 25). Therefore a surface-catalysed  $\text{S}_\text{N}1'$  mechanism cannot contribute to the rearrangement mechanism. However, there remains the possibility that  $\text{Et}_4\text{NCl}$  catalysed rearrangement and the  $\text{Et}_4\text{NCl}$  catalysed component of elimination involves nucleophilic attack on substrate adsorbed on the surface.

Making the assumption that the homogeneous reaction is unimportant; if the surface is saturated with substrate, the rate of rearrangement should be independent of the substrate concentration of the solution and the rate should increase on increasing the surface area of the reaction tubes, i.e., the first-order rate constant should vary with both the substrate concentration and the surface area of the reaction tubes. As only a 5% increase in the first-order rate constant is observed on packing the reaction tubes and as the rates of both rearrangement and elimination are proportional to the substrate concentration over a threefold change in its concentration, (see Run 37B), the surface cannot be saturated. Now, if  $n=1$  and  $x$  is directly proportional to  $c$ , as is required by the results of Run 37B, then  $x$  and hence  $k_1'$  should be proportional to  $m$ , but, as the variation of

$k_1'$  with  $m$  is very small, this possibility is untenable. Finally, if there were insufficient reactant to cover the surface of the reaction tubes at the highest substrate concentration used, then the results of Runs 36B and 37B would hold, if  $n=0$ ; but the results of Run 38B, which show the "first-order" reactions to be dependent on the surface area of the reaction tubes, show that the surface cannot accommodate all the reactant at 0.1M concentration - the standard one used - so that this possibility is also ruled out. Therefore the possibility remains, of an  $S_N2'$  reaction occurring on the surface at a rate comparable with that in homogeneous solution.

Although the possibility of polarisation of the double bond for nucleophilic attack caused by interaction of the chlorine substituent with an electrophilic surface is feasible, the stereochemical requirements of the cis transition state may counteract the facilitating effect of this polarisation, as the  $\delta$ -carbon atom may be protected from cis attack by an ion in solution. Cis attack by an adjacent adsorbed chloride ion would of course be quite possible.

In further attempts to probe for a surface reaction, Runs 37C and 37D were carried out. The former was carried out using soda glass ampoules. Soda glass contains no boron, to which Dittmer and Marcantonio assigned an electrophilic interaction with the substrate chlorine atom,<sup>150</sup> so it was considered that a heterogeneous  $S_N2'$  reaction dependent on boron-chlorine interaction and making a significant contribution to the (assumed homogeneous) rearrangement reaction, might be detectable using this method. It may be seen from

Table XL, that the rate constants for rearrangement are in good agreement for the runs in both Pyrex and soda glass tubes, with no evidence for a differentiating effect. The relative rates of rearrangement and elimination are also in good agreement.

In Run 37D the soda glass ampoules were coated with silicone grease in a further attempt to alter the nature of the surface of the reaction tubes. Silicone grease was chosen as one of the few available compounds likely to stay on the glass surface in the presence of acetonitrile at the reaction temperature required. This surface lacks the various cations present in soda glass, which presumably could interact with substrate chlorine. Here, a depression of about 7% in  $k_1$  is observed and this rate depression seems to apply also to the elimination reaction, as the product ratio appears to be unchanged, although a trend causing a change in the ratio of about 10% cannot be ruled out. (See below). Two interpretations are possible:

(a) a surface-catalysed component of the  $S_N2'$  mechanism, faster than the homogeneous component is suppressed, or (b) the silicone grease contains some impurity which slightly inhibits the reaction, possibly by interacting with the nucleophile. If the former is true, it appears, by comparison with the effect of soda glass tubes, that non-specific cation catalysis of the reactions is involved.

As such a contribution is small, judging by the effect of glass wool and of silicone grease and as it would merely entail increased activation of the substrate for nucleophilic attack due to initial polarisation of the double bond, it is not considered to affect the

validity of assigning an  $S_N2^i$  mechanism to the rearrangement reaction.

It may be noted that the kinetics of both rearrangement and elimination have been demonstrated by Runs 37A and 37B to be first-order in substrate. There may be a tendency for the elimination rate to be approximately 10% lower than expected, but a trend of this magnitude is of the order of the experimental error in determining the product ratios and is therefore inconclusive. The decrease of approximately 6% in the rate constant for rearrangement of the latter run at 31%  $\delta$ -isomer formation may be attributed to the enhanced proportion of hydrogen chloride to chloride ions and the resultant reduction in effective nucleophile concentration.

In Runs 37A-D and 36A and B, the relative rates of the rearrangement and elimination reactions remain, to within  $\sim 10\%$ , constant, as shown by the product ratios. As the error in determining the  $\left(\frac{\delta}{\text{But.}}\right)$  ratio is of this order, no trend of this magnitude can be attributed any significance. This does not of course, apply to  $\left(\frac{\alpha}{\gamma}\right)$  ratios.

Considering Runs 38A and B; Pyrex glass wool increases the rate of the rearrangement reaction, in the absence of  $\text{Et}_4\text{NCl}$ , by a factor of about 4.6, and that of the elimination reaction by a factor of about 2.3. Part of the catalysis of the former reaction can no doubt be assigned to increased catalysis by hydrogen chloride, due to the increased rate of production of this compound, by the accelerated elimination reaction. The "first-order" elimination reaction is

therefore a surface-catalysed reaction, which may involve cis removal of a hydrogen chloride molecule with, or without, nucleophilic assistance from a solvent molecule attacking the  $\alpha$ -carbon atom in a "merged" substitution-elimination reaction.<sup>185</sup> Such a mechanism could account for the absence of salt effects and significant autocatalysis discussed in Section XII. It is interesting that Dittmer and Mercantonio observed no elimination in toluene at 80°C.<sup>150</sup>

If this surface-catalysed reaction is unaffected by the presence of  $\text{Et}_4\text{NCl}$ , i.e., if  $\text{Et}_4\text{NCl}$  does not compete with substrate for the surface, the two-fold increase in rate should produce an increase of about 23% in the overall elimination rate in the presence of  $\text{Et}_4\text{NCl}$  and the same weight per ml. of glass wool. Comparison of the product ratios for Runs 36A and 36B does not reveal such a trend. It may be, therefore, that the "first-order" elimination rate in the absence of  $\text{Et}_4\text{NCl}$ , is suppressed in the presence of  $\text{Et}_4\text{NCl}$ , to some 50% or less of its measured value, due to competition from this compound for the surface. The above discussion involves 0.05M  $\text{Et}_4\text{NCl}$ . Also, if the "first-order" component of elimination is unaffected by competition from  $\text{Et}_4\text{NCl}$  for the surface, a rate depression of about 18% in the overall elimination rate might be expected for Runs 37C and 37D, if the reaction is specifically dependent on boron atom catalysis. No trend of this magnitude is observed in the product ratios, so that it appears that either  $\text{Et}_4\text{NCl}$  does compete, or any of the surfaces employed, including silicone grease, are effective catalysts (cf. page 205).

There is a slight tendency, inconclusive/<sup>for</sup>the reasons given above, for the elimination rate for Run 37D to be depressed.

In conclusion, a homogeneous  $S_N2'$  mechanism is assigned to the chloride ion catalysed rearrangement reaction, and a surface-catalysed mechanism to the elimination reaction in the absence of  $Et_4NCl$ . Therefore, " $k_1^E$ " is dependent on the surface area of the reaction tubes and possibly also on the substrate concentration, depending on the type of adsorption isotherm obeyed. Both of these were kept essentially constant throughout the kinetic runs described in this chapter. The chloride ion catalysed component of the elimination reaction is assigned a homogeneous bimolecular mechanism and a magnitude which may vary by about 20%, depending on whether the "E1" component operates in the presence of  $Et_4NCl$ . The "uncatalysed" rearrangement reaction in its initial stages may be partly a surface-catalysed reaction and partly due to traces of hydrogen chloride, or it may be entirely due to traces of hydrogen chloride produced by the elimination reaction.

Surface-catalysed bimolecular components appear to make only a small contribution to the homogeneous mechanisms.

XIV The Activation Parameters for the Rearrangement Reactions(i) Introduction

It being established that the  $S_N2'$  mechanism of rearrangement best explains the experimental data, a determination of the activation parameters for the rearrangement reactions of both isomers was carried out.

(ii) Procedure

Runs were carried out at 81.0, 111.0 and 126.0°C for  $\alpha$ -methylallyl chloride and 126.0°C for  $\gamma$ -methylallyl chloride, the 126°C runs being carried out in duplicate for each isomer. The values of  $k_2'$  which were obtained, together with those obtained previously for 96.0°C, (Runs 30, 31, 34, 35), after dissection into  $k_2'^\alpha$  and  $k_2'^\gamma$  values, allowed the parameters to be calculated.

The equilibrium constant at 126.0°C was evaluated by the methods discussed in Section XI for the evaluation at 96.0°C and details of this are given in the next section. The value obtained by method (a) was used in calculations of the rate constants at 126°C, and appropriate values, interpolated from the data at 96°C and 126°C, were used for the other reaction temperatures.

Corrections for solvent expansion were made using the data tabulated by Timmermans for acetonitrile.<sup>155</sup> The values used for the density of acetonitrile at the various temperatures, interpolated from

The parameters were determined by applying the method of least squares to the data.<sup>38</sup> The relevant equations are given below.<sup>156</sup>

$$\log_{10} k_2'^{\alpha(\gamma)} = \log_{10} A - \frac{E_a}{2.30RT}$$

$$\log_{10} \frac{k_2'^{\alpha(\gamma)}}{T} = \log_{10} \frac{K}{h} + \frac{\Delta S^\ddagger}{2.30R} - \frac{\Delta H^\ddagger}{2.30RT}$$

The rate constants used in the calculations are shown in Table XLVIII, these being the mean of values for duplicate runs, for the temperatures 96.0 and 126.0°C. An error of 3% in  $k_2'^{\alpha(\gamma)}$  was assumed in calculating errors in the activation parameters, while the error in temperature was assumed to be negligible. The errors were calculated using the method discussed by Peterson, Markgraf and Ross.<sup>195</sup> The value of 3% was deduced from a consideration of the standard deviations of the rate constants for the various runs, the reproducibility of rate constants for pairs of runs and the deviations of the experimental rate constants from the least squares Arrhenius plot.

#### (iii) Results and Discussion

The kinetic results for Runs 39-44 are shown in Tables XLII-XLVII and values for  $E_a$ ,  $\log_{10} A$ ,  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  are shown in Table XLVIII. Plots of  $\log_{10} k_2'$  versus  $\frac{1}{T}$  are shown in Fig. 12. The values of  $X_e$  used in the calculations of the rate constants at the various temperatures are shown in the tables.

TABLE XIII

Run 39. The  $\alpha$ -Methylallyl Chloride/Et<sub>4</sub>NCI Reaction in  
Acetonitrile (81°C)

Time (min.)	% $\alpha$ -MAC	$\log_{10}(X_{\infty}-X)$ ( $X_{\infty} = 71.1$ )	$10^6 k_1'$ (sec. <sup>-1</sup> )
0	0.26	1.8502	-
470	3.43	1.8304	1.62
946	6.70	1.8089	1.68
1665	11.05	1.7786	1.65
2687	16.7	1.7356	1.64
3420	20.8	1.7016	1.67
4725	27.4	1.6405	1.70
7155	36.1	1.5441	1.64
9916	43.5	1.4409	1.58
12772	50.9	1.3054	1.64

$$[\alpha\text{-MAC}] = 0.1043M$$

$$[\text{Et}_4\text{NCI}] = 0.1230M$$

$$T = 81.05^\circ\text{C}$$

$$\text{Mean (8) } k_1' = 1.65 \pm 0.04 \times 10^{-6} \text{ sec.}^{-1}$$

$$k_2' = 1.34 \times 10^{-5} M^{-1} \text{ sec.}^{-1}$$

$$k_2'^{\alpha} = 9.53 \times 10^{-6} M^{-1} \text{ sec.}^{-1}$$

TABLE XLIII

Run 40. The  $\alpha$ -Methylallyl Chloride/ $\text{Et}_4\text{NCl}$  Reaction in Acetonitrile(111°C)

Time (min.)	% $\alpha$ -MAC	$\log_{10}(X_e - X)$ ( $X_e = 69.9$ )	$10^5 k_1'$ (sec. <sup>-1</sup> )
0	0.43	1.8418	-
60	3.22	1.8240	1.14
140	6.93	1.7992	1.17
210	9.88	1.7783	1.16
330	14.9	1.7404	1.18
465	20.6	1.6928	(1.23)
590	24.1	1.6609	1.18
835	30.9	1.5911	1.15
1135	37.6	1.5092	1.13
1710	48.3	1.3345	1.14

$$[\alpha\text{-MAC}] = 0.1108M$$

$$[\text{Et}_4\text{NCl}] = 0.0537M$$

$$T = 111.10^\circ\text{C}$$

$$\text{Mean (7) } k_1' = 1.16 \pm 0.02 \times 10^{-5} \text{ sec.}^{-1}$$

$$k_2' = 2.15 \times 10^{-4} M^{-1} \text{ sec.}^{-1}$$

$$k_2'^{\alpha} = 1.50 \times 10^{-4} M^{-1} \text{ sec.}^{-1}$$

TABLE XLIV

Run 41. The  $\alpha$ -Methylallyl Chloride/Et<sub>4</sub>NCl Reaction in Acetonitrile  
(126°C)

Time (min.)	% $\alpha$ -MAC	$\log_{10}(X_e - X)$ ( $X_e = 69.3$ )	$10^5 k_1'$ (sec. <sup>-1</sup> )
0.0	0.76	1.8360	-
18.0	3.63	1.8174	3.97
38.0	6.56	1.7976	3.88
68.0	10.69	1.7680	3.84
107.0	15.5	1.7308	3.77
150.0	21.1	1.6830	3.91
200.0	25.7	1.6395	3.77
276.0	32.3	1.5682	3.72
385.0	41.1	1.4502	3.85
480.0	44.5	1.3945	3.53
570.0	48.1	1.3263	3.43

[ $\alpha$ -MAC] = 0.1025M

[Et<sub>4</sub>NCl] = 0.0546M

T = 126.22°C

Mean (7)  $k_1' = 3.84 \pm 0.09 \times 10^{-5} \text{ sec.}^{-1}$

$k_2' = 7.03 \times 10^{-4} \text{ M}^{-1} \text{ sec.}^{-1}$

$k_2'^{\alpha} = 4.87 \times 10^{-4} \text{ M}^{-1} \text{ sec.}^{-1}$

TABLE XLV

Run 42. The  $\alpha$ -Methylallyl Chloride/Et<sub>4</sub>NCl Reaction in Acetonitrile  
(126°C)

Time (min.)	% $\alpha$ -MAC	$\log_{10}(X_{\infty} - X)$ ( $X_{\infty} = 69.3$ )	$10^5 k_1'$ (sec. <sup>-1</sup> )
0	1.43	1.8317	-
27.0	5.12	1.8074	3.45
66.0	10.21	1.7716	3.49
108.0	15.3	1.7324	3.53
150.0	19.9	1.6937	3.53
200.0	24.1	1.6551	3.39
275.0	31.1	1.5821	3.48
390.0	38.3	1.4914	3.35
575.0	47.8	1.3324	3.33

$$[\alpha\text{-MAC}] = 0.0993M$$

$$[\text{Et}_4\text{NCl}] = 0.0516M$$

$$T = 126.12^\circ\text{C}$$

$$\text{Mean (6) } k_1' = 3.48 \pm 0.05 \times 10^{-5} \text{ sec.}^{-1}$$

$$k_2' = 6.74 \times 10^{-4} M^{-1} \text{ sec.}^{-1}$$

$$k_2'^{\alpha} = 4.67 \times 10^{-4} M^{-1} \text{ sec.}^{-1}$$

TABLE XLVI

Run 43. The  $\gamma$ -Methylallyl Chloride/Et<sub>4</sub>NCl Reaction in Acetonitrile  
(126°C)

Time (min.)	% $\alpha$ -MAC	$\log_{10}(X_e - X)$ ( $X_e = 30.7$ )	$10^5 k_1'$
0	0.92	1.4740	-
23.0	3.34	1.4371	6.16
55.0	6.26	1.3881	5.99
91.0	9.30	1.3304	6.06
135.0	12.57	1.2584	6.13
190.0	15.8	1.1732	6.08
253.0	18.1	1.1004	5.67
400.0	23.0	0.8865	5.64

$$[\gamma\text{-MAC}] = 0.1000M$$

$$[\text{Et}_4\text{NCl}] = 0.0913M$$

$$T = 126.13^\circ\text{C}$$

$$\text{Mean (6) } k_1' = 6.01 \pm 0.18 \times 10^{-5} \text{ sec.}^{-1}$$

$$k_2' = 6.58 \times 10^{-4} M^{-1} \text{ sec.}^{-1}$$

$$k_2'^{\gamma} = 2.02 \times 10^{-4} M^{-1} \text{ sec.}^{-1}$$

TABLE XLVII

Run 44. The  $\delta$ -Methylallyl Chloride/Et<sub>4</sub>NCl Reaction in Acetonitrile  
(126°C)

Time (min.)	% $\alpha$ -MAC	$\log_{10}(X_e - X)$ ( $X_e = 30.7$ )	$10^5 k_1'$ (sec. <sup>-1</sup> )
0	1.02	1.4725	-
23.0	3.74	1.4308	6.96
48.0	6.74	1.3795	7.44
77.0	9.10	1.3345	6.88
112.0	12.66	1.2562	7.41
128.0	13.4	1.2380	7.03
154.0	14.9	1.1987	6.82
206.0	18.0	1.1038	6.87
340.0	23.1	0.8808	6.68

$$[\delta\text{-MAC}] = 0.1039M$$

$$[\text{Et}_4\text{NCl}] = 0.1102M$$

$$T = 126.02^\circ\text{C}$$

$$\text{Mean (7) } k_1' = 7.06 \pm 0.26 \times 10^{-5} \text{ sec.}^{-1}$$

$$k_2' = 6.40 \times 10^{-4} M^{-1} \text{ sec.}^{-1}$$

$$k_2'^{\delta} = 1.96 \times 10^{-4} M^{-1} \text{ sec.}^{-1}$$

TABLE XLVIIIThe Activation Parameters for Rearrangement

Isomer	$\Delta H^*$ (kcal.mole <sup>-1</sup> )	$\Delta S^*$ (cal.deg. <sup>-1</sup> mole <sup>-1</sup> )
$\alpha$ -MAC	24.2 $\pm$ 0.4	-13.4 $\pm$ 1.1
$\gamma$ -MAC	24.3 $\pm$ 0.6	-14.9 $\pm$ 1.6
	$E_a$ (kcal.mole <sup>-1</sup> )	$\log_{10} A$ (A in M <sup>-1</sup> sec. <sup>-1</sup> )
$\alpha$ -MAC	24.9 $\pm$ 0.4	10.41 $\pm$ 0.2
$\gamma$ -MAC	25.0 $\pm$ 0.6	10.07 $\pm$ 0.4

TABLE XLVIII

The Rate Constants Used to Calculate the Activation Parameters for  
Rearrangement

	Temp. (°C)	$k_2'^{\alpha(\gamma)}$ (M <sup>-1</sup> sec. <sup>-1</sup> )
A	81.05	$1.04 \times 10^{-5}$
	95.87	$4.34 \times 10^{-5}$
	111.10	$1.72 \times 10^{-4}$
	126.17	$5.61 \times 10^{-4}$
B	95.87	$1.77 \times 10^{-5}$
	126.07	$2.34 \times 10^{-4}$

$$k_2'(A) = k_2'^{\alpha}$$

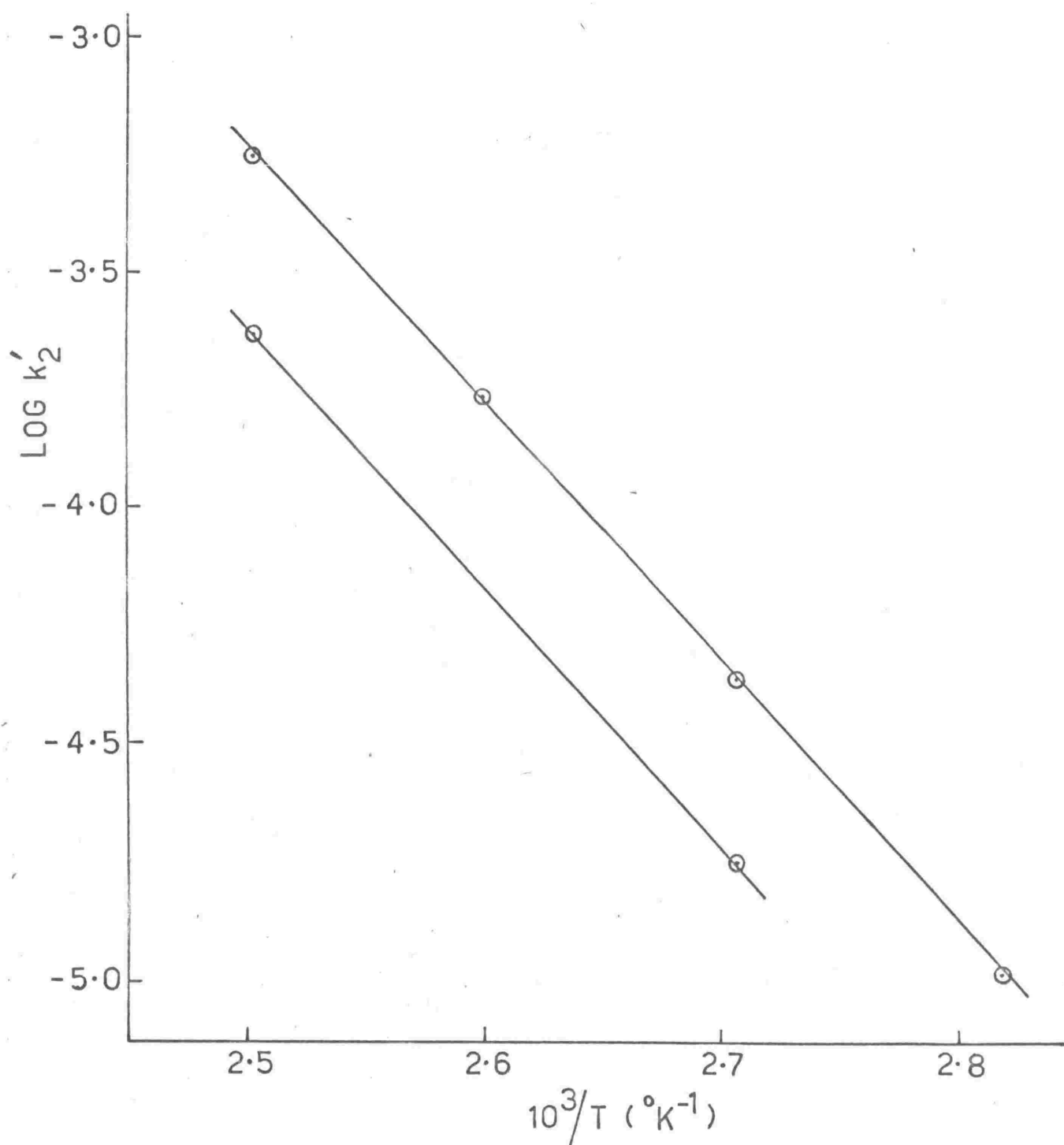
$$k_2'(B) = k_2'^{\gamma}$$

All  $k_2'$  values have been corrected for solvent expansion.

At 96°C and 126°C the  $k_2'$  values are the mean of values for duplicate runs.

FIG. 12

Arrhenius Plots for the Rearrangement Reactions  
in AN



No discoloration of the reaction mixtures, indicative of polymerisation, was observed at  $126^{\circ}\text{C}$  - the highest temperature used.

The runs at  $126^{\circ}\text{C}$  starting from the  $\gamma$ -isomer show a fall-off in the rate constant after about 50% reaction, similar to that observed in the runs at  $96^{\circ}\text{C}$ . The magnitude of the depression is smaller than at  $96^{\circ}\text{C}$ ,  $k_2'$  being depressed approximately 5% at 20%  $\alpha$ -isomer formation, 8% at 22.5% and 10% at 25%.

These runs provide no additional explanations for this behaviour to those already proposed in Section X, except perhaps that the magnitude of the depression of the rate constants was enhanced by experimental error in the runs at  $96^{\circ}\text{C}$ .

As observed at  $96^{\circ}\text{C}$ , the mean values of the composite rate constants -  $k_2'$  - for the approach to equilibrium starting from either isomer, are in reasonably good agreement at  $126^{\circ}\text{C}$ , when calculated using the value for the equilibrium constant evaluated from measurements of the isomer ratio at equilibrium at  $126.0^{\circ}\text{C}$ . (See Runs 41-44). The difference in  $\text{Et}_4\text{NCl}$  concentration can be neglected for the reason given in Section XI.

The activation parameters for each isomer are in close agreement.

For a reversible first-order or pseudo-first-order reaction, for which the order with respect to each reactant is the same as its coefficient in the stoichiometric equation, the equilibrium constant  $K_{(\text{eq.})}$  gives the ratio of the forward and reverse rate constants and the difference in the magnitude of these is dependent upon the difference in the free energy of formation of the compounds, which may be calculated from  $K_{(\text{eq.})}$ .<sup>18,160</sup>

$$\Delta G^{\circ} = -2.30RT \log_{10} K_{(eq.)}$$

This calculation for the methylallyl chloride isomers at 96.0°C gives a value of  $\Delta G^{\circ} = -639 \text{ cal.mole}^{-1}$  for the reaction:



Thus the  $\gamma$ -isomer has a lower free energy and is therefore more stable than the  $\alpha$ -isomer. This has been attributed to methyl hyperconjugation with the double bond,<sup>11</sup> and as the entropy of the two isomers should be similar, the difference in free energy should be mainly due to the difference in enthalpy caused by electron delocalisation through hyperconjugation.

This implies that the activation enthalpy of the  $\gamma$ -isomer  $\rightarrow$   $\alpha$ -isomer reaction should be approximately  $0.5 \text{ kcal.mole}^{-1}$  greater than that of the reverse reaction, resulting in an increase in the ratio of  $k_2^{\gamma}$  to  $k_2^{\alpha}$  and an increase in the proportion of the  $\alpha$ -isomer at equilibrium, as the temperature is raised. However, an activation enthalpy difference of this magnitude is of the order of the experimental error of the activation enthalpy determinations for the two isomers, so it would be undetectable.

Further discussion of the parameters and the significance of their magnitude, is postponed until after the sections on the symmetrical halide ion exchange reactions of the two isomers.

XV Determination of the Equilibrium Constant at 126.0°C(1) Introduction

It has been shown in the previous section that  $\gamma$ -methylallyl chloride has a lower free energy and is therefore more stable than the  $\alpha$ -isomer. The enthalpy contribution to this extra stability may be determined from the temperature dependence of the equilibrium constant:<sup>18,160</sup>

$$\log_{10} \frac{K_2}{K_1} = \frac{\Delta H^\circ}{2.30R} \left[ \frac{1}{T_1} - \frac{1}{T_2} \right]$$

A determination of the value for the equilibrium constant at 126.0°C was carried out to enable (a) an assessment of  $\Delta H^\circ$  to be made, and (b) the composite rate constants for the two isomers to be derived (and dissected into their components) more accurately, from the experimental data obtained at the various reaction temperatures.

(ii) Procedure

Four determinations of the equilibrium constant at 126.0°C were performed by analysing the isomer ratio at equilibrium, three starting from the  $\gamma$ -isomer and one starting from the  $\alpha$ -isomer. The experimental procedure was the same as that outlined in Section XI.

A further kinetic determination was available from the duplicate runs for each isomer at 126.0°C.

(111) Results and Discussion

The results are shown in Table XLIX together with  $\Delta G^\circ$  and  $\Delta H^\circ$  values.

Errors have been calculated using the standard deviation in  $K_{(eq.)}$ , which corresponds to an error of 0.5% in the percentage of  $\alpha$ -isomer at equilibrium. The four values show a spread of 1.2% in the percentage of  $\alpha$ -isomer present at equilibrium. The equilibrium constant is again invariant with time and independent of the reactant isomer, (within the limits of experimental error), indicating that equilibrium had been reached. The reaction times used, were, as for the determinations at  $96.0^\circ\text{C}$ , considerably longer than ten half-lives, which corresponded to about thirty hours, to allow for the fall-off in the rate constants near equilibrium.

The mean value for the equilibrium constant at  $126.0^\circ\text{C}$  is 2.26 compared with that of 2.39 at  $96.0^\circ\text{C}$ . This corresponds to 30.7%, compared with 29.5%, of the  $\alpha$ -isomer present in the equilibrium mixture.

$\Delta H^\circ$  for the reaction:



is approximately  $-545 \text{ cal.mole}^{-1}$ , which is close to  $\Delta G^\circ$  for the reaction, this being  $-646 \text{ cal.mole}^{-1}$  at  $126.0^\circ\text{C}$ . However, the large experimental error in determining a 1.2% increase in the percentage of the  $\alpha$ -isomer present in the equilibrium mixture means that the error in  $\Delta H^\circ$  is also large. For example, a 0.5% change in the value for the equilibrium percentage of  $\alpha$ -isomer at one temperature changes the value of  $\Delta H^\circ$  by  $226 \text{ cal.mole}^{-1}$ .

TABLE XLIX

The Equilibrium Constant at 126.0°C (Method (a))

Reaction Time (day)	$K_{\text{(cal.)}}$ (GIC detector)	$(\alpha)_{\text{R.M.}}$	% $\alpha$ -MAC	Reactant Isomer	$K_{\text{(eq.)}}$
6.5	0.705	3.29	30.1	$\gamma$ -MAC	2.32
7	0.763	2.87	31.3	$\gamma$ -MAC	2.19
11	0.737	3.00	31.1	$\gamma$ -MAC	2.22
6	0.725	3.14	30.5	$\alpha$ -MAC	2.28

N<sub>2</sub>

$$[\text{MAC}] = 0.1\text{M}$$

$$[\text{Et}_4\text{NCl}] = 0.1\text{M}$$

$$\text{Mean } K_{\text{(eq.)}} = 2.26 \pm 0.06$$

$$\Delta G^\circ = -646 \pm 18 \text{ cal.mole}^{-1}$$

$$\Delta H^\circ = -545 \pm 226 \text{ cal.mole}^{-1}$$

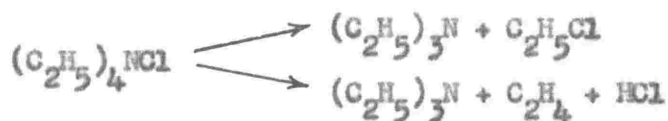
These results are similar to those obtained by Winstein and Young for the methylallyl bromides in the pure state, for which  $\Delta G^\circ$  at  $20^\circ\text{C}$  was  $-1.1 \text{ kcal.mole}^{-1}$ .<sup>157,160</sup>  $\Delta G^\circ$  at  $50.0^\circ\text{C}$  for the methylallyl bromides in acetone was  $-706 \text{ cal.mole}^{-1}$ .<sup>79</sup>

Values for the equilibrium percentages of the isomers at the other reaction temperatures were calculated from the data for  $96.0^\circ\text{C}$  and  $126.0^\circ\text{C}$ .

A noteworthy feature of the determinations of  $K_{(\text{eq.})}$  at  $126.0^\circ\text{C}$  was the presence of a large unknown peak just behind the butadiene peak on the gas chromatograms. This peak, much smaller in size, was also observed in determinations of  $K_{(\text{eq.})}$  at  $96.0^\circ\text{C}$  and a very small peak was also noted near the end of kinetic runs at  $126^\circ\text{C}$ .

The reaction tube which was heated for 11 days at  $126^\circ\text{C}$  (Table XLIX) also showed two other small peaks, one in front of the butadiene peak and one behind the unknown peak, on the gas chromatograms.

This large unknown peak was suspected to be a decomposition product of  $\text{Et}_4\text{NCl}$ .  $\text{Et}_4\text{NCl}$  can decompose as follows:<sup>121</sup>

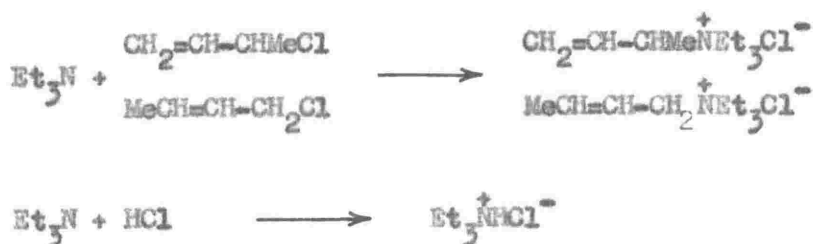


Ethylene has a retention time less than that for butadiene and no evidence for its formation was observed except in the reaction tube heated for 11 days at 126°C.

Bromination of an equilibrium reaction mixture with excess liquid bromine resulted in complete removal of the butadiene peak, leaving the unknown unchanged. After 24 hours, only the unknown and acetonitrile peaks were present on the gas chromatograms.

A solution of ethyl chloride in acetonitrile was prepared and analysed, and this compound had a retention time of approximately one minute, i.e., identical with that of the unknown peak. Small volumes of this solution and a reaction mixture at equilibrium were mixed together and samples were analysed. These gave an enhanced peak behind the butadiene peak. This was considered sufficient evidence to identify the unknown peak as being due to ethyl chloride. (b.p. = 12.5°C at 760 mm.).<sup>207</sup>

Preparation of a solution of triethylamine in acetonitrile (b.p.=89.4°C)<sup>207</sup> and analysis of this gave a peak with a retention time in between that of  $\alpha$ -methylallyl chloride and acetonitrile. A peak attributable to this compound was not observed on the chromatograms for equilibrium tube analyses. However, being a nucleophilic compound, it has considerable opportunity for reaction:



so that its absence from the chromatograms would not be unexpected.

Young, Clement and Shih have studied the reaction between trimethylamine and  $\alpha$ -methylallyl chloride in acetone, which forms partially rearranged quaternary ammonium chlorides, so a similar reaction with triethylamine in acetonitrile is feasible.<sup>84b</sup>

Obviously, the situation at "equilibrium" is not without ambiguities. Despite the stable value of the isomer ratio, especially at 96.0°C, the system is far from being at equilibrium with respect to side reactions. Not only is elimination of hydrogen chloride from the  $\alpha$ -isomer to form butadiene still occurring, but also decomposition of the  $\text{Et}_4\text{NCl}$  to form ethyl chloride and triethylamine, which, being a nucleophile, can attack the allylic chlorides. Assuming a bimolecular mechanism the primary halide would be expected to react faster in this case.<sup>85,92b</sup>

The presence of these side reactions throws some doubt on the validity of the assumption that the measured value for  $K_{(\text{eq.})}$  is simply the ratio of the rate constants for the forward and reverse reactions, as for an uncomplicated pseudo-first-order reaction. In such a situation a kinetic evaluation of  $K_{(\text{eq.})}$  at the two temperatures 96°C and 126°C should be informative.

It has already been mentioned in the text, that the values of  $K_{(eq.)}$  required for kinetic agreement of the composite rate constants starting from either isomer, are (within experimental error) those actually measured. (See Runs 30, 31, 34, 35, 41, 42, 43, 44). The agreement between the composite rate constants for the approach to equilibrium starting from either isomer is shifted from exact to 7% out by an error of 1% in the percentage composition of the equilibrium mixture, and the nature of the rate constants for the approach to equilibrium starting from the  $\gamma$ -isomer is sensitive to the value for  $K_{(eq.)}$ . Thus it would seem in order to choose a value for  $K_{(eq.)}$  satisfying the requirements of (a) agreement between the composite rate constants, and (b) reasonable rate constants for the  $\gamma$ -isomer, as these should be uncomplicated over the region where elimination of hydrogen chloride from the product is negligible. That this value should agree (within experimental error) with the values obtained by measuring the isomer ratio at "equilibrium", suggests that the overall effect of side-reactions does not alter the equilibrium position from its true value by a significant amount.

CHAPTER IVTHE KINETICS AND MECHANISM OF THE CHLORINE-36 ISOTOPE EXCHANGEREACTIONS OF  $\alpha$ - AND  $\delta$ -METHYLALLYL CHLORIDE IN ACETONITRILEI Introduction

To realise one of the aims of this project, namely, the determination of the relative rates of bimolecular substitution by chloride ions at saturated and  $\pi$ -bonded carbon for the  $\alpha$ - and  $\delta$ -methylallyl chlorides, a study of the kinetics and mechanism of chloride ion attack at saturated carbon, for both  $\alpha$ - and  $\delta$ -methylallyl chloride reacting with  $\text{Et}_4\text{NCl}$  in acetonitrile, was required.

As the products of  $\text{S}_{\text{N}}2$  substitution by chloride ions at the saturated  $\alpha$ -carbon atom are identical with the reactants, the reactions can only be followed by using the radioactive isotope of chlorine - chlorine-36. Consequently,  $\text{Et}_4\text{NCl}$  labelled with chlorine-36 was used as the nucleophile. e.g.,



It was expected that the mechanisms of the isotope exchange reactions would be bimolecular, because a unimolecular mechanism of exchange would give a unimolecular mechanism of rearrangement, which has not been observed, unless bimolecular rearrangement was faster

than exchange. This is obviously contradictory to all the known behaviour of  $S_N2'$  and  $S_N2$  reactions. Various workers have studied halide ion exchange reactions of alkyl and allyl halides, usually in the dipolar aprotic solvent acetone, and have established the preference of primary and secondary halides for the  $S_N2$  mechanism.<sup>92b,116,158,161,120</sup>

The integrated rate equation for an isotope exchange reaction:

$$k_2^{(obs.)} = \frac{2.303}{(a+b)t} [\log_{10}(X_{\infty} - X_0) - \log_{10}(X_{\infty} - X_t)]$$

(See Appendix II for the derivation), gives no indication of the order of the reaction. However,  $R = k_2^{(obs.)} ab$  can be equated to the sum of first-order and second-order components:<sup>142</sup>

$$R = k_2^{(obs.)} ab = k_1 a + k_2 \alpha a b$$

and by varying the concentration of  $b$  (the nucleophilic reagent) values for  $k_1$  and  $k_2$  can be obtained by plotting  $\frac{R}{a}$  versus  $\alpha b$ . (See page 152).

The work in the following sections therefore involves:

- (a) determination of the rate constants for the exchange reactions of both the isomers at a suitable temperature and an investigation of the reproducibility of the runs,
- (b) variation of the nucleophile concentration to establish the rate law followed by the reactions,

- (c) determinations of the rate constants at various temperatures to enable the activation parameters for the reactions to be calculated, and
- (d) product analyses by gas chromatography.

## II The Chlorine- $^{36}$ Isotope Exchange Reaction of $\alpha$ -Methylallyl Chloride in Acetonitrile

### (i) Introduction

The programme outlined in the introduction to this chapter was carried out for the exchange reaction of  $\alpha$ -methylallyl chloride with  $\text{Et}_4\text{NCl}^{36}$  ( $\text{Et}_4^*\text{NCl}$ ) in acetonitrile.

### (ii) Procedure

Duplicate runs at  $60.0^\circ\text{C}$  were carried out to determine the reproducibility of the rate data, and further runs at  $75.0^\circ\text{C}$  and  $45.0^\circ\text{C}$  to determine the activation parameters were also carried out. To determine the dependence of the rate constant on the concentration of the nucleophilic reagent, two "half-runs" were performed. i.e., half the number of reaction tubes for a normal run were filled with a reaction mixture containing a given concentration of  $\text{Et}_4^*\text{NCl}$ , while the other half were filled with a reaction mixture containing  $\text{Et}_4\text{NCl}$  at about four times this concentration.

The activation parameters were calculated by applying the method of least squares to the data and an error of  $\frac{3}{\%}$  in the rate constants was assumed in calculating the errors in the parameters, using the method of Peterson, Markgraf and Ross.<sup>195</sup> As for the rearrangement runs, the value of  $\frac{3}{\%}$  was deduced from the standard deviations of the rate constants for the various runs, the reproducibility of the rate constants for the runs and the deviations of the

experimental rate constants from the least squares Arrhenius plot. (See Section XIV, Chapter III for the relevant equations). Timmermans' data<sup>155</sup> on the density of acetonitrile at various temperatures was used to correct the rate constants for solvent expansion and the values which were used for the density at the various reaction temperatures are shown in Appendix IV. The corrected rate constants are shown in Table LXIII. Those for Runs 46, 48 and 49 were used to calculate the parameters.

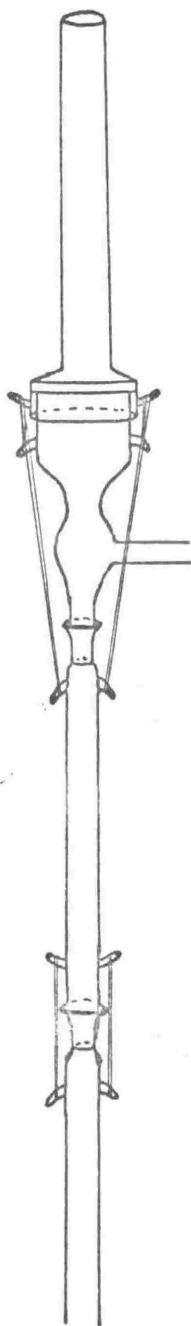
### (iii) Experimental

#### (a) Preparation of Reaction Mixtures and Performance of Runs

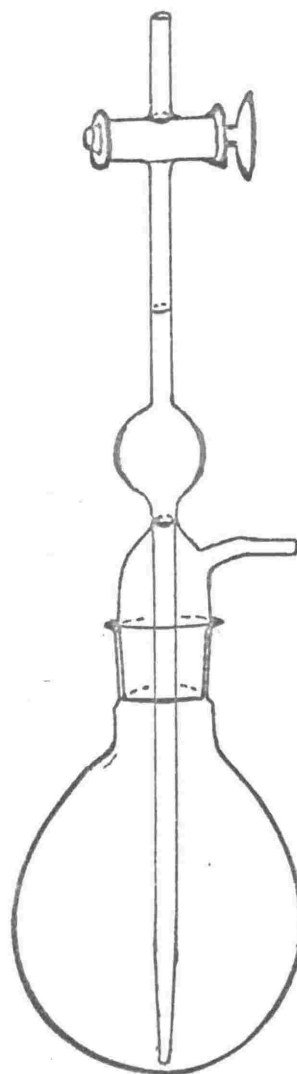
A preliminary run showed that the exchange reaction between  $\alpha$ -methylallyl chloride and  $\text{Et}_4\text{NCl}^*$  in acetonitrile, with reactant concentrations of approximately 0.1M for the substrate and 0.04M for the nucleophile, went at a suitable rate for kinetic study at 60°C. This meant that the rate at room temperature was slow enough to allow the runs to be carried out by the sealed tube technique, as negligible reaction occurred in the time interval between preparing the reaction mixture and sealing the reaction tubes. Consequently, reaction mixtures were prepared and reaction tubes were filled and sealed, by the method described in detail for the rearrangement runs. (Section VII). Precautions were of course taken, against accidents and contamination, in the handling of  $\text{Et}_4\text{NCl}^*$ .

FIG. 10

Injection System



Special Pipette



The only deviation from the method described in Section VII was the use of a specially designed pipette to deliver the reaction mixture to the reaction tubes. (See Fig. 10). This 5 ml. calibrated bulb pipette, which was filled to the mark by increasing the pressure on the reaction mixture by means of a 10 ml. syringe connected to the side-arm and turning off the tap when the mark was reached, enabled an accurately known and reproducible volume to be delivered in the dry-box.

Although an exactly known volume was not required in the reaction tubes, it was convenient, and an improvement, to be able to deliver an exact aliquot to tubes destined for analysis for initial reactant concentrations, because the less a volatile reaction mixture is handled in between sampling and analysis the fewer are the volatility errors introduced. Also, the pressure method of filling the pipette was considered more satisfactory than sucking, for volatile compounds.

Runs were carried out at  $75.0^{\circ}\text{C}$ ,  $60.0^{\circ}\text{C}$  and  $45.0^{\circ}\text{C}$ . The reaction tubes were immersed simultaneously in the thermostat and after a few minutes to allow attainment of thermal equilibrium, a tube was quenched for analysis as the zero-time tube. The reaction tubes were quenched in ice water and then transferred to liquid air to await analysis.

#### (b) Analytical Technique

Each tube was removed from liquid air, cracked open with a hot glass point and the contents, when melted, were poured into a

6" x 1" B24 "Quickfit" tube cooled in liquid air. A splash bulb was inserted and connected to a collection trap by means of a special adaptor, which had a short side-arm fitted with a stopcock, through which air could be admitted to the apparatus. The collection trap was cooled in liquid air and connected through another liquid-air trap to a "Hyvac" pump and manometer. The apparatus was evacuated and the tube and its contents were warmed up slowly by shaking the tube in an ethanol-bath. The solvent and  $\alpha$ -methylallyl chloride distilled over at about  $-15^{\circ}\text{C}$  leaving the  $\text{Et}_4\text{NCl}^*$  as a white deposit. The apparatus was then brought back to atmospheric pressure, by admitting air through the tap on the special adaptor, and "Analar" acetone (ca. 5 ml.) was added to the salt through the splash bulb. The tube was refrozen and the evaporation process was repeated. A further 5 ml. of acetone was then added and the process was repeated. Finally, air was admitted through the tap and the apparatus was then pumped down for 10 minutes.

This procedure ensured complete separation of the two isotopically-labelled compounds. The tube was then disconnected and the  $\text{Et}_4\text{NCl}^*$  was dissolved up in usually  $\sim 23$  ml. of distilled water and transferred to a 50 ml. conical flask. Homogeneity was ensured by tipping the solution to and fro between two of these flasks.

#### (c) The Counting Assembly<sup>205</sup>

A typical counting assembly was used, consisting of a high voltage supply and pre-amplifier unit, a scaling unit, a quench unit and an M5H liquid counter (20th Century Electronics Ltd.) housed in a

lead "castle". The operating voltage was  $\sim 400$  volts, the exact voltage used being determined by the plateau of the counter. The quench times of the quench units used were  $0.5 \times 10^{-5}$  and  $1 \times 10^{-5}$  minutes, as determined by a cathode-ray oscilloscope. Timing of the period required to register a given number of counts was done with a stopclock, which had been checked against an electric clock. The background counting rate in the assembly was 12 ct./min., determined from counts over a long period of time.

The assembly was checked each day before use, for faults in performance, with a standard solution of lithium chloride in water.

(d) Counting of Samples and Analysis for Chloride Ions

Each sample was analysed for activity by counting it in the assembly described above and determining its chloride ion concentration.

An MGH liquid counter was filled with the sample (ca. 10 ml.) and then placed in the lead castle of the counting assembly. The time required for  $10^4$  counts to be recorded was determined at least three times and the mean counts per minute (ct./min.) was calculated. This counting rate (C/R) was then corrected for the quench time of the quench unit and the background counting rate of 12 ct./min., to give the true counting rate of the sample. The error in the counting rate should thus be within 2%.<sup>205</sup>

The remainder of the sample (ca. 10 ml.) was accurately weighed into a beaker, and after dilution and adding a little nitric acid (dil.), it was titrated for chloride ions with standard silver

nitrate solution (ca. 0.014M), by the potentiometric titration method. A 10 ml. burette was used and the end-point was estimated from a graph of E.M.F. versus titre. The total analysis error was  $\sim 0.5\%$ . From this data, the volume of silver nitrate required to titrate 10 gm. of water containing  $\text{Et}_4^*\text{NCl}$  at the concentration of the sample was calculated.

The counting rate of each sample was then adjusted to the value it would be, if the titre of the sample were the same as that of the sample chosen as the standard for comparison. This standard titre was usually the titre of the sample giving the initial activity of the  $\text{Et}_4^*\text{NCl}$  and sometimes that of the sample giving the zero-time activity.

$$\text{i.e. } C/R = C/R_{(\text{expt'l.})} \times \frac{\text{ml. AgNO}_3 \text{ (of standard)}}{\text{ml. AgNO}_3 \text{ (of sample)}}$$

Therefore, a series of values was obtained for the activity of the  $\text{Et}_4^*\text{NCl}$  isolated at various times during the exchange reaction. The difference between these values and that for the initial activity of the  $\text{Et}_4^*\text{NCl}$  was of course the activity of the substrate, i.e.

$$Z - Y = X$$

which was required for substitution in the rate equation. These values are proportional to the specific activity of the labelled compounds, which it was not necessary to calculate.

The zero-time Y value was used to correct for any reaction occurring during the preparation of the run and the thermal equilibration period.

The initial activity of the  $\text{Et}_4\text{NCl}^*$  was determined by taking a sample of the salt in acetonitrile, before addition of the substrate, during the preparation for a run, and isolating and analysing it by the same method as used for a reaction tube.

(e) Analysis of Initial Reactant Concentrations

(1)  $\text{Et}_4\text{NCl}^*$  - two 5 ml. aliquots of the reaction mixture were sealed up in tubes during the preparation of the run, to be used for determining the initial  $\text{Et}_4\text{NCl}^*$  concentration. The contents of each tube and washings were added to an extraction mixture of 30 ml. of *n*-pentane and 20 ml. of water in a separating funnel, which was then vigorously shaken to extract the substrate into the organic layer. The aqueous layer was run off into a 150 ml. conical flask, made faintly alkaline with sodium hydroxide and evaporated down using a water-bath, while being flushed with nitrogen. The cold solution was then acidified with nitric acid (dil.) and titrated with standard silver nitrate by the potentiometric titration method. The analysis error was 0.5%.

(2)  $\alpha$ -Methylallyl Chloride - three 5 ml. aliquots of the reaction mixture were added to three constricted test tubes of 10 ml. capacity during the preparation for a run. To each of these was added sodium methoxide in methanol (ca. 5 ml. of ca. 1M) before sealing off. The tubes were then heated in a boiling-water bath for times equal to, and two and three times that estimated to be sufficient for complete reaction, to ensure that this was so. The contents of each tube were

then made up to 25 ml. in a standard flask and 10 ml. aliquots were titrated with silver nitrate as above. This analysis data gave the total chlorine concentration of the solution. Subtraction of the  $\text{Et}_4\text{NCl}$  concentration, determined as above, gave the initial substrate concentration. The analysis error was 0.5%.

(f) Calculation of Rate Constants

The equation used for calculating the rate constants was:

$$k_2 = \frac{2.303}{(a+b)t} [\log_{10}(X_{\infty} - X_0) - \log_{10}(X_{\infty} - X_t)]$$

which is derived and defined in Appendix II.

Substitution of the X values determined as described above,  $X_{\infty} = (\frac{a}{a+b}) Z$  and  $(a+b)$  = the total chlorine concentration of the solution, into the equation, enabled the rate constants to be calculated.

(iv) Results and Discussion

The results for all runs are shown in Tables L-LIV and the activation parameters in Table LX. A plot of  $\log_{10} k_2$  versus  $\frac{1}{T}$  is shown in Fig. 13. The standard deviation of the rate constants from the mean value is shown in the tables.

The agreement between the mean values of the rate constants for duplicate runs is good and the rate constants show no deviations

from constancy for 93% of the theoretical exchange. Analysis by gas chromatography showed less than 1% rearrangement at 93% exchange, which is in accord with the calculated value of  $\sim 0.5\%$  rearranged product.

Variation of the  $\text{Et}_4\text{NCl}^*$  concentration has little effect on the  $k_2$  values. A straight line, passing on extrapolation close to the origin, was obtained from a plot of  $k_2$  versus  $b$  and this is shown in Fig. 14. A straight line plot of zero intercept on extrapolation to zero  $\text{Et}_4\text{NCl}^*$  concentration is required by a pure bimolecular mechanism. (See page 158 ).

The close approximation of the plot to a straight line of zero intercept justifies the assumption that  $(\alpha)$ , the degree of dissociation of  $\text{Et}_4\text{NCl}^*$ , over a two to three-fold change in the concentration of the latter, does not vary by an amount significantly greater than the experimental error in determining the rate constants, and hence it may be regarded as being constant. Consequently, considering the approximations made, the results are consistent with pure second-order kinetics. (The number of tubes for Run 47B was reduced by experimental mishap and time was not available to repeat this experiment.)

Discussion of the activation parameters is reserved until Chapter V.

TABLE L

Run 45. The  $\alpha$ -Methylallyl Chloride/ $\text{Et}_4\text{NCl}$  Reaction in Acetonitrile ( $60^\circ\text{C}$ )

Time (min.)	Y (ct./min.)	$\log_{10}(X_\infty - X)$ ( $X_\infty = 1151$ )	% R	$10^4 k_2$ ( $\text{M}^{-1} \text{sec}^{-1}$ )
0	1547	3.0535	1.7	-
112	1429	3.0055	12.0	(1.12)
225	1313	2.9528	22.1	(1.17)
402	1143	2.8615	36.8	1.25
582	1015	2.7774	48.0	1.24
822	891	2.6767	58.7	1.20
1307	696	2.4472	75.7	1.21
1662	605	2.2765	83.6	1.22

240.

$$[\alpha\text{-MAC}] = 0.1077\text{M} \quad \text{Mean (5) } k_2 = 1.22 \pm 0.02 \times 10^{-4} \text{ M}^{-1} \text{ sec}^{-1}$$

$$[\text{Et}_4\text{NCl}] = 0.0390\text{M} \quad Z = 1567 \text{ ct./min.} = X + Y$$

$$T = 59.95^\circ\text{C}$$

TABLE II

Run 46. The  $\alpha$ -Methylallyl Chloride/ $\text{Et}_4\text{NCl}$  Reaction in Acetonitrile ( $60^\circ$ )

Time (min.)	Y (ct./min.)	$\log_{10}(X_\infty - X)$ ( $X_\infty = 124.0$ )	% R	$10^4 k_2$ ( $\text{M}^{-1} \text{sec.}^{-1}$ )
0	1658	3.0859	1.7	-
122	1503	3.0270	14.1	1.23
224	1387	2.9768	23.5	1.24
301	1313	2.9415	29.5	1.22
404	1218	2.8915	37.2	1.23
590	1069	2.7993	49.2	1.23
830	932	2.6928	60.2	1.21
1070	798	2.5551	71.0	1.26
1319	726	2.4579	76.8	1.21
1799	609	2.2304	86.3	1.21
2390	525	1.9345	93.1	1.23

 $[\alpha\text{-MAC}] = 0.1112\text{M}$  $T = 59.80^\circ\text{C}$ Mean  $k_2 = 1.23 \pm 0.02 \times 10^{-4} \text{ M}^{-1} \text{sec.}^{-1}$  $[\text{Et}_4\text{NCl}] = 0.0394\text{M}$  $Z = 1679 \text{ ct./min.}$

TABLE III

Run 47. Dependence of the Rate Constant on Nucleophile Concentration (60°C)

Time (min.)	Y (ct./min.)	$\log_{10}(X_{\infty} - X)$ ( $X_{\infty} = 1552$ )	% R	$10^4 k_2$ ( $M^{-1} \text{sec.}^{-1}$ )
0	2966	3.1881	0.6	-
124	2753	3.1235	14.4	1.20
277	2532	3.0444	28.6	1.20
457	2318	2.9513	42.4	1.20
675	2123	2.8445	55.0	1.18
1210	1783	2.5551	76.9	1.21
				Mean = $1.20 \pm 0.01$
(A)				
0	1662	3.1485	1.2	-
660	984	2.8633	48.8	1.26
1025	761	2.7050	64.4	1.26
				Mean = 1.26
(B)				
[ $\alpha$ -MAC] = 0.0866M (A)      0.1116M (B)      Z = 2976 ct./min. (A)				
[Et <sub>4</sub> NCl] = 0.0794M (A)      0.0199M (B)      Z = 1679 ct./min. (B)				
T = 59.80°C				

TABLE LIII

Run 48. The  $\alpha$ -Methylallyl Chloride/ $\text{Et}_4\text{NCl}$  Reaction in Acetonitrile (75°C)

Time (min.)	Y (ct./min.)	$\log_{10}(X_{\infty} - X)$ ( $X_{\infty} = 954$ )	% R	$10^4 k_2$ ( $\text{M}^{-1} \text{sec.}^{-1}$ )
0.0	1313	2.9708	2.0	-
28.0	1210	2.9201	12.8	4.88
60.0	1101	2.8591	24.2	5.02
96.0	1006	2.7980	34.2	4.85
138.0	905	2.7218	44.7	4.86
187.0	810	2.6355	54.7	4.83
248.0	712	2.5237	65.0	4.86
326.0	622	2.3874	74.4	4.83
435.0	530	2.1818	84.1	4.89

243.

$$\text{Mean } k_2 = 4.88 \pm 0.06 \times 10^{-4} \text{ M}^{-1} \text{ sec.}^{-1}$$

$$Z = 1332 \text{ ct./min.}$$

$$[\alpha\text{-MAC}] = 0.1020\text{M}$$

$$[\text{Et}_4\text{NCl}] = 0.0404\text{M}$$

$$T = 75.20^\circ\text{C}$$

TABLE LIV

Run 49. The  $\alpha$ -Methylallyl Chloride/ $\text{Et}_4\text{NCl}$  Reaction in Acetonitrile ( $45^\circ\text{C}$ )

Time (min.)	Y (ct./min.)	$\log_{10}(X_\infty - X)$ ( $X_\infty = 954$ )	% R	$10^5 k_2$ ( $\text{M}^{-1} \text{sec.}^{-1}$ )
0	1332	2.9795	0.0	-
417	1246	2.9385	9.0	2.65
880	1161	2.8938	17.9	2.63
1404	1070	2.8401	27.5	2.68
2004	971	2.7731	37.8	2.78
2724	891	2.7101	46.2	2.67
3660	783	2.6075	57.5	2.74
4735	692	2.4969	67.1	2.75
7160	556	2.2504	81.3	2.75

Mean  $k_2 = 2.71 \pm 0.06 \times 10^{-5} \text{ M}^{-1} \text{sec.}^{-1}$  $Z = 1332 \text{ ct./min.}$  $[\alpha\text{-MAC}] = 0.102\text{M}$  $[\text{Et}_4\text{NCl}] = 0.0404\text{M}$  $T = 45.10^\circ\text{C}$

FIG. 13

Arrhenius Plot for the  $\alpha\text{-MAC/Et}_4\text{NCl}^{36}$  Exchange  
Reaction in AN

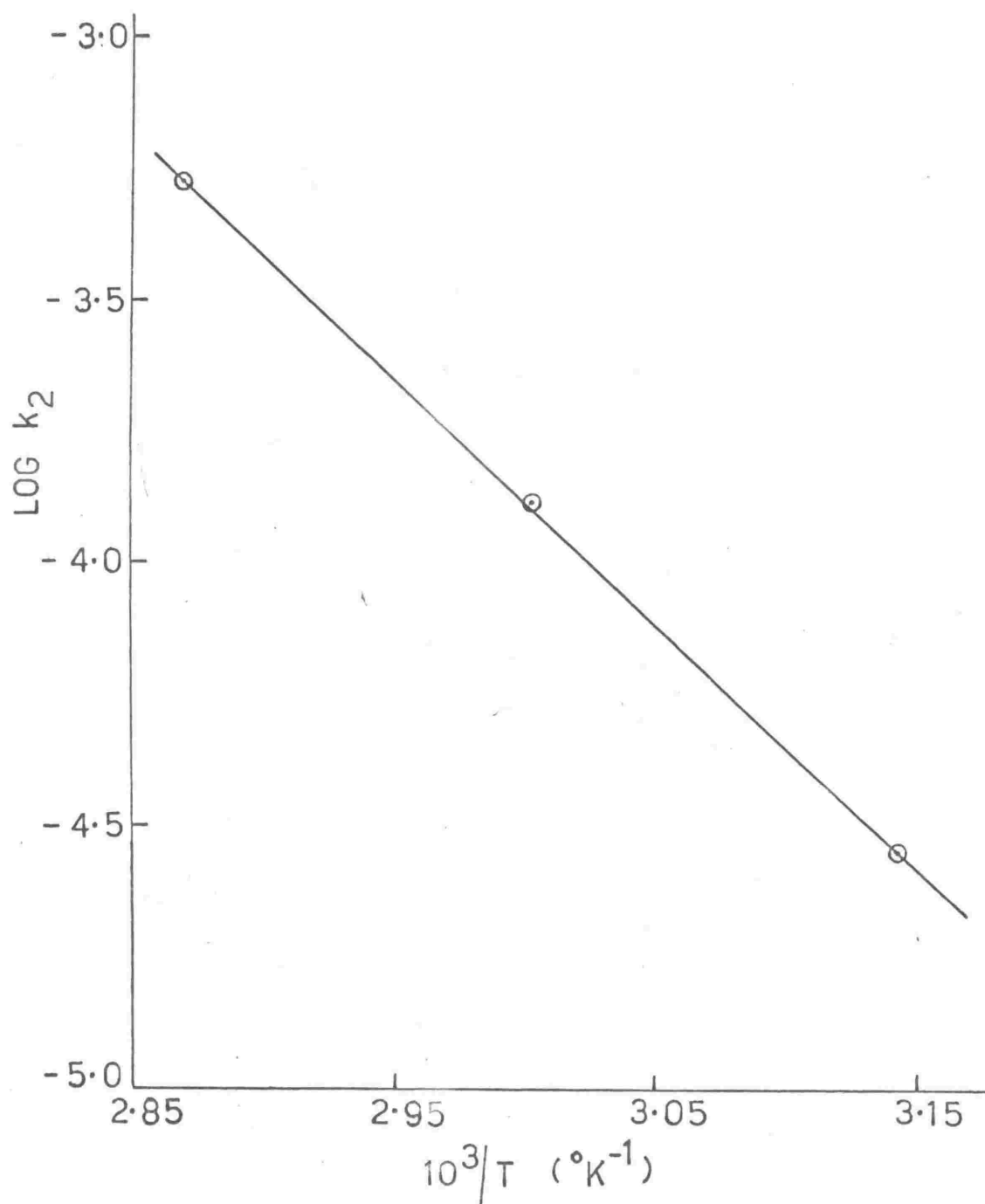
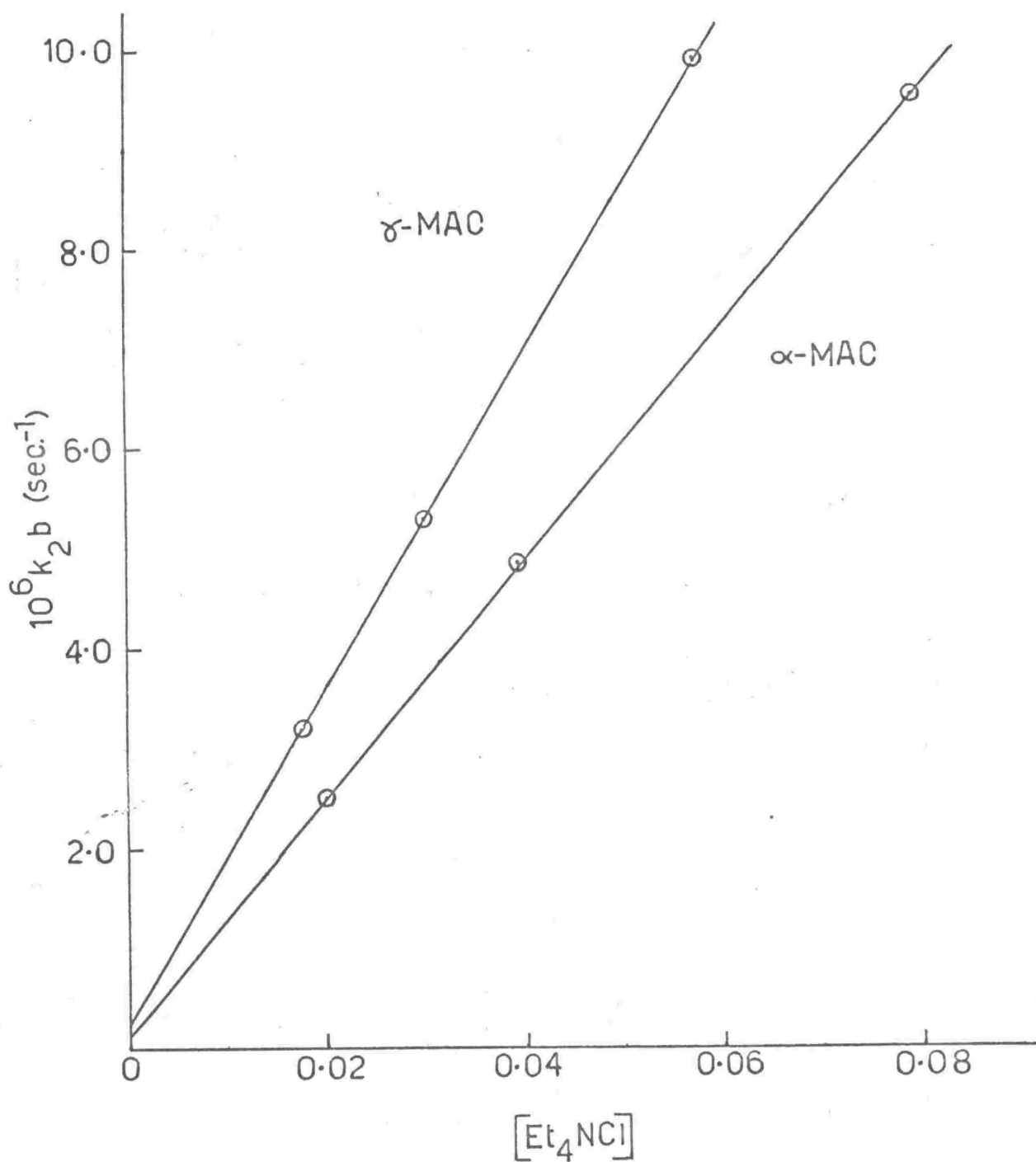


FIG. 14

Kinetic Order of the Isotope Exchange Reactions  
in AN



### III The Chlorine-36 Isotope Exchange Reaction of $\delta$ -Methylallyl Chloride in Acetonitrile

#### (i) Introduction

A parallel investigation to that for  $\alpha$ -methylallyl chloride was carried out for the exchange reaction of  $\delta$ -methylallyl chloride with  $\text{Et}_4^*\text{NCl}$  in acetonitrile.

#### (ii) Procedure

Duplicate runs at  $30.0^\circ\text{C}$  were carried out to determine the reproducibility of the rate data and further runs at  $17.5^\circ\text{C}$  and  $0.0^\circ\text{C}$  to determine the activation parameters were also carried out. Two half-runs (as described in Section II) were carried out to determine the dependence of the rate constant on the concentration of the nucleophile. These involved a three-fold change in the concentration of  $\text{Et}_4^*\text{NCl}$  and the reaction temperature used was  $20.0^\circ\text{C}$ .

#### (iii) Experimental

##### (a) Preparation of Reaction Mixtures and Performance of Runs

The rate of the reaction of  $\delta$ -methylallyl chloride with  $\text{Et}_4^*\text{NCl}$  over the convenient temperature range chosen for the study was too high, except at the lowest temperature used ( $0.0^\circ\text{C}$ ), for the sealed tube technique of carrying out runs to be employed.

The "Y tube" technique, which is suitable for moderately fast reactions, was therefore adopted. A set of reaction tubes in the form of an inverted Y, with side-arms of about 8 ml. capacity, and a short neck of about 8 ml. capacity surmounted by a  $B_{14}$  socket, were used.  $B_{14}$  stoppers were held in place by springs attached to small hooks drawn from the glass.

Solutions of the two reactants (a)  $\delta$ -methylallyl chloride in acetonitrile, and (b)  $Et_4N^+Cl^-$  in acetonitrile, were prepared in the dry-box in two 100 ml. round-bottom  $B_{24}$  flasks. Two 5 ml. pipettes of the special design described in Section II were used to transfer 5 ml. aliquots of each reactant to the Y tubes, which were then closed with  $B_{14}$  stoppers greased with silicone grease. Aliquots to be used for determining the initial concentrations of the reactants were placed in constricted test tubes of the required capacity. The reaction tubes were then immersed in a thermostat at the required temperature up to the bottom of the socket joint, by means of short holders, to attain thermal equilibrium.

After a suitable time had elapsed, each tube was removed from the thermostat and inverted quickly five times, to ensure complete mixing of the reagents, before being replaced in the thermostat. The tubes were inverted in the same order as that in which they were immersed in the thermostat, which gave a constant equilibration time. The last tube inverted was allowed to react for usually 1-2 minutes, before being quenched. This tube was used as the zero-time tube, to correct for any reaction prior to inversion, due to distillation of

the volatile reactant, and for any other errors in the technique.

This technique of performing runs was used for the runs at 30.0°C, 20.0°C and 17.5°C. At 0.0°C, the conventional sealed tube technique described in Section II was used, two tubes being taken for analysis at zero time to correct for reaction up to this time.

(b) Thermostats

At 17.5°C and 20.0°C the correct temperature was maintained in a thermostat of conventional design by means of a large copper coil through which tap water was circulated. At 0.0°C a large Dewar flask of 8 inch diameter, containing a stirred ice-water mixture and covered with an insulating lid, was found to be suitable.

(c) Analytical Techniques

Two methods were used for separating the reaction products - an extraction method and an evaporation method.

(1) The Evaporation Method

This method was used for the run carried out at 17.5°C as a check on the extraction method.

The contents of each Y tube were poured into a tube immersed in liquid air to quench the reaction. This tube was then put on the vacuum line and treated as described for the runs in Section II. Preparation of the sample for analysis for activity and  $\text{Et}_4\text{NCl}$  concentration was also the same as described in Section II.

## (2) The Extraction Method

This technique was used for the runs carried out at 30.0°C, 20.0°C and 0.0°C.

For the runs at the first two temperatures, the contents of the Y tubes were poured into a separating funnel containing 30 ml. each of *n*-pentane and water to quench the reaction. The funnel was then stoppered and vigorously shaken to extract the substrate into the organic phase. The aqueous phase was run off into a 150 ml. conical flask, covered and put aside to await further treatment.

The reaction tubes for the 0.0°C run were cooled in liquid air to quench the reaction, cracked open using a hot glass point and the melted contents (-40°C) were then poured into an extraction mixture and treated as above.

The equivalent of 0.05 gm. of potassium hydroxide (A.R.) was added to the contents of each conical flask, which were then evaporated down, while being flushed with nitrogen, to a very small volume, to remove acetonitrile and traces of the organic phase. Each evaporated sample (2-4 ml.) was made up to a suitable volume with distilled water, usually ~23 ml., and its activity and chloride ion concentration were analysed as for the runs in Section II.

The contents of the tubes used for determining the initial concentration and activity of  $\text{Et}_4\text{N}^+\text{Cl}^-$  were added to 30 ml. of water and evaporated down, as described above, before analysis. This procedure applied of course, only to the Y tube technique of carrying out the runs.

The initial substrate concentration was determined in the same way as described for the runs in Section II, differing only in that, for the runs by the Y tube technique, only the substrate was present in the reaction tubes, so that its concentration was given directly.

Allylic halides are hydrolysed by water to the alcohol and hydrochloric acid. It was therefore expected that during the extraction and evaporating down procedure for reaction mixtures, some hydrolysis of the substrate would occur. Previous experiments, as mentioned in Section VII, Chapter III indicated that this involved not more than 1% of the substrate, with a concentration of  $\sim 0.1M$  for the substrate solution. As a further test, 5 ml. aliquots of each reactant solution were sealed up in tubes, during the preparation for a run by the Y tube technique. The aliquot containing  $\text{Et}_4\text{NCl}^*$  was then added to an extraction mixture and shaken up. After addition of the aliquot containing the substrate, the extraction mixture was treated as for a reaction tube. Subsequent analysis gave an activity for the sample 1% less than that of the initial activity of the  $\text{Et}_4\text{NCl}^*$ . A decrease of 3% in the activity would have been expected for 1% solvolysis of the substrate, with the reactant concentrations used. Thus the expected change in the activity of the sample was hardly outside the error in analysis.

It seemed therefore, that a figure of 1% was a reasonable assessment of the extent of solvolysis occurring during isolation of the products of the reaction. Consequently, the correction for solvolysis described below was applied to runs analysed by the extraction method.

$$\text{Corrected activity of Et}_4\text{NCl}^* = \left[ \frac{[\text{substrate}]}{[\text{Et}_4\text{NCl}]} + 100 \right] \times \frac{Y}{10^2}$$

where Y is the experimental activity of the  $\text{Et}_4\text{NCl}^*$ . This assumes that all the chloride ions produced by solvolysis of the substrate are inactive.

Let this activity of the  $\text{Et}_4\text{NCl}^*$  be  $Y_s$  then:

$$X_s = Z - Y_s$$

where  $X_s$  is the activity of the substrate and Z is the initial activity of the  $\text{Et}_4\text{NCl}^*$ .

Now, to correct for the activity of the solvolysed substrate 1% of  $X_s$  is subtracted from  $Y_s$  to give  $Y_{(\text{corr.})}$  i.e.

$$Y_{(\text{corr.})} = Y_s - \frac{X_s}{100} \quad \text{and} \quad \therefore X_{(\text{corr.})} = Z - Y_{(\text{corr.})}$$

The zero-time Y values for runs analysed using the extraction method tended to be lower than expected and the above correction for substrate solvolysis brought these into closer agreement with that obtained for the run at  $17.5^\circ\text{C}$ , which was analysed using the evaporation method.

Whether the zero-time analysis data, together with the Y values, is used directly to determine the rate constants, or whether the above correction for an arbitrary 1% solvolysis of the substrate is applied, the rate constants obtained are closely similar in magnitude and character. Therefore, as the latter method does not assume (a) that there

is no solvolysis, or (b) that all the chloride ions produced by solvolysis, for analyses throughout the run, are inactive, (which they cannot be as exchange proceeds), it was considered a more valid treatment for the data.

The  $Y_{(\text{corr.})}$  values for runs analysed using the extraction method are recorded in the Tables. The  $Y$  values for these runs are shown in Table LXI.

The rate constants were calculated by substituting the relevant data in the integrated rate equation of Appendix II, as described in Section II.

#### (iv) Results and Discussion

The results for Runs 50-54 are shown in Tables LV-LIX and the activation parameters are shown in Table LX. The method of calculation for the latter was the same as that described in the previous section and relevant data is shown in Appendix IV and Table LXIII. The rate constants for Runs 51, 52 and 53 were used in the calculations. An error in the rate constants of 3% was assumed in calculating the errors in the activation parameters, this value being estimated by the method previously described. (See Section II).

Analysis by gas chromatography showed that  $\delta$ -methylallyl chloride was the exclusive product at >90% theoretical exchange.

As for  $\alpha$ -methylallyl chloride, a plot of  $k_2 b$  versus  $b$  was a straight line passing on extrapolation, close to the origin, which again is indicative of second-order kinetics, and only a small variation,

TABLE IV

Run 50. The  $\gamma$ -Methylallyl Chloride/ $\text{Et}_4\text{NCl}$  Reaction in Acetonitrile (30°C)

Time (min.)	$Y_{(\text{corr.})}$ (ct./min.)	$\log_{10}(X_{\infty} - X)$ ( $X_{\infty} = 1565$ )	% R	$10^4 k_2$ ( $\text{M}^{-1} \text{sec.}^{-1}$ )
0.0	1967	3.1810	3.1	-
28.1	1790	3.1274	14.4	(5.70)
44.0	1739	3.1103	17.6	(4.77)
61.0	1632	3.0727	24.5	5.27
104.0	1446	2.9983	36.4	5.22
141.0	1306	2.9325	45.3	5.23
184.0	1170	2.8573	54.0	5.22
283.0	935	2.6857	69.0	5.20

$$[\gamma\text{-MAC}] = 0.100\text{M}$$

$$\text{Mean (5) } k_2 = 5.23 \pm 0.03 \times 10^{-4} \text{ M}^{-1} \text{ sec.}^{-1}$$

$$[\text{Et}_4\text{NCl}] = 0.0288\text{M}$$

$$Z = 2015 \text{ ct./min.} = X_{(\text{corr.})} + Y_{(\text{corr.})}$$

$$T = 30.03^\circ\text{C}$$

TABLE IWI

Run 51. The  $\delta$ -Methylallyl Chloride/ $\text{Et}_4\text{NCl}$  Reaction in Acetonitrile ( $30^\circ$ )

Time (min.)	$Y_{\text{(corr.)}}$ (ct./min.)	$\log_{10}(X_\infty - X)$ ( $X_\infty = 1500$ )	% R	$10^4 k_2$ ( $\text{M}^{-1} \text{sec.}^{-1}$ )
0.0	1945	3.1741	0.5	-
26.8	1792	3.1271	10.7	5.16
60.7	1591	3.0565	24.1	(5.69)
103.8	1419	2.9854	35.5	5.33
143.7	1273	2.9143	45.3	5.31
188.8	1138	2.8363	54.3	5.25
228.7	1037	2.7672	61.0	5.22
282.8	919	2.6693	68.8	5.24
374.8	782	2.5185	78.0	5.13
529.8	649	2.2915	86.9	4.87

 $[\delta\text{-MAC}] = 0.1005\text{M}$  $[\text{Et}_4\text{NCl}] = 0.0302\text{M}$  $T = 29.97^\circ\text{C}$ Mean (7)  $k_2 = 5.23 \pm 0.07 \times 10^{-4} \text{ M}^{-1} \text{sec.}^{-1}$  $Z = 1952 \text{ ct./min.}$

TABLE LVII

Run 52. The  $\delta$ -Methylallyl Chloride/ $\text{Et}_4\text{NCl}$  Reaction in Acetonitrile (17.5°C)

Time (min.)	Y (ct./min.)	$\log_{10}(X_\infty - X)$ ( $X_\infty = 1574$ )	% R	$10^4 k_2$ ( $\text{M}^{-1} \text{sec.}^{-1}$ )
0	1989	3.1900	1.6	-
94	1837	3.1453	11.2	1.40
199	1692	3.0976	20.5	1.37
219	1661	3.0867	22.4	1.39
318	1544	3.0429	29.9	1.36
459	1384	2.9750	40.0	1.38
675	1178	2.8681	53.1	1.40
899	1046	2.7825	61.5	1.33
1232	866	2.6294	72.9	1.34
1735	707	2.4265	83.0	1.29

 $[\delta\text{-MAC}] = 0.1020\text{M}$  $T = 17.5^\circ\text{C}$ Mean (8)  $k_2 = 1.37 \pm 0.03 \times 10^{-4} \text{ M}^{-1} \text{ sec.}^{-1}$  $[\text{Et}_4\text{NCl}] = 0.0285\text{M}$  $Z = 2014 \text{ ct./min.}$

TABLE IN III

Run 53. The  $\delta$ -Methylallyl Chloride/Et<sub>4</sub>NCl Reaction in Acetonitrile (0°C)

Time (min.)	Y <sub>(corr.)</sub> (ct./min.)	$\log_{10}(X_{\infty}-X)$ ( $X_{\infty} = 1119$ )	% R	$10^5 k_2$ ( $M^{-1} \text{sec.}^{-1}$ )
0	1385	3.0037	9.8	-
739	1281	2.9566	19.1	1.57
1560	1174	2.9020	28.7	1.60
2519	1066	2.8398	38.3	1.61
3464	970	2.7738	46.9	1.63
4860	861	2.6857	56.7	1.61
6480	762	2.5866	65.5	1.58
8469	661	2.4548	74.5	1.59
11340	564	2.2742	83.2	1.58
16219	489	2.0531	89.9	1.44

[ $\delta$ -MAC] = 0.1170M

T = 0.00°C

Mean (8)  $k_2 = 1.60 \pm 0.02 \times 10^{-5} M^{-1} \text{sec.}^{-1}$ [Et<sub>4</sub>NCl] = 0.0393M

Z = 14.95 ct./min.

TABLE I.XX

Run 54. Dependence of the Rate Constant on Nucleophile Concentration (20°C)

Time (min.)	$Y_{(corr.)}$ (ct./min.)	$\log_{10}(X_{\infty} - X)$ ( $X_{\infty} = 2315$ )	% R	$10^4 k_2$ ( $M^{-1} \text{sec.}^{-1}$ )
0	3559	3.3543	2.3	-
169	3006	3.2324	26.2	1.74
281	2704	3.1479	39.3	1.77
412	2457	3.0641	49.9	1.70
568	2191	2.9509	61.4	1.71
819	1888	2.7709	74.5	1.72
				Mean = $1.73 \pm 0.03$

256.

 $(X_{\infty} = 1154)$ 

0	1355	3.0622	0	-
284	1005	2.9053	30.3	1.77
439	855	2.8156	43.3	1.80
769	623	2.6253	63.4	1.82
				Mean = 1.80

 $[\delta\text{-MAC}] = 0.1020M$  (A) 0.1020M (B)  $Z = 3613$  ct./min. (A) $[\text{Et}_3\text{NCl}] = 0.0572M$  (A) 0.0478M (B)  $Z = 1355$  ct./min. (B) $T = 19.90^\circ\text{C}$

TABLE IX

## The Activation Parameters for Isotope Exchange

Isomer	$E_a$ (kcal.mole <sup>-1</sup> )	$\Delta H^\ddagger$ (kcal.mole <sup>-1</sup> )	$\log_{10} A$ (A in M <sup>-1</sup> sec. <sup>-1</sup> )	$\Delta S^\ddagger$ (cal.deg. <sup>-1</sup> mole <sup>-1</sup> )
$\alpha$ -MAC	21.5 <sup>±</sup> 0.4	20.8 <sup>±</sup> 0.4	10.22 <sup>±</sup> 0.3	-13.9 <sup>±</sup> 1.4
$\gamma$ -MAC	19.4 <sup>±</sup> 0.3	18.8 <sup>±</sup> 0.3	10.68 <sup>±</sup> 0.3	-11.6 <sup>±</sup> 1.2

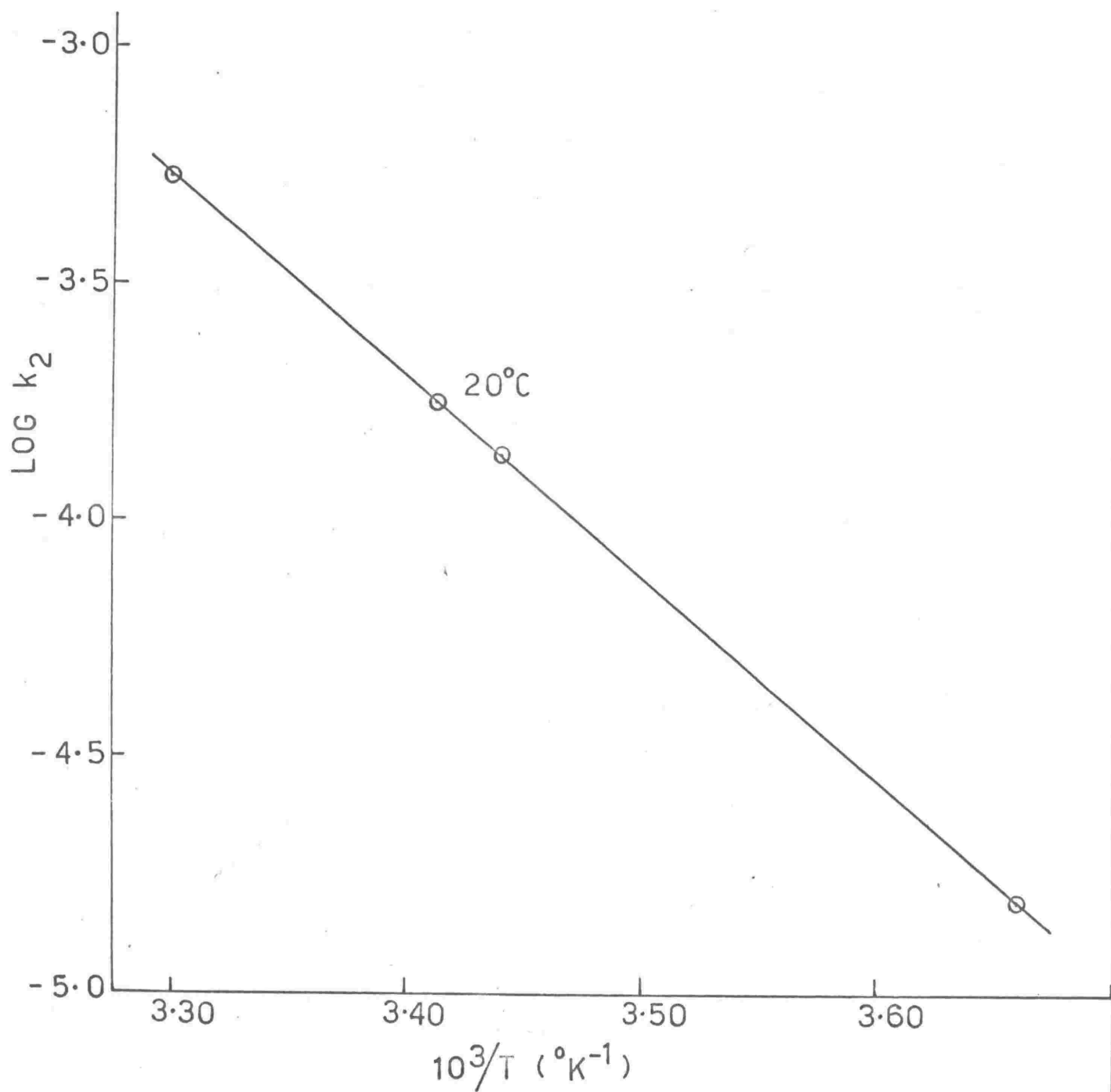
TABLE LXI

Collected "Y Values" for Runs 50, 51, 53 and 54

Run 50 (ct./min.)	Run 51 (ct./min.)	Run 53 (ct./min.)	Run 54A (ct./min.)	Run 54B (ct./min.)
1901	1884	1346	3497	1282
1732	1736	1247	2959	953
1683	1544	1143	2666	813
1581	1378	1039	2425	596
1403	1239	947	2166	
1269	1109	842	1872	
1138	1012	747		
914	899	650		
	768	556		
	641	485		

FIG. 15

Arrhenius Plot for the  $\alpha$ -MAC/ $\text{Et}_4\text{NCl}^{36}$  Exchange  
Reaction in AN



of approximately the magnitude of the experimental error in determining the rate constants, in the degree of dissociation of  $\text{Et}_4\text{NCl}^*$  for a two to three-fold variation in the latter's concentration. The plot is shown in Fig. 14. Data from Runs 54A and B and Run 51 was used. As the temperature of the latter run differed from that of the former, the rate constant at the same temperature was obtained from the activation parameter data.

The rate constants for duplicate runs are again in good agreement, while the plot of  $\log_{10} k_2$  versus  $\frac{1}{T}$  gives a good straight line. (See Fig. 15). The mean value for  $k_2$  at  $20^\circ\text{C}$  ( $1.77 \times 10^{-4} \text{ M}^{-1} \text{ sec.}^{-1}$ ), although not used in calculating the activation parameters, is shown on the plot in Fig. 15 and it agrees closely with that expected ( $1.78 \times 10^{-4} \text{ M}^{-1} \text{ sec.}^{-1}$ ). Discussion of the activation parameters is reserved until Chapter V.

One unexpected feature of the runs was a tendency for the rate constants to fall off after about 80% of the theoretical exchange had taken place.

Both the sealed tube and Y tube techniques of performing the runs, and both the extraction and evaporation methods of analysis, had no effect on this downwards drift, which therefore appears to be independent of the kinetic technique.

Intensive v.p.c. analyses of the  $\gamma$ -methylallyl chloride used for the runs and of reaction mixtures reacted to "infinity" showed the presence of no extra peaks, with the chromatograph column run at  $20-75^\circ\text{C}$ .

An "infinity" tube analysis gave the theoretical activity, within experimental error, after a reaction time of 100 half-lives, i. e. , 383 ct./min. compared with the theoretical value of 376 ct./min. No  $\alpha$ -methylallyl chloride or acid was detected in the reaction mixture.

Quantitative solvolysis of weighed samples of  $\delta$ -methylallyl chloride, by reaction with methoxide ions in methanol, and subsequent analysis for chloride ions by potentiometric titration and gravimetric analysis, gave a chlorine content 99% of the theoretical.

England postulated the presence of a trace impurity, not removed by fractionation, to account for downwards drifting rate constants in the exchange reactions of the methylallyl bromides in acetone.<sup>120</sup>

However, no evidence was obtained for the presence of an impurity in  $\delta$ -methylallyl chloride, by the most sensitive method of analysis - gas chromatography - so the reason for the downwards drift in the rate constants is not clear. Postulation of the presence of an impurity of low volatility, or of a non-volatile impurity, is precluded by the fact that samples of  $\delta$ -methylallyl chloride were bulb to bulb distilled before use.

A possible explanation is that the sample of  $\delta$ -methylallyl chloride was not pure trans-isomer but contained some of the cis-isomer. For reasons not well defined, this isomer reacts faster with iodide ions in acetone and ethoxide ions in ethanol than does the trans-isomer.<sup>116,158</sup> In the former case the rate ratio is  $\sim 6$  and in the latter  $\sim 1.4$ .

The behaviour is similar for a  $\gamma$ -methyl, ethyl, isopropyl or t-butyl group, except for the latter which shows the reverse effect with ethoxide ions in ethanol.

Hatch and Li<sup>116</sup> report that the kinetic effects approximate to those expected from the London theory, so that the enhanced reactivity of the cis-isomer may be due to London interactions between the attacking nucleophile and the nearby cis-alkyl group, resulting in a reduction in transition state free energy.

One would expect these interactions to be much smaller with the smaller and less polarisable chloride ion. However, if some cis-isomer were present in the  $\gamma$ -methylallyl chloride and if it reacts with chloride ions faster than the trans-isomer, then a fall-off in the rate constant would be expected.

An attempt was made to see if the single peak observed for  $\gamma$ -methylallyl chloride using the PYE Argon Chromatograph could be split using an instrument capable of higher resolution. A Perkin-Elmer Model 800 chromatograph was used with a 12 foot packed column run at 50°C. The liquid phase was polypropyleneglycol (P.P.G.). A single peak with a retention time of 50 minutes was obtained. Whereas a splitting of the peak would have suggested the presence of two components of similar retention time, a negative result could mean either that the peak is representative of the sample which contains only one component, or that the column is not capable of resolving the peak into its components.

Hollis and Hayes separated all the isomeric monochlorobutenes on a 100 foot squalane coated capillary column,<sup>159</sup> so the above failure to observe two components is inconclusive.

Obviously, a study of the relative reactivity of the cis- and trans-isomers of  $\gamma$ -methylallyl chloride would have been of considerable value and interest, but as this project had to be terminated at this stage it could not be attempted. Hatch and Noyes have suggested caution in the use of isomerically impure samples (with respect to geometrical isomerism) for kinetic studies with  $\gamma$ -methylallyl halides.<sup>167</sup>

Both exchange reactions have been shown, by varying the  $\text{Et}_4\text{NCl}$  concentration, to follow second-order kinetics. This, together with the virtually exclusive formation of the normal products, establishes a bimolecular mechanism for the exchange reactions, as a unimolecular mechanism would result in a mixture of normal and rearranged products.

As mentioned in the introduction to this chapter, the  $\text{S}_{\text{N}}2$  mechanism is preferred for the halide ion exchange reactions of these compounds and it requires the more  $\text{S}_{\text{N}}1$  promoting benzyl and benzhydryl compounds to bring about  $\text{S}_{\text{N}}1$  or concurrent  $\text{S}_{\text{N}}1$ - $\text{S}_{\text{N}}2$  exchange in dipolar aprotic solvents.<sup>126,162,163</sup>

Even 3-phenylallyl chloride exchanges by the  $\text{S}_{\text{N}}2$  mechanism in dimethylformamide.<sup>141</sup> A 1-phenyl group promotes competing  $\text{S}_{\text{N}}1$  rearrangement and exchange.<sup>140,141</sup>

The relative rates of the two exchange processes at 25°C is 110. (See Chapter V). This is in accord with the known effects of  $\alpha$ -methyl and  $\delta$ -methyl substituents on the reactivity of allyl chloride, namely, that an  $\alpha$ -methyl group retards  $S_N2$  substitution by sterically hindering nucleophilic attack, while a  $\delta$ -methyl group accelerates it by hyperconjugative stabilisation of the transition state.<sup>85,92b</sup>

As observed for the rearrangement reaction, the dependence of the second-order rate constants on the concentration of  $Et_4NCl^*$  is very small, the variation being no more than 5% for a four-fold change in concentration. This is considerably less than would be expected from the calculations for the degree of dissociation of  $Et_4NCl^*$  at 25°C, which are given in Section VII of the previous chapter. It would seem therefore, that in these reactions the reactivity of an ion-pair is not negligible compared with that of the "free" ion.

TABLE LXII

## Summary of Rate Constants

Run	Temp. (°C)	$[\text{Et}_4\text{NClO}_4]$ (M)	$k_1$ (sec. <sup>-1</sup> )	
24	95.93	0.0	$3.44 \times 10^{-8}$	$(k_1^*)(\alpha\text{-MAC})$
25	95.93	0.0507	$3.94 \times 10^{-8}$	$(k_1^*)(\alpha\text{-MAC})$
24	95.93	0.0	$3.45 \times 10^{-8}$	$(k_1^E)(\alpha\text{-MAC})$
25	95.93	0.0507	$3.53 \times 10^{-8}$	$(k_1^E)(\alpha\text{-MAC})$
33	95.89	0.0	$2.22 \times 10^{-8}$	$(k_1^*)(\gamma\text{-MAC})$

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The reactant isomer is indicated in brackets.

$k_1$  is the rate constant indicated in brackets uncorrected for solvent expansion.

TABLE LXIII

Summary of Rate Constants

Run	Temp. (°C)	[Et <sub>4</sub> NCl] (M)	k <sub>2</sub> (M <sup>-1</sup> sec. <sup>-1</sup> )	k <sub>2</sub> (corr.) (M <sup>-1</sup> sec. <sup>-1</sup> )	
26	95.83	0.0485	5.61 x 10 <sup>-5</sup>	4.42 x 10 <sup>-5</sup>	(k <sub>2</sub> <sup>α</sup> )
27	95.85	0.0485	5.42 x 10 <sup>-5</sup>	4.28 x 10 <sup>-5</sup>	(k <sub>2</sub> <sup>α</sup> )
26 + 27	95.85	0.0485	3.15 x 10 <sup>-6</sup>	3.52 x 10 <sup>-6</sup>	(k <sub>2</sub> <sup>E</sup> )
28	95.88	0.0259	5.72 x 10 <sup>-5</sup>	4.51 x 10 <sup>-5</sup>	(k <sub>2</sub> <sup>α</sup> )
29	95.92	0.0249	5.59 x 10 <sup>-5</sup>	4.41 x 10 <sup>-5</sup>	(k <sub>2</sub> <sup>α</sup> )
30	95.88	0.0470	5.55 x 10 <sup>-5</sup>	4.38 x 10 <sup>-5</sup>	(k <sub>2</sub> <sup>α</sup> )
31	95.86	0.0970	5.45 x 10 <sup>-5</sup>	4.30 x 10 <sup>-5</sup>	(k <sub>2</sub> <sup>α</sup> )
32	95.88	0.0207	6.04 x 10 <sup>-5</sup>	4.76 x 10 <sup>-5</sup>	(k <sub>2</sub> <sup>α</sup> )
34	95.85	0.1080	5.40 x 10 <sup>-5</sup>	1.78 x 10 <sup>-5</sup>	(k <sub>2</sub> <sup>γ</sup> )
35	95.89	0.0993	5.33 x 10 <sup>-5</sup>	1.76 x 10 <sup>-5</sup>	(k <sub>2</sub> <sup>γ</sup> )
39	81.05	0.1230	1.34 x 10 <sup>-5</sup>	1.04 x 10 <sup>-5</sup>	(k <sub>2</sub> <sup>α</sup> )
40	111.10	0.0537	2.15 x 10 <sup>-4</sup>	1.72 x 10 <sup>-4</sup>	(k <sub>2</sub> <sup>α</sup> )
41	126.22	0.0546	7.03 x 10 <sup>-4</sup>	5.73 x 10 <sup>-4</sup>	(k <sub>2</sub> <sup>α</sup> )
42	126.12	0.0516	6.74 x 10 <sup>-4</sup>	5.49 x 10 <sup>-4</sup>	(k <sub>2</sub> <sup>α</sup> )
43	126.13	0.0913	6.58 x 10 <sup>-4</sup>	2.38 x 10 <sup>-4</sup>	(k <sub>2</sub> <sup>γ</sup> )
44	126.02	0.1102	6.40 x 10 <sup>-4</sup>	2.30 x 10 <sup>-4</sup>	(k <sub>2</sub> <sup>γ</sup> )
45	59.95	0.0390	1.22 x 10 <sup>-4</sup>	1.29 x 10 <sup>-4</sup>	(k <sub>2</sub> <sup>α</sup> )
46	59.80	0.0394	1.23 x 10 <sup>-4</sup>	1.30 x 10 <sup>-4</sup>	(k <sub>2</sub> <sup>α</sup> )
47	59.80	( 0.0794 0.0199	( 1.20 x 10 <sup>-4</sup> 1.26 x 10 <sup>-4</sup>	( 1.27 x 10 <sup>-4</sup> 1.33 x 10 <sup>-4</sup>	( k <sub>2</sub> <sup>α</sup> ) ( k <sub>2</sub> )

/cont...

Table LXIII (cont.)Summary of Rate Constants

Run	Temp. (°C)	[Et <sub>4</sub> NCl] (M)	k <sub>2</sub> (M <sup>-1</sup> sec. <sup>-1</sup> )	k <sub>2</sub> (corr.) (M <sup>-1</sup> sec. <sup>-1</sup> )	
48	75.20	0.0404	4.88 x 10 <sup>-4</sup>	5.28 x 10 <sup>-4</sup>	(k <sub>2</sub> <sup>α</sup> )
49	45.10	0.0404	2.71 x 10 <sup>-5</sup>	2.81 x 10 <sup>-5</sup>	(k <sub>2</sub> <sup>α</sup> )
50	30.03	0.0288	5.23 x 10 <sup>-4</sup>	5.30 x 10 <sup>-4</sup>	(k <sub>2</sub> <sup>γ</sup> )
51	29.97	0.0302	5.23 x 10 <sup>-4</sup>	5.30 x 10 <sup>-4</sup>	(k <sub>2</sub> <sup>γ</sup> )
52	17.57	0.0285	1.37 x 10 <sup>-4</sup>	1.36 x 10 <sup>-4</sup>	(k <sub>2</sub> <sup>γ</sup> )
53	0.00	0.0393	1.60 x 10 <sup>-5</sup>	1.56 x 10 <sup>-5</sup>	(k <sub>2</sub> <sup>γ</sup> )
54	19.90	0.0572	1.73 x 10 <sup>-4</sup>	1.73 x 10 <sup>-4</sup>	(k <sub>2</sub> <sup>γ</sup> )
		0.0178	1.80 x 10 <sup>-4</sup>	1.80 x 10 <sup>-4</sup>	(k <sub>2</sub> <sup>δ</sup> )

k<sub>2</sub> = the second-order rate constant (undissected and uncorrected for solvent expansion).

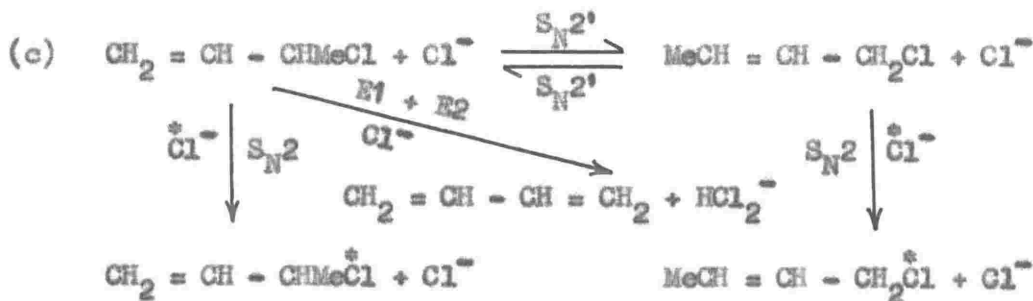
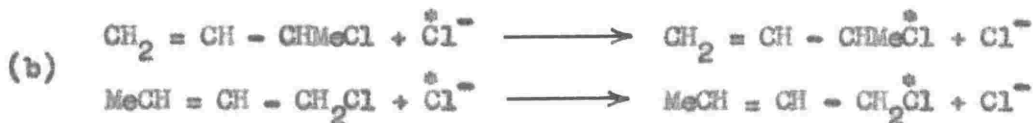
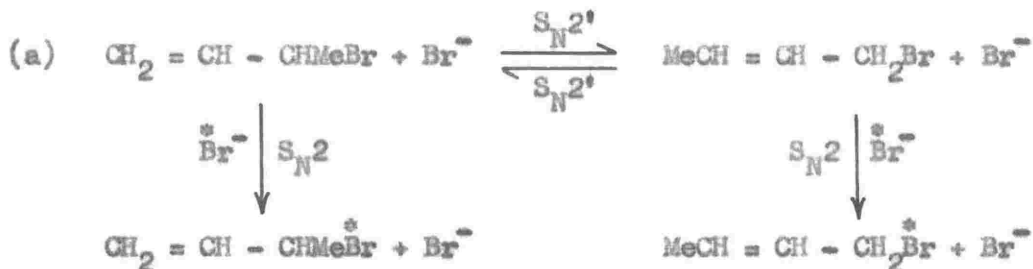
k<sub>2</sub>(corr.) = the rate constant corrected for solvent expansion and dissected when composite, into the component indicated.

CHAPTER V

A COMPARISON OF THE REACTIONS OF THE ISOMERIC METHYLALLYL  
BROMIDES AND CHLORIDES IN ACETONE AND THE ISOMERIC  
METHYLALLYL CHLORIDES IN ACETONITRILE

(1) Introduction

In this chapter a comparison of the systems:



is made. Data from the work of England and Hughes<sup>76b,79,120</sup> on the  $S_N2$  and  $S_N2'$  reactions of the methylallyl bromides in acetone and the  $S_N2$  reactions of the methylallyl chlorides in acetone has been used for comparison with that obtained in this project for the methylallyl chlorides in acetonitrile.

#### (11) Rate Ratios and the Isokinetic Temperature

Table LXIV shows the rate ratios, (or rate constant ratios), for all the relevant binary combinations of the bimolecular reactions undergone by these allylic halides in acetone and acetonitrile, at two temperatures 25°C and 100°C. The rate constants at 25°C and 100°C and the activation parameters for these reactions are shown in Table LXV.

Except for the ratios marked with an asterisk, none of the reactions compared are near their isokinetic temperature, as shown by the large values for their rate ratios and the fact that a 75°C change in temperature does not alter the relative rates sufficiently to invert them.<sup>173,174</sup> (The isokinetic temperature for a pair of reactions is the temperature at which their rate constants are identical). An increase in temperature decreases the rate ratios which means that the reactions are below their isokinetic temperatures or in the region of control by  $\Delta H^\ddagger$ . In this region, the reaction of lower activation enthalpy is the faster reaction.<sup>173,174</sup> Those ratios marked with an asterisk apparently involve reactions above their isokinetic temperature and this will be discussed later.

TABLE LXIV

$$\frac{k_2^{\alpha-\text{Br}}(\text{A})}{k_2^{\alpha-\text{Br}}(\text{AN})} = \frac{160(25^\circ\text{C})}{83(100^\circ\text{C})} \quad \frac{k_2^{\alpha-\text{Cl}}(\text{A})}{k_2^{\alpha-\text{Cl}}(\text{AN})} = \frac{125(25^\circ\text{C})}{31(100^\circ\text{C})} \quad \frac{k_2^{\alpha-\text{Cl}}(\text{AN})}{k_2^{\alpha-\text{Cl}}(\text{AN})} = \frac{110(25^\circ\text{C})}{53(100^\circ\text{C})}$$

$$\frac{k_2^{\alpha-\text{Br}}(\text{A})}{k_2^{\alpha-\text{Br}}(\text{AN})} = \frac{59(25^\circ\text{C})}{23(100^\circ\text{C})} \quad \frac{k_2^{\alpha-\text{Cl}}(\text{AN})}{k_2^{\alpha-\text{Cl}}(\text{AN})} = \frac{246(25^\circ\text{C})}{67(100^\circ\text{C})}$$

$$\frac{k_2^{\alpha-\text{Br}}(\text{A})}{k_2^{\alpha-\text{Cl}}(\text{AN})} = \frac{306(25^\circ\text{C})}{60(100^\circ\text{C})} \quad \frac{k_2^{\alpha-\text{Br}}(\text{A})}{k_2^{\alpha-\text{Cl}}(\text{AN})} = \frac{44.7(25^\circ\text{C})}{94(100^\circ\text{C})} \quad \frac{k_2^{\alpha-\text{Br}}(\text{A})}{k_2^{\alpha-\text{Cl}}(\text{AN})} = \frac{1120(25^\circ\text{C})}{175(100^\circ\text{C})}$$

$$\frac{k_2^{\alpha-\text{Cl}}(\text{AN})}{k_2^{\alpha-\text{Cl}}(\text{A})} = \frac{12(25^\circ\text{C})}{16(100^\circ\text{C})} \quad \frac{k_2^{\alpha-\text{Cl}}(\text{AN})}{k_2^{\alpha-\text{Cl}}(\text{A})} = \frac{11(25^\circ\text{C})}{28(100^\circ\text{C})} \quad \frac{k_2^{\alpha-\text{Br}}(\text{A})}{k_2^{\alpha-\text{Cl}}(\text{A})} = \frac{3820(25^\circ\text{C})}{976(100^\circ\text{C})} \quad \frac{k_2^{\alpha-\text{Br}}(\text{A})}{k_2^{\alpha-\text{Cl}}(\text{A})} = \frac{4890(25^\circ\text{C})}{2630(100^\circ\text{C})}$$

$\alpha, \gamma$  denotes the isomer

(A) = acetone

Cl, Br denotes the leaving group

(AN) = acetonitrile

TABLE LXV

Substrate	Mechanism	Solvent	$k_2$ ( $M^{-1} \text{ sec.}^{-1}$ )	$E_a$ (kcal.mole $^{-1}$ )	$\log_{10} A$ ( $M^{-1} \text{ sec.}^{-1}$ )	$\Delta H^\ddagger$ (kcal.mole $^{-1}$ )	$\Delta S^\ddagger$ (cal.deg. $^{-1}$ mole $^{-1}$ )
$\alpha$ -MAC	$S_N2$	MeCN	$2.87 \times 10^{-6}$ (25°C) $4.21 \times 10^{-3}$ (100°C)	24.5	10.22	20.8	-13.9
$\gamma$ -MAC	$S_N2$	MeCN	$3.15 \times 10^{-4}$ (25°C) $2.23 \times 10^{-1}$ (100°C)	19.4	10.68	18.8	-11.6
$\alpha$ -MAC	$S_N2^*$	MeCN	$1.33 \times 10^{-8}$ (25°C) $6.28 \times 10^{-5}$ (100°C)	24.9	10.41	24.2	-13.4
$\gamma$ -MAC	$S_N2^*$	MeCN	$5.31 \times 10^{-9}$ (25°C)	25.0	10.07	24.3	-14.9
$\alpha$ -MAC	$S_N2$	Me <sub>2</sub> CO	$2.30 \times 10^{-7}$ (25°C) $2.57 \times 10^{-4}$ (100°C)	20.6	8.47	19.9	-22.1
$\gamma$ -MAC	$S_N2$	Me <sub>2</sub> CO	$2.88 \times 10^{-5}$ (25°C) $7.94 \times 10^{-3}$ (100°C)	16.5	7.56	15.8	-26.2
$\alpha$ -MABr	$S_N2$	Me <sub>2</sub> CO	$8.79 \times 10^{-4}$ (25°C) $2.51 \times 10^{-1}$ (100°C)	16.5	9.06	15.9	-19.1
$\gamma$ -MABr	$S_N2$	Me <sub>2</sub> CO	$1.44 \times 10^{-1}$ (25°C) $2.09 \times 10^1$ (100°C)	14.7	9.93	14.1	-15.0
$\alpha$ -MABr	$S_N2^*$	Me <sub>2</sub> CO	$1.49 \times 10^{-5}$ (25°C) $1.10 \times 10^{-2}$ (100°C)	19.4	9.40	18.8	-17.7

MAC = Methylallyl Chloride

MABr = Methylallyl Bromide

Therefore it may be concluded that trends in rate ratios, unchanged over this temperature range, provide a valid basis for discussion.

(iii) The S<sub>N</sub>2 Reactions - Effect of a Methyl Substituent

Consider first the S<sub>N</sub>2 rate ratios -  $\frac{k_2^\gamma}{k_2^\alpha}$ . The ratio for the methylallyl bromides in acetone and those for the methylallyl chlorides in acetone and acetonitrile are 160, 125, 110 respectively at 25°C and 83, 31, 53 at 100°C. Therefore, the ratio for the chlorides in both solvents is similar to and smaller than that for the bromides.

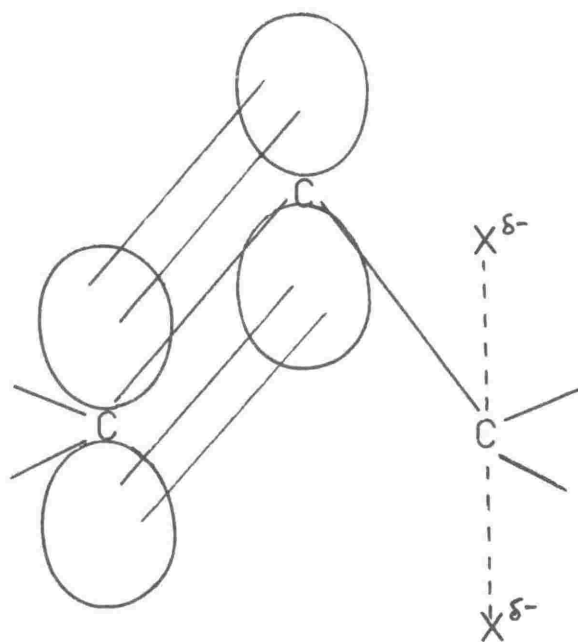
Two factors governing the relative rates of the S<sub>N</sub>2 reactions of allyl halides with α- and γ-methyl substituents are considered to be steric hindrance to nucleophile attack by an α-methyl substituent and transition state stabilisation by hyperconjugative electron release from a γ-methyl substituent.<sup>92b</sup> For example, γ-methylallyl chloride reacts 2.62 times faster than allyl chloride with ethoxide ions in ethanol at 44.6°C and 2.52 times faster with chloride ions in acetone at the same temperature, while allyl chloride reacts 20 times faster than α-methylallyl chloride with ethoxide ions and 32 times faster with chloride ions.<sup>92b</sup> Two methyl substituents are even more effective, completely suppressing an S<sub>N</sub>2 reaction when in the α-position and causing a large increase in rate, of the order of fifteen-fold, when in the γ-position.<sup>54</sup>

The smaller ratios for the chlorides in acetone and acetonitrile, compared with that for the bromides, could be due partly to reduced

steric hindrance to  $S_N2$  attack by the smaller chloride ion on  $\alpha$ -methylallyl chloride, compared with  $S_N2$  attack by the larger bromide ion on the corresponding bromide.<sup>175</sup>

However, Dostrovsky, Hughes and Ingold consider steric hindrance to be less dependent on nucleophile and leaving group size than on alkyl homology, because a larger entering group, although more capable of interaction, sets itself further from the reaction centre.<sup>176,177</sup>

In the case of allyl compounds, if nucleophilic attack involves the configuration of the molecule given below,<sup>100a</sup> then some interaction of the nucleophile and leaving group with the  $\pi$  electrons of the double bond may occur and the interaction in a reaction involving an  $\alpha$ -methyl group may increase relative to that in a reaction involving no  $\alpha$ -methyl group, as the size of the attacking nucleophile, or anion, and leaving group increases, possibly due to restriction of bending away from the  $\pi$  orbital.



The differences between the ratios are small, so that another possible contributing factor could be differences in initial state solvation between members of the isomeric pairs.<sup>5</sup>

(iv) the Correction of Ratios for Ion-Pairing of the Nucleophilic Reagent

The rate constant ratios for  $\alpha$ -methylallyl halide pairs and  $\gamma$ -methylallyl halide pairs are distorted, due to the high degree of ion-association for lithium halides in acetone, which markedly reduces the effective concentration of the nucleophilic reagent.<sup>13,178</sup>

(See rows 3 and 4 of Table LXIV). Large salt effects were observed by England and Hughes for the reactions in acetone, so the rate constants for the reactions of the bromides were adjusted to a constant concentration of lithium bromide, (0.04M). The  $S_N2$  reactions of the chlorides were studied at an approximately constant lithium chloride concentration. (ca. 0.025M).<sup>79,120</sup>

Calculations of the degree of dissociation ( $\alpha$ ) for lithium bromide in acetone (0.04M), lithium chloride in acetone (0.025M), and tetraethylammonium chloride in acetonitrile (0.025M and 0.04M) were carried out, using values for the dissociation constants at 25°C of  $2.19 \times 10^{-4}$ ,  $3.3 \times 10^{-6}$  and  $2.88 \times 10^{-2}$ .<sup>131,178</sup> (The method used was the same as that described in Section VIII, Chapter III). Values of  $1.0 \times 10^{-1}$ ,  $1.3 \times 10^{-2}$ ,  $7.5 \times 10^{-1}$  and  $6.9 \times 10^{-1}$  were obtained, which were used to adjust the rate constants for the reactions carried out in acetone, to the values they would have if the degree of

dissociation of the nucleophiles were the same as that for  $\text{Et}_4\text{NCl}$  in acetonitrile at the same concentration. These rate constants were then used to calculate the corrected rate ratios given in Table LXVI.

The above corrections were made in the conventional way using the "dual hypothesis" of Acree,<sup>35</sup> represented by the equation:

$$k_2^{\text{obsd.}} = \alpha k_f + (1-\alpha)k_p$$

with the assumption that  $k_p$  is negligible so that  $k_2^{\text{corr.}} = k_2^{\text{obsd.}}/\alpha$ . Subject to the limitations of the above equation and within the limits of the assumptions that (a) the variation of the degree of dissociation with temperature does not distort the value of  $E_a$  significantly from its true value thus giving a distorted value for  $k_2$  on extrapolation to  $25^\circ\text{C}$ , (b) that the ion-pairs of tetraethylammonium chloride, lithium chloride and lithium bromide have negligible reactivity and (c) that an ion-pair defined by conductance is kinetically significant,<sup>144</sup> the corrected ratios can be compared. The further assumption that  $(\alpha)$  is constant from  $25^\circ\text{C}$  to  $100^\circ\text{C}$  is made in calculating the ratios at  $100^\circ\text{C}$ .

(v) Solvent Effects on the  $S_N2$  Reactions of the Isomeric Chlorides

It may be seen from the above ratios that the  $S_N2$  reactions of the allylic chlorides are approximately five times faster in acetone than in acetonitrile at  $25^\circ\text{C}$ .

Large rate differences for a change of solvent from one member of the dipolar aprotic group to another are not expected, as anion -

TABLE LXVI

$$\frac{k_2^{\alpha-\text{Br}}(\text{A})}{k_2^{\alpha-\text{Cl}}(\text{AN})} = \frac{2115(25^\circ\text{C})}{412(100^\circ\text{C})} = \frac{k_2^{\gamma-\text{Br}}(\text{A})}{k_2^{\gamma-\text{Cl}}(\text{AN})} = \frac{3090(25^\circ\text{C})}{646(100^\circ\text{C})} = \frac{k_2^{\delta-\text{Br}}(\text{A})}{k_2^{\delta-\text{Cl}}(\text{AN})} = \frac{7730(25^\circ\text{C})}{1209(100^\circ\text{C})}$$

$$\frac{k_2^{\alpha-\text{Cl}}(\text{AN})}{k_2^{\alpha-\text{Cl}}(\text{A})} = \frac{0.216(25^\circ\text{C})}{0.284(100^\circ\text{C})} = \frac{k_2^{\gamma-\text{Cl}}(\text{AN})}{k_2^{\gamma-\text{Cl}}(\text{A})} = \frac{0.189(25^\circ\text{C})}{0.486(100^\circ\text{C})} = \frac{k_2^{\delta-\text{Br}}(\text{A})}{k_2^{\delta-\text{Cl}}(\text{A})} = \frac{636(25^\circ\text{C})}{342(100^\circ\text{C})}$$

solvation ability, dielectric constants and ionising and dissociating powers do not differ greatly.<sup>8,15,16</sup> A higher rate in acetone would be in accord with the Hughes-Ingold theory of solvent effects.<sup>2</sup> A similar result was obtained for the  $S_N2$  (assumed) reaction of allyl chloride with lithium chloride in acetone and dimethyl sulphoxide, which also involved a rate decrease on transfer to a more polar solvent. (See Chapter II).

It is interesting to compare these results with those for the exchange reactions of substituted benzhydryl thiocyanates with thiocyanate ions in acetone and acetonitrile.<sup>48</sup> The ratio of the second-order rate constants in acetone and acetonitrile was greater than 1 for strongly electron-withdrawing substituents and decreased to values smaller than 1 as the electron-withdrawing power decreased. This behaviour was correlated with a change in transition state character from near equivalent bond-breaking and making to bond-breaking considerably ahead of bond-making.

Both Fava and Parker (and their co-workers) have drawn attention to the fact that ion-pairing corrections must be treated with caution, because (a) the reactivity of ion-pairs is not necessarily negligible compared with that of the "free ion", and (b) ion-pairing of the transition state with the cation of the nucleophilic reagent may not be negligible, especially with small transition states, so that corrections based on kinetic data or known values of  $K_{(eq.)}$  may be seriously in error.<sup>33b,48</sup>

The corrected rate ratios at the two temperatures show that the reactions of the chlorides in acetone and acetonitrile, which were apparently above their isokinetic temperature as recorded in Table LXIV, are really below it, with ion-pairing distortion of their relative absolute rates being responsible for the observed ratios.

(vi) Rate-Controlling Factors

Two of the factors controlling the rate of a bimolecular nucleophilic substitution reaction are the strength of the bond to the leaving group and the nucleophilicity of the nucleophile,<sup>12,179</sup> The faster rate of reaction of the allylic bromides compared with the chlorides is therefore in accord with the weaker carbon-bromine bond, which has a bond energy of 45.5 kcal.mole<sup>-1</sup> compared with that for the carbon-chlorine bond, which is 59.3 kcal.mole<sup>-1</sup>.<sup>180</sup>

There is some tendency towards a nucleophilicity order of  $F^- > Cl^- > Br^- > I^-$  for the halide ions in dipolar aprotic solvents in  $S_N2$  reactions with alkyl halides and *p*-toluenesulphonates, when corrections are made for ion-pairing of the nucleophilic reagent.<sup>13,21,37</sup> If the above order holds in the present case, the difference in reactivity between the bromide and chloride ions must be small compared with the difference in the ease of breaking the bond to the leaving group.

The data in dipolar aprotic solvents available for comparison indicates a reactivity for the chloride ion of the order of 0.5 times that of the bromide ion.<sup>13,21,37</sup>

(vii) The Effect of Variables by Comparison with Reference Reactions

If the relative rates of the  $S_N2$  exchange reactions of  $\gamma$ -methylallyl bromide and  $\gamma$ -methylallyl chloride in acetone and acetonitrile respectively, can be taken as a measure of the effect of change of solvent, nucleophile and leaving group on attack at saturated carbon under conditions of low steric hindrance, then variations in the relative rates of the  $S_N2$  reactions of the  $\alpha$ -methylallyl halides and the  $S_N2'$  reactions of both the  $\alpha$ - and  $\gamma$ -compounds from this ratio may be discussed in terms of a number of factors.

The ratio  $\frac{k_2^{\alpha-\text{Br}(A)}}{k_2^{\gamma-\text{Br}(A)}}$  is much less than the ratio  $\frac{k_2^{\alpha-\text{Cl}(AN)}}{k_2^{\gamma-\text{Cl}(AN)}}$ ,

being 59 at 25°C and 23 at 100°C compared with 216 and 67 at the same temperatures, while the ratios  $\frac{k_2^{\alpha-\text{Br}(A)}}{k_2^{\alpha-\text{Cl}(AN)}}$ ,  $\frac{k_2^{\gamma-\text{Br}(A)}}{k_2^{\gamma-\text{Cl}(AN)}}$  and  $\frac{k_2^{\gamma-\text{Br}(A)}}{k_2^{\alpha-\text{Cl}(AN)}}$  are 2115, 3090 and 7730 respectively at 25°C and 412, 646 and 1209 at 100°C.

It appears therefore, that the  $S_N2'$  reaction of  $\alpha$ -methylallyl chloride competes less effectively with the  $S_N2$  reaction, than does the  $S_N2'$  reaction of  $\alpha$ -methylallyl bromide with the corresponding  $S_N2$  reaction. The ratios show that, not only is the  $S_N2'$  reaction of  $\alpha$ -methylallyl chloride considerably slower than expected from the relative rates of the  $S_N2$  reactions of the  $\gamma$ -methylallyl halides and the rate of the  $S_N2'$  reaction of  $\alpha$ -methylallyl bromide, but also that the rate of the  $S_N2$  reaction of  $\alpha$ -methylallyl chloride is somewhat higher than expected, this having been discussed previously.

Reduced steric hindrance to the  $S_N2$  reaction of  $\alpha$ -methylallyl chloride by the  $\alpha$ -methyl group, compared with that to the  $S_N2$  reaction of  $\alpha$ -methylallyl bromide, due to the smaller size of the nucleophile (as discussed previously) may contribute to the observed behaviour. It has been demonstrated that substituents on the  $\alpha$ -carbon atom of an allylic halide can change the reaction mechanism from exclusive  $S_N2$  to exclusive  $S_N2'$ .<sup>80e,181</sup>

The relative effect of the solvent change - acetone to acetonitrile - on the two transition state types should also be important. If the  $S_N2'$  transition state undergoes a smaller increase in stabilisation than the  $S_N2$  when the polarity of the solvent is increased, then, as the initial state solvation is the same for reaction by both mechanisms, the rate and proportion of reaction by the  $S_N2'$  mechanism would fall relative to the  $S_N2$  reaction on transfer from acetone to the more polar acetonitrile. This effect is analogous to the effect of a change of solvent on  $S_N2/E2$  ratios.<sup>3</sup> Also, the range of influence of the  $S_N2$  transition state on solvent molecules should show a greater change for the solvent change, than that of the  $S_N2'$ , resulting in a larger relative entropy change and hence rate, for the  $S_N2$  reaction in the more polar solvent.

The  $\frac{k_2(S_N2)}{k_2(S_N2')}$  ratio for the reaction of 3,3-dichloroprop-1-ene with sodium thiophenoxide in ethanol increases on transfer to 75% aqueous ethanol.<sup>92a</sup>

More efficient solvent stabilisation of the less dispersed and more accessible charge on the  $S_N2$  transition state is not unlikely.

Another factor which may reduce the rate of the  $S_N2'$  reaction relative to that of the  $S_N2$  by a larger amount for the chlorides than for the bromides, is electrostatic repulsion between the entering and leaving groups in the cis transition state postulated for the  $S_N2'$  reaction. This repulsion may be greater for the chlorides than for the bromides due to the smaller size, and therefore higher charge density and lower polarisability, of the chloride ion.<sup>175,182</sup>

The ratio  $\frac{k_2^{\gamma\text{-Br(A)}}}{k_2^{\gamma\text{-Cl(AN)}}} = 6460$  at  $25^\circ\text{C}$  is also considerably higher than expected on the basis of the reference ratio. The slow rate of the  $S_N2'$  reaction of  $\gamma$ -methylallyl chloride compared with that of  $\gamma$ -methylallyl bromide is of course reflected in the  $\frac{k_2^{\gamma\text{-Cl(AN)}}}{k_2^{\gamma\text{-Br(A)}}$  and  $\frac{k_2^{\gamma\text{-Br(A)}}}{k_2^{\gamma\text{-Cl(AN)}}$  ratios, which are 59,300 and 28,400 respectively at  $25^\circ\text{C}$ .

The factors discussed for the  $S_N2$  and  $S_N2'$  reactions of the  $\alpha$ -methylallyl halides, with the exception of steric effects at the  $\alpha$ -carbon atom, are equally valid here.

(viii) The  $S_N2/S_N2'$  Rate Ratios of the Isomers

The large difference in the  $\frac{k_2(S_N2)}{k_2(S_N2')}$  ratios for the  $\alpha$ - and  $\gamma$ -methylallyl halides reflects the differentiating effects of steric hindrance to nucleophilic attack and hyperconjugative stabilisation of the transition state, of an  $\alpha$ -methyl substituent compared with a  $\gamma$ -methyl substituent, on the rates of  $S_N2$  reactions. The rates of the  $S_N2'$  reactions of both isomers are of course, similar,

$\frac{k_2^{\alpha\text{-Br(A)}}}{k_2^{\gamma\text{-Br(A)}}} = 3.0, \quad \frac{k_2^{\alpha\text{-Cl(AN)}}}{k_2^{\gamma\text{-Cl(AN)}}} = 2.4$  being determined by the small difference in initial-state free energies.<sup>18,53</sup>

These ratios stress the fact that the  $S_N2'$  mechanism cannot compete with the  $S_N2$  in poorly activated and hindered substrates (see Chapter I), when the nucleophile is an anion of moderate size, and that fairly vigorous reaction conditions are necessary to achieve a reasonable rate of reaction by the mechanism, in probably the only reaction type allowing unambiguous study of this substrate group (in "Group B" type reactions), i.e., isomeric rearrangement reactions in dipolar aprotic solvents. (See page 33 ).

The absolute rate of reaction by the  $S_N2'$  mechanism, i.e., of nucleophilic attack at  $\pi$ -bonded carbon, may be compared with that by the  $S_N2$  mechanism at unhindered saturated carbon using analogues from two reaction types - those of allylic and aliphatic compounds. The relative merits of possible reference compounds is debatable, but as the relevant data on the saturated compounds and the unsubstituted allylic compounds is incomplete, it is probably sufficient to note that the vinyl group increases the reactivity of an unsubstituted allyl halide by a factor of at least 14 above that for the alkyl analogue.<sup>92b</sup> As a  $\gamma$ -methyl substituent in an allyl halide increases the reactivity by a factor of about 3 and an  $\alpha$ -methyl substituent decreases it by a factor of about 30,<sup>92b</sup> the rate of  $S_N2$  attack on saturated reference compounds such as the *n*-propyl halides and on the unsubstituted allyl halides would be greater by factors of  $2-6 \times 10^2$  and  $3-8 \times 10^3$  than

that of  $S_N2'$  attack. Therefore any of these reference compounds show that the reactivity of halide anions towards saturated carbon is much greater than that towards vinylic (or  $\pi$ -bonded) carbon.

(ix) Halide Ion Nucleophilicity and Transition State Character

Although the bromide ion in acetone is more effective in promoting the  $S_N2'$  mechanism than the chloride ion in acetonitrile, no information about the nucleophilicity order of halide ions, for reaction by the  $S_N2'$  mechanism with this type of substrate in dipolar aprotic solvents, can be obtained from the present project and the work of England and Hughes. As mentioned previously, virtually nothing is known about the comparative reactivity of various anions towards vinylic carbon for  $S_N2'$  reactions of any substrate type.<sup>54,77</sup>

The transition state for these isomeric rearrangement reactions is unlikely to have appreciable carbonium ion character because the substrates are poorly activated and the solvents although polar, are poor anion solvators, (see page 36 ), so that the driving forces for bond heterolysis are not great.

The isomeric bromides, which contain the better leaving group,<sup>54,77,100a</sup> could be expected to show greater carbonium ion character in the transition state than the isomeric chlorides, while the latter should have greater initial polarisation of the double bond due to the greater electronegativity of chlorine. However, the more polar solvent, acetonitrile, should favour a more advanced heterolysis of the carbon-chlorine bond in comparison with acetone.

(x) The Relative Efficiency of Anionic and Neutral Nucleophiles

A noteworthy comparison is that of the relative rates of the  $S_N2$  and  $S_N2'$  reactions of  $\alpha$ -methylallyl chloride with chloride ions in acetonitrile, and of  $\alpha$ -methylallyl bromide with bromide ions in acetone, with those of  $\alpha$ -methylallyl chloride with trimethylamine in acetone. <sup>81b</sup>

TABLE LXVII

Reaction	Solvent	Mechanism	$k_2 (M^{-1} \text{sec.}^{-1})$ (25°C)	$\frac{k_2(S_N2)}{k_2(S_N2')}$
$\alpha$ -MAC/ $Cl^-$	MeCN	$S_N2$	$2.87 \times 10^{-6}$	216
"	"	$S_N2'$	$1.33 \times 10^{-8}$	
$\alpha$ -MABr/ $Br^-$	Me <sub>2</sub> CO	$S_N2$	$8.79 \times 10^{-4}$	59
"	"	$S_N2'$	$1.49 \times 10^{-5}$	
$\alpha$ -MAC/Me <sub>3</sub> N	Me <sub>2</sub> CO	$S_N2$	$8.38 \times 10^{-7}$	0.51
"	"	$S_N2'$	$1.65 \times 10^{-6}$	
$\alpha$ -MAC/ $Cl^-$	Me <sub>2</sub> CO	$S_N2$	$2.30 \times 10^{-7}$	150*
"	"	$S_N2' *$	-	

Allowing for a degree of dissociation for lithium chloride of 0.013 at 25°C, the absolute value of  $k_2$  for the exchange reaction in acetone is  $1.77 \times 10^{-5} M^{-1} \text{sec.}^{-1}$ , so that the reaction with trimethylamine is slower by a factor of about 20 than the exchange reaction. Assuming an  $S_N2/S_N2'$  rate ratio of 150 for acetone, the  $S_N2'$  reaction of the amine may be seen to be about 300 times more effective than that of the

chloride ion in competing with the  $S_N2$  reaction and about 120 times more effective than that of the bromide ion.

This comparison clearly shows the less discriminating nature of uncharged nucleophiles such as amines, which has been discussed in Chapter I.

A comparison of the activation parameters for the  $S_N2$  and  $S_N2'$  reactions with trimethylamine in acetone, with those for the  $S_N2$  and  $S_N2'$  reactions with halide ions in acetone and acetonitrile, is of interest.  $\Delta H^\ddagger$  is 12.8 and 13.9 kcal.mole<sup>-1</sup> for the  $S_N2$  and  $S_N2'$  reactions respectively, while  $\Delta S^\ddagger$  is -45 and -38 cal.deg.<sup>-1</sup>mole<sup>-1</sup> respectively.

Comparison with Table LXV shows that the difference in the enthalpy of activation for the two mechanisms is much smaller for the Group C reaction (see Table II), while the difference in the entropy of activation is much greater - so much so, that the enthalpy of activation, which favours a faster  $S_N2$  reaction, is outweighed by the more favourable entropy of activation for the  $S_N2'$  reaction, resulting in a faster rate of reaction by the  $S_N2'$  mechanism than by the  $S_N2$ .

The smaller difference in activation enthalpies may reflect the absence of electrostatic repulsion between entering and leaving groups in the cis transition state of the  $S_N2'$  reaction and the absence of electrostatic assistance to leaving group departure in the  $S_N2$  transition state. Steric hindrance to  $S_N2$  attack, due to the bulk of the amine nucleophile, may also be a levelling factor.

The more favourable entropy of activation for the  $S_N2'$  reaction, which is also observed for the  $S_N2'$  reaction of 1,1-dimethylallyl

chloride with thiourea in acetone, by comparison with the value for the  $S_N2$  reaction of the isomeric 3,3-dimethylallyl chloride in the same reaction medium,<sup>41</sup> may be indicative of a self-stabilised transition state requiring less solvent stabilisation than the  $S_N2$  transition state, rather than of greater charge dispersal in the  $S_N2'$  transition state requiring less solvent stabilisation.

The difference in  $\Delta S^\ddagger$  described above does not appear to extend to the protic solvent methanol, as the  $\Delta S^\ddagger$  values for the  $S_N2$  and  $S_N2'$  reactions of the various allylic halides reacting with thiourea in methanol, studied by Bordwell and co-workers,<sup>100a</sup> are in close agreement. In the better ion-solvating protic solvent of higher dielectric constant, the degree of ordering of solvent molecules by a polar transition state should be smaller and this differentiating effect should be reduced.

#### (xi) The Activation Parameters

A comparison of the activation parameters for the reactions of the allylic bromides in acetone and the allylic chlorides in acetonitrile (see Table LXV) shows that the enthalpies of activation for the latter reactions are approximately 5 kcal.mole<sup>-1</sup> higher than those for the corresponding reactions of the bromides. For both systems the activation enthalpies for the  $S_N2$  reactions of the isomers differ by about 2 kcal.mole<sup>-1</sup>, while those for the  $S_N2$  and  $S_N2'$  reactions of the  $\alpha$ -isomer differ by about 3 kcal.mole<sup>-1</sup>.

The enthalpy of activation for the exchange reaction of  $\alpha$ -methylallyl chloride in acetonitrile is only 1 kcal.mole<sup>-1</sup> higher than the value for

the reaction in acetone, but that for the exchange reaction of the  $\gamma$ -isomer is 3 kcal.mole<sup>-1</sup> higher in acetonitrile than in acetone.

The  $\log_{10}A$  values (or the  $\Delta S^\ddagger$  values) for each of the systems - the methylallyl bromides in acetone and the methylallyl chlorides in acetonitrile - are closely similar, with the value for the  $S_N2$  reaction of the  $\gamma$ -isomer being the greatest and that for the  $S_N2$  reaction of the  $\alpha$ -isomer being the smallest. The value for the  $S_N2'$  reaction lies in between, which means that the formation of the three transition states involves a similar loss of entropy, which is least for the  $S_N2$  reaction of the  $\gamma$ -isomer and closely similar for both  $S_N2$  and  $S_N2'$  types of transition state.

The values for the methylallyl bromide system are lower in magnitude than those for the methylallyl chloride system and show a greater spread.

The somewhat lower values for the  $S_N2$  and  $S_N2'$  reactions of the  $\alpha$ -methylallyl halides may be indicative of steric restriction of rotational freedom in the transition state for the former reaction, caused by the  $\alpha$ -methyl group and loss of rotational freedom caused by partial double-bond formation in the transition state for the latter.<sup>3</sup> The greater spread for the bromides may be indicative of greater interaction. However, as these trends are of the order of the experimental error of the determinations, no definite significance can be attributed to them.

The close similarity of the  $\Delta S^\ddagger$  values for the two types of transition state is in accord with the work of Bordwell and co-workers (discussed on page 27), who found that restriction of the possible conformations of a system to those suitable for  $S_N2'$  attack had little effect on the activation parameters for  $S_N2$  attack.<sup>100,100a</sup>

Differences in rate in the two reaction systems are therefore due almost entirely to differences in activation enthalpies.

The slow rate of the  $S_N2'$  reactions is consequently due to a higher enthalpy of activation than that for the  $S_N2$  reactions, the difference being about 3 kcal.mole<sup>-1</sup> for the  $\alpha$ -methylallyl halides and about 5 kcal.mole<sup>-1</sup> for the  $\gamma$ -methylallyl halides. This can no doubt be largely attributed to nucleophile repulsion by the  $\pi$  electrons of the double bond and electrostatic repulsion between the partial negative charges on the entering and leaving groups in the cis transition state. (See page 20).

The enthalpy of activation difference for the  $S_N2$  reactions reflects the effect of a methyl substituent in the  $\gamma$ -position compared with one in the  $\alpha$ -position. (See Section iii).

#### (xii) Deviations of the Methylallyl Chlorides

The activation parameters for the  $S_N2$  reactions of the isomeric chlorides in acetone and acetonitrile show marked differences. The activation enthalpies for the isomers differ by 4.1 kcal.mole<sup>-1</sup> in acetone compared with only 2.0 kcal.mole<sup>-1</sup> in acetonitrile, while the  $\log_{10} A$  values differ by 0.91 in acetone compared with 0.46 in

acetonitrile. The value of 0.9 is similar to that for the isomeric bromides in acetone, but it is in the reverse order to that observed for the other systems. Therefore a low value for the activation enthalpy of the  $S_N2$  reaction of the  $\gamma$ -isomer in acetone is counteracted by a very low value for the entropy of activation, resulting in a rate ratio for the isomers similar to that observed in acetonitrile.

England attributed the low  $\log_{10} A$  value for the  $\gamma$ -isomer in acetone to the requirements of a linear system for hyperconjugative stabilisation of the transition state and considered this stabilisation to be greater for  $\gamma$ -methylallyl chloride than for  $\gamma$ -methylallyl bromide due to the greater electronegativity of chlorine.<sup>120</sup> The absence of this behaviour in the results for the  $S_N2$  reactions of the isomeric chlorides in acetonitrile casts some doubt on this explanation, as such an effect would hardly show great solvent sensitivity, especially to a change only from one member of a solvent class to another. No plausible explanation is readily available.

#### (xiii) Correction of $\log_{10} A$ Values for Ion-Pairing

The  $\log_{10} A$  values for the reactions in acetone are much lower, especially those for the isomeric chlorides, than those for the corresponding reactions in acetonitrile. This may be shown to be largely due to distortion of the absolute values for the rate constants of the reactions, caused by ion-pairing of the nucleophilic reagents. If the rate constants for the reactions in acetone are corrected for ion-pairing, by adjusting their values to what they would

be if the degree of dissociation of the nucleophilic reagent was the same as that for  $\text{Et}_4\text{NCl}$  in acetonitrile at the same concentration, they may then be used to calculate  $\log_{10} A$  values suitable for comparison with those for the reactions in acetonitrile. (See page 159 for the method used).

The corrected values and those for acetonitrile are shown in Table LXVIII.

TABLE LXVIII

Compound	$\alpha$ -methylallyl chloride	$\gamma$ -methylallyl chloride	$\alpha$ -methylallyl chloride
Mechanism/Solvent	$\text{S}_{\text{N}}2/\text{MeCN}$	$\text{S}_{\text{N}}2/\text{MeCN}$	$\text{S}_{\text{N}}2'/\text{MeCN}$
$\log_{10} A$	10.22	10.68	10.41
Compound	$\alpha$ -methylallyl bromide	$\gamma$ -methylallyl bromide	$\alpha$ -methylallyl bromide
Mechanism/Solvent	$\text{S}_{\text{N}}2/\text{Me}_2\text{CO}$	$\text{S}_{\text{N}}2/\text{Me}_2\text{CO}$	$\text{S}_{\text{N}}2'/\text{Me}_2\text{CO}$
$\log_{10} A$	9.88	10.76	10.23
Compound	$\alpha$ -methylallyl chloride	$\gamma$ -methylallyl chloride	
Mechanism/Solvent	$\text{S}_{\text{N}}2/\text{Me}_2\text{CO}$	$\text{S}_{\text{N}}2/\text{Me}_2\text{CO}$	
$\log_{10} A$	10.22	9.31	

Bearing in mind the assumptions and approximations inherent in these corrections (see page 273), the values of  $\log_{10} A$  are seen to be closely similar for the  $S_N2$  and  $S_N2'$  reactions of the  $\alpha$ -methylallyl halides, and also for the  $S_N2$  reactions of  $\gamma$ -methylallyl chloride and bromide in acetonitrile and acetone respectively. The value for the  $S_N2$  reaction of  $\gamma$ -methylallyl chloride in acetone deviates from the pattern established by the other reactions, by 1.4 units.

The variables in the reactions compared above, namely, different solvent members of the same solvent class and different nucleophiles and leaving groups, which are anions of closely similar type, would not be expected to cause large differences in the entropies of activation and hence  $\log_{10} A$ .

The activation parameters for the  $S_N2'$  reactions of the  $\gamma$ -methylallyl halides are of course closely similar to those for the  $\alpha$ -methylallyl halides.<sup>18</sup> (See page 219 ).

The agreement of the corrected values suggests that the ion-pairing corrections may be reasonably accurate, and this, together with the lower values for  $\Delta H^\ddagger$  in acetone, suggests that the direction of the effect of the change of solvent on the  $S_N2$  reactions of the isomeric chlorides, deduced in Sections iv and v, is valid.

It is noteworthy that the value of  $\log_{10} A$  for the  $S_N2$  reaction of allyl chloride in dimethyl sulphoxide is 10.32.

(xiv) Dissociation of Nucleophilic Reagents

The large differences between the degree of dissociation of  $\text{Et}_4\text{NCl}$  in acetonitrile and lithium chloride and bromide in acetone at the same concentration is noteworthy. The dissociation constants are  $2.88 \times 10^{-2}$ ,  $3.3 \times 10^{-6}$  and  $2.19 \times 10^{-4}$  at  $25^\circ\text{C}$ ,<sup>131,178</sup> which means that tetraethylammonium chloride is approximately 58 times more dissociated than lithium chloride and 7 times more than lithium bromide in solutions of similar concentration. As both the small halide ions are poorly solvated in dipolar aprotic solvents,<sup>24,182</sup> this must be largely due to differences in cation stability.

The tetraethylammonium cation is large and its positive charge is well shielded by the ethyl groups, while the lithium cation is very small with no shielding groups, (radius  $\sim 4.0\text{\AA}$ , cf. radius  $\sim 0.60\text{\AA}$ ).<sup>40</sup> Therefore, the interaction of the latter ion with an anion would be expected to be much greater than that for the former and the strength of the interaction should increase with decrease in anion size and decreasing polarity of the solvent.<sup>144,183,184</sup> The following examples of dissociation constants for some tetra-alkyl ammonium salts in acetone and acetonitrile and lithium salts in acetone illustrate these points.

$\text{Bu}_4\text{NCl}$  has a dissociation constant of  $16.6 \times 10^{-4}$  in acetone compared with  $0.033 \times 10^{-4}$  for lithium chloride, while  $\text{Bu}_4\text{NBr}$  has a dissociation constant of  $32.9 \times 10^{-4}$  in the same solvent compared with  $2.19 \times 10^{-4}$  for lithium bromide.<sup>119b,178,186</sup> In acetonitrile,  $\text{Bu}_4\text{NBr}$  has a dissociation constant of  $9.4 \times 10^{-2}$ , while in the same solvent  $\text{Et}_4\text{NBr}$  has one of  $6.9 \times 10^{-2}$ .<sup>153</sup>

The solvating power of dipolar aprotic solvents is high for cations, especially with oxygen donors such as dimethylformamide and dimethyl sulphoxide and the order  $\text{Me}_2\text{SO}, \text{Me}_2\text{Nac} > \text{Me}_2\text{NCHO}, \text{H}_2\text{O} > \text{Me}_2\text{CO} \gg \text{MeCN}, \text{MeNO}_2$  has been quoted by Parker.<sup>25</sup> Therefore acetone is a better donor than acetonitrile, which is poor because it has an unfavourable donor atom. Lithium salts are reported to form solvates with acetone and dimethylsulphoxide.<sup>25</sup>

Therefore, although the cation solvating-power of acetone is fairly good and the cation-solvent interaction is strong, the degree of dissociation of lithium salts is low, so that cation-anion interaction must still be sufficient to prevent ion-dipole stabilisation, and shielding of the ions by solvent molecules, from dissociating an ion-pair.

#### (xv) The Nucleophilicity of Ion-Pairs

The nucleophilic reactivity of ion-pairs is usually considered negligible compared with that of the free ion, when corrections are made to rate constants for incomplete dissociation of the nucleophilic reagent.<sup>13,21,37,143</sup> As mentioned before, (see page 160), Fava and co-workers have criticised this assumption, especially for reactions in which the transition state has considerable carbonium ion character.<sup>48</sup>

Hughes, Ingold and Parker have also commented on this assumption for lithium halides in acetone,<sup>189</sup> while Lichtin and Rao have examined ion-pairing in liquid sulphur dioxide and shown the reactivity of ion-pairs to be dependent upon cation size.<sup>144</sup>

It has been shown in Chapters III and IV, that the rate constants for the  $S_N2$  and  $S_N2'$  reactions of the isomeric chlorides with  $Et_4NCl$  in acetonitrile are almost independent of salt concentration, over a range of concentrations large enough for a salt effect of the magnitude expected to be readily observed. However, this low sensitivity to  $Et_4NCl$  concentration is not attributed to a high degree of carbonium ion character in the transition states for the reactions, but rather to the high dissociation constant for  $Et_4NCl$  and to a low interaction energy in the  $Et_4NCl$  ion-pair, which does not reduce the nucleophilicity of the chloride ion to a negligible value compared with that of the "free" ion.<sup>144,145</sup> The reactions of the isomeric bromides in acetone, the transition states for which should resemble fairly closely those for the isomeric chlorides in acetonitrile, show very marked salt effects,<sup>79</sup> which are probably due to a high interaction energy in the lithium bromide ion-pair which markedly reduces the nucleophilicity of the bromide ion compared with that of the "free" ion. Also, because the degree of dissociation of  $Et_4NCl$  is much greater than that for lithium bromide, the expected salt effect for a given change in the concentration of the nucleophilic reagent is larger for the latter.

Theoretically, the reactivity of ion-pairs can be determined to some extent from the calculated and observed dependence of the rate constant on the concentration of the nucleophilic reagent.<sup>142,143,144</sup> These calculations involve the use of the Acree equation, the Ostwald equation, equilibrium constants from conductivity measurements and the Debye-Hückel equation with various values for  $a^0$ . However, as the

calculated dependence is itself dependent on the accuracy of the value for the dissociation constant (and few dissociation constant determinations are made at temperatures other than 25°C) and on the accuracy of activity coefficient approximations, such estimations need treating with caution.<sup>144,187</sup>

Attempts to correct rate constants for ion-pairing of the nucleophilic reagent tend to indicate a low reactivity for the ion-pair, in reactions in which a lithium halide in a dipolar aprotic solvent is the nucleophilic reagent.<sup>13,142,143,188</sup> For example, Evans and Sugden corrected their data for the exchange reactions of *n*-butyl and *sec.*-octyl bromide with lithium bromide in acetone for ion-pairing and obtained reasonably constant rate constants, compared with the strongly salt-dependent values obtained from the raw data, and a low value for ion-pair reactivity.<sup>143</sup> It would be reasonable to expect the small lithium cation to form less reactive ion-pairs than larger cations.

It is interesting to compare their corrected rate constants for the *sec.*-octyl bromide reaction at 65.5°C with those for the  $S_N2'$  reaction of  $\alpha$ -methylallyl bromide at 60.2°C, corrected using the same values for the degree of dissociation of lithium bromide in acetone at the various salt concentrations. Values for the degree of dissociation were interpolated from a plot of  $(\alpha)$  versus  $c$ . (The effect of the temperature difference of the two studies on  $(\alpha)$  is neglected). The results are compared in the Table below.

TABLE LXIX

$(\alpha)^A$	$10^3 k_2^A$ ( $M^{-1} \text{sec.}^{-1}$ )	$(\alpha)^B$	$10^4 k_2^B$ ( $M^{-1} \text{sec.}^{-1}$ )
0.198	13.3	0.186	34.2
0.161	9.5	0.143	38.3
0.130	10.1	0.120	42.0
0.106	10.7	0.104	43.1
0.082	10.1	0.095	49.2
0.077	10.7	0.087	48.0
0.057	13.4	0.075	51.3
		0.069	58.6

$(\alpha)$  = the degree of dissociation of lithium bromide

A labels data for the sec.-octyl bromide reaction

B labels data for the  $\alpha$ -methylallyl bromide reaction

The corrections give reasonably constant values for A but tend to overcompensate for B, which may imply that ion-pairing of the nucleophilic reagent has less effect on the  $S_N2^1$  reaction than on the  $S_N2$  reaction. Far more data would be required in order to refute or substantiate the above trend.

(xvi) Criticism of England and Hughes' Demonstration of the  $S_N2'$  Mechanism

The demonstration by England and Hughes,<sup>79</sup> of the operation of the  $S_N2'$  mechanism in the rearrangement reaction of  $\alpha$ -methylallyl bromide with bromide ions in acetone has been criticised by de Wolfe and Young,<sup>190</sup> on the grounds that neither a lithium ion catalysed  $S_N1'$  or  $S_Ni'$  mechanism was excluded. Both of these possible mechanisms would be more favoured by the small lithium cation, than by other larger cations such as tetra-alkylammonium,<sup>40</sup> as shown by the work of Winstein and co-workers on specific salt-promoted ionisation in a number of solvents.<sup>42b,154a,b</sup>

England and Hughes considered the magnitude of the effect of lithium bromide on the rate of rearrangement to be too large for it to be due to a salt effect on an  $S_N1'$  mechanism, as 0.04M lithium bromide caused a forty-fold increase in the rate of rearrangement. The decrease in the second-order rate constant with increasing salt concentration, which they also observed, was consistent with the salt effects observed for  $S_N2$  reactions and attributed to incomplete dissociation of the nucleophilic reagent.

The close similarity between the reactions of the isomeric bromides in acetone and those of the isomeric chlorides in acetonitrile, for which an  $S_N1'$  mechanism has been ruled out, is further evidence against the  $S_N1'$  mechanism.

The possibility of a lithium ion catalysed  $S_N1'$  mechanism, as a special case of the  $S_N2'$ , and involving nucleophilic attack by the bromide ion of an ion-pair and electrophilic assistance to leaving group departure by the lithium ion, cannot be refuted and such a path may contribute to the rearrangement mechanism. However, this mode of nucleophilic attack merely entails polarisation and hence activation of the double bond by interaction of the halogen substituent with the lithium cation and needs no differentiation from other types of activation facilitating operation of the  $S_N2'$  mechanism. (See page 33).

There is a possibility that the greater effectiveness of the  $S_N2'$  reaction of  $\alpha$ -methylallyl bromide in acetone in competing with the  $S_N2$ , compared with that of  $\alpha$ -methylallyl chloride in acetonitrile, is partially due to lithium ion facilitation of the former reaction.

(xvii) Elimination Reactions of Allylic Halides

The reaction of  $\alpha$ -methylallyl chloride with  $Et_4NCl$  in acetonitrile constitutes probably the first system in which the operation of concurrent  $S_N2$ ,  $S_N2'$  and E2 mechanisms can be observed and the rate constants for all three measured.

The first two mechanisms are considered to be established for this system and the latter best explains the data for the  $Et_4NCl$  catalysed elimination reaction. The rate constant for the elimination reaction is not known with great accuracy and may be distorted to some extent (see pages 134, 207), but the error should be no greater than 30%. ( $\pm 10\%$  and  $\pm 20\%$  depending on the behaviour of the surface-catalysed

reaction). Therefore, the relative reactivity of chloride ions in acetonitrile towards saturated carbon, vinylic carbon and hydrogen can be roughly compared and the rate constant ratios are given below.

TABLE LXX

$$\frac{k_2(S_N2)}{k_2(S_N2')} = 67^{(100^\circ\text{C})} \quad \frac{k_2(S_N2')}{k_2(E2)} \sim 12^{(96^\circ\text{C})} \quad \frac{k_2(S_N2)}{k_2(E2)} \sim 875^{(96^\circ\text{C})}$$

The chloride ion in acetonitrile is therefore far more reactive towards saturated carbon and even vinylic carbon, than towards hydrogen, with this substrate.

The value above for the  $\frac{k_2(S_N2)}{k_2(E2)}$  ratio can be compared with that of approximately 10, obtained by Vernon for the reaction of ethoxide ions in ethanol with the same substrate at  $44.6^\circ\text{C}$ .<sup>92b</sup> No rearranged product was obtained, so that  $\frac{k_2(S_N2)}{k_2(S_N2')} \geq 100$  and therefore

$$\frac{k_2(S_N2')}{k_2(E2)} \leq \frac{1}{10}.$$

The ethoxide ion in ethanol is therefore more reactive towards hydrogen than towards vinylic carbon in contrast to the chloride ion in acetonitrile. Unfortunately both elimination reactions have been studied at only one temperature, so that the ratios cannot be compared at a common temperature and are subject to the limitations of this. However, it could be deduced from the v.p.c. analysis data that the  $\frac{k_2(S_N2')}{k_2(E2)}$  ratio increases as the temperature decreases, so that at  $44.6^\circ\text{C}$  the ratio for

the chloride ion catalysed reactions in acetonitrile would be even larger.

Some indication of the reluctance of  $\gamma$ -methyl substituted allylic halides to undergo 1:4 elimination may be obtained from the work of Nesmeyanov and co-workers,<sup>112</sup> who obtained only a small amount of elimination product from the reaction of  $\text{Me}_2\text{C}=\text{CH}-\text{CCl}_3$  with "hydroxide" ions in methanol, the major product being that of the  $\text{S}_{\text{N}}2'$  reaction. The  $-\text{CCl}_3$  group in this compound should increase the acidity of the methyl-group hydrogens by inductively promoting inductive and hyperconjugative electron release from the methyl group.

No elimination of hydrogen bromide from  $\alpha$ -methylallyl bromide was observed by England in the reaction of this substrate with lithium bromide in acetone.<sup>79</sup> To check for elimination, he took reaction mixtures for the rearrangement reaction which had attained equilibrium, separated the volatile components by evaporating them from the inactive lithium bromide at low temperature and pressure and collected them at  $-80^\circ\text{C}$ . He then reacted them with radioactive lithium bromide at  $-80^\circ\text{C}$ . (See page 43 ). No exchange was observed, within the limits of experimental error.

There appear to be three possible reasons for the absence of a concurrent elimination reaction accompanying the  $\text{S}_{\text{N}}2'$  reaction of  $\alpha$ -methylallyl bromide. (a) The bromide ion is a poorer hydrogen nucleophile than the chloride ion in comparison to its reactivity towards vinylic carbon, (b) the rate of addition of hydrogen bromide to butadiene is faster, compared with the rate of elimination of hydrogen

bromide from  $\alpha$ -methylallyl bromide, than that of hydrogen chloride to butadiene compared with the rate of elimination of hydrogen chloride from  $\alpha$ -methylallyl chloride and it is less retarded by bromide ions than the latter is by chloride ions, so that back addition of the elimination products was essentially complete when the rearrangement reaction was near equilibrium - this really implies fast back addition and slow elimination, and (c) the evaporation procedure for removal of the volatile components of a reaction mixture from the lithium bromide left the hydrogen bromide behind as the salt  $\text{LiHBr}_2$ .

No conclusions derived from experimental data can be drawn about possibility (a).

The behaviour of hydrogen halides in acetone and acetonitrile is complex and has been discussed in various papers by Janz and Danyluk, and Kolthoff and co-workers.<sup>124,170</sup> The general conclusion is that they are weak electrolytes, but the conductance of freshly prepared solutions changes as the solutions age, attributed to the formation of various complexes, and in the case of acetone to acid-catalysed condensation of the solvent. The dissociation constants for the acids in acetonitrile quoted below were determined using freshly prepared solutions.

Hydrogen bromide is a stronger acid than hydrogen chloride in dipolar aprotic solvents. For example, the  $\text{pK}_a$  value for hydrogen bromide is 5.5 in acetonitrile compared with that of 8.9 for hydrogen chloride.<sup>124,171</sup> Unfortunately the dissociation constants for the hydrogen halides in acetone have not been measured due to the instability of these compounds in this solvent with which they react,<sup>170</sup> therefore

the strength of hydrogen bromide in acetone and hydrogen chloride in acetonitrile cannot be compared. However, the rate of addition of hydrogen bromide to isobutylene in nitromethane is faster than that of hydrogen chloride and less retarded by  $\text{Et}_4\text{NBr}$  than the latter is by  $\text{Et}_4\text{NCl}$ ,<sup>134,135,193</sup> so that possibility (b) is feasible. It is also possible that lithium bromide, which is quite highly associated in acetone,<sup>178</sup> is less effective in forming dihalide ions than a tetraalkylammonium salt and therefore less effective at preventing back addition.<sup>193</sup>

It is unlikely that  $\text{LiHBr}_2$  would be stable at the low pressures used to evaporate the volatile components of the rearrangement reaction mixture, because the lithium cation is so small, whereas the stability of the complex halide ions increases with the size of the cation and is dependent on this being large and organic.<sup>194</sup>

No conclusions regarding the above possibilities may be drawn from the existing data.

#### (xviii) General Conclusion

The two complete systems which are involved in the greater part of the discussion above, namely, that comprised of the bromide ion catalysed rearrangement and isotope exchange reactions of the methylallyl bromides in acetone and that comprised of the chloride ion catalysed rearrangement and isotope exchange reactions of the methylallyl chlorides in acetonitrile, are similar in behaviour. Therefore, the results for the system studied in this project have confirmed the expectation that

the variables involved between the two systems - different solvents which are members of the same solvent class and different nucleophile and leaving group, which are anions of closely similar type - would not have a large differentiating effect on the mechanisms operating or on their relative importance.

The more detailed investigation which has been possible with the more stable isomeric chlorides in acetonitrile and with present day methods of analysis, such as the one employed - gas chromatography - which enabled the whole range of isomer ratios to be accurately measured, has confirmed the pattern of behaviour for  $S_N2'$  reactions of this substrate type with small anionic nucleophiles in dipolar aprotic solvents, which was indicated by the results of England and Hughes for the isomeric bromides. It has also extended the data on these reactions, which involve nucleophilic attack on a substrate poorly activated for attack on  $\pi$ -bonded carbon and moderately hindered or unhindered for attack on saturated carbon.

Consequently, this project has established the slow rate of nucleophilic attack at poorly activated vinylic carbon (as defined in Chapter I) in isomeric rearrangement reactions of allylic halides compared with the rate of attack at saturated carbon, either moderately hindered or unhindered in allylic compounds and unhindered in aliphatic compounds. It has also provided data for another quantitative comparison of relative reactivities involving a Group B reaction.

As well as being able to compare the rates of nucleophilic attack at the different types of carbon for these systems, a deviation

in the behaviour of the system studied in this project from that of the isomeric bromides, consisting of a minor concurrent elimination reaction accompanying the rearrangement reaction of the  $\alpha$ -isomer, has enabled the comparison to be extended to the rate of nucleophilic attack on hydrogen. Therefore the tentative deduction possible from the behaviour of the system comprised of the isomeric bromides, namely, that halide ions are very weak nucleophiles with respect to attack at hydrogen in the  $\alpha$ -methylallyl halides, gains confirmation and a quantitative comparison with nucleophilicity towards carbon from the data for  $\alpha$ -methylallyl chloride in acetonitrile.

The necessity for a solvent of low nucleophilicity, high stability and low water content for studies of Group B  $S_N2'$  reactions in dipolar aprotic solvents has been shown by the results for the reactions of allylic chlorides in dimethyl sulphoxide and dimethylformamide obtained in the present project, and by those obtained by England and Hughes for the reactions of  $\alpha$ -methylallyl chloride in acetone.<sup>120</sup> It is also significant that no peak of appreciable size attributable to butadiene was observed on the chromatograms for v.p.c. analyses carried out during the investigation of dimethyl sulphoxide and dimethylformamide in the early stages of this project. As hydrogen chloride is reported to be a strong acid in both of these solvents,<sup>192,216,220</sup> back addition of the products of an elimination reaction would not be inhibited by dihalide ion formation.

Both the  $Et_4NCl$ -acetonitrile reaction medium and acetonitrile itself appear to be quite stable and non-destructive towards substrates over fairly prolonged periods at fairly high reaction temperatures.

Therefore, this medium, and mediums consisting of other tetraalkylammonium salts in acetonitrile, may be of considerable value for studying reactions requiring the above conditions, one such type being, of course,  $S_N2'$  reactions classified as Groups A and B.

It is also quite probable that acetonitrile would be a useful solvent for  $S_N2'$  reactions involving neutral nucleophiles, namely, Group C and Group D  $S_N2'$  reactions.

ADDENDA

No worthwhile speculation about the nature of the transition state for the  $\text{Et}_4\text{NCl}$  catalysed elimination reaction in terms of recent theories of transition state types in E2 reactions, which involve varying degrees of bond-making and bond-breaking in the transition state and transition states which have some of the transition state character of an  $\text{S}_{\text{N}}2$  substitution reaction,<sup>223,224</sup> is possible using the data obtained in this project.

A very recent theory advanced by Lesnini, Buckley and Noyes<sup>225</sup> to account for the  $\text{Et}_4\text{NCl}$  catalysed racemisation reaction of 5-methyl-2-cyclohexenyl chloride in acetonitrile is of considerable interest. Racemisation is postulated to involve a "sandwich" transition state in which a chloride ion on the opposite side of the ring promotes racemisation of a cis allylic chloride molecule. The kinetics are second-order, but the allylic rearrangement occurs by migration of the original chlorine substituent rather than by displacing this substituent. A significant contribution from this mechanism to the isomeric allylic rearrangement reactions of poorly activated substrates is an interesting possibility.

CHAPTER VIPREPARATION AND PURIFICATION OF SOLVENTSAND REAGENTS. ANALYTICAL REAGENTSI Solvents(1) Acetonitrile

The B.D.H. or M. & B. product was shaken with saturated potassium hydroxide solution (25 ml./litre for 15 seconds), dried over anhydrous sodium carbonate (100 gm./litre) and distilled through a 4 foot vacuum-jacketed column packed with glass helices.<sup>107,124,197</sup> The still head was of conventional design. All joints were greased with silicone grease. Fractions were analysed by gas chromatography for purity and the fraction with b.p. = 81.4-81.5°C at 760 mm. was collected for kinetic use. (lit. b.p. = 81.6°C/760mm.)<sup>196</sup>

This fraction was then dried by distillation from phosphorus pentoxide (5-10 gm./litre) through a 30-inch long vacuum-jacketed Vigreux column, at least three times in succession.<sup>107,197</sup>

All the apparatus for these distillations was carefully dried each time, by baking it in an oven and cooling it in a desiccator or stream of dry nitrogen where possible. The column was dried in a stream of dry nitrogen and then attached to a flask containing phosphorus pentoxide, to remove any remaining traces of water.

The distillate was finally collected in 500 ml. flasks, which were closed with greased stoppers (silicone grease) and stored, shielded from light, in the dry-box. b.p. = 81.3-81.4°C/760mm.,  $n_D^{25} = 1.3410$  (lit. b.p. = 81.6°C/760mm., lit  $n_D^{25} = 1.3416$ )<sup>196</sup>

A v.p.c. check of the purity of the final product was carried out.

This drying procedure is reported to give a product containing less than 36 mgm. of water per litre<sup>107,197</sup> but, as a check on this, kinetic runs using solvent which had been dried by three and five successive distillations from phosphorus pentoxide were carried out. These gave identical rate constants within experimental error, (cf. Runs 26, 27, 30 and 34), indicating the two batches of solvent to be kinetically indistinguishable. This result, together with the stability of allyl chloride in the solvent, was considered to be proof that the drying procedure was satisfactory. For the effect of added water on reaction rate, see Table XXX.

#### (ii) Dimethyl Sulphoxide

The B.D.H. product was dried using two different methods.

(a) It was passed through a column of molecular sieves ("Linde" type 4A) into a still pot and then distilled through a 4 foot column packed with glass helices, under reduced pressure in an atmosphere of nitrogen. The middle fraction was collected for kinetic use.

b.p. = 80°C/15mm., m.p. = 18.45-18.50°C (lit. b.p. = 90°C/20mm., lit. m.p. = 18.52-18.55°C)<sup>210,218</sup>  $n_D^{25} = 1.4760$  (lit.  $n_D^{25} = 1.4765$ )<sup>8</sup>

The melting-point of dimethyl sulphoxide is a good criterion of the purity and dryness of the solvent, as the molal freezing-point-depression constant is large ( $4.36^{\circ}\text{C}/\text{mole}$ )<sup>213</sup>. Murto has purified this solvent by recrystallisation and used the melting-point as a criterion of purity.<sup>23</sup>

The melting-points of batches of solvent used in this project were determined with a Beckmann freezing-point apparatus, flushed with dry nitrogen to prevent uptake of atmospheric moisture.

(b) The solvent was refluxed with calcium oxide (28gm./litre) for several hours and then distilled from it, through the 4 foot fractionating column, as described in (a) above.<sup>219</sup> m.p. =  $18.50^{\circ}\text{C}$ .

(iii) Dimethylformamide

The B.D.H. product was dried using three different methods.

(a) After preliminary drying over anhydrous sodium sulphate,<sup>142</sup> it was passed through a column of molecular sieves into a still pot and then distilled through a 4 foot column packed with glass helices, under reduced pressure in an atmosphere of nitrogen.<sup>8</sup> The middle fraction was collected for use. b.p. =  $60^{\circ}\text{C}/25\text{mm.}$ ,  $n_D^{25} = 1.4269$  (lit. b.p. =  $62^{\circ}\text{C}/25\text{mm.}$ ,  $n_D^{25} = 1.4269$ )<sup>142,196</sup>

(b) The solvent was shaken with barium oxide for several hours, decanted and then distilled as described above.<sup>220</sup>

(c) The solvent was refluxed with calcium oxide and distilled. It was then refluxed with fresh calcium oxide and fractionated as described in (a) above.

(iv) Methanol

Methanol was dried by the magnesium turnings method of Lund and Bjerrum,<sup>208</sup> and distilled. "Analar" methanol was used directly for some purposes.

(v) n-Pentane

The B.D.H. product (b.p. =  $35-37^{\circ}\text{C}$ ) was checked for interfering impurities by shaking 30 ml. with 30 ml. of distilled water and testing the aqueous layer for hydrogen and chloride ions. (lit. b.p. =  $36.0^{\circ}\text{C}$ )<sup>207</sup>

(vi) n-Hexane

The B.D.H. product (boiling range  $60-80^{\circ}\text{C}$ ) was tested as above for interfering impurities. (lit. b.p. =  $68.9^{\circ}\text{C}$ )<sup>207</sup>

## II Reagents

(1)  $\alpha$ - and  $\gamma$ -Methylallyl Chloride

A 50% mixture of the two isomers (L. Light & Co.) was dried over anhydrous potassium carbonate and distilled through a 4 foot column packed with glass helices, at reduced pressure in an atmosphere

of nitrogen. A trace of diphenylamine was added to the still pot to try to reduce rearrangement.<sup>120</sup> Ice water was pumped through the condenser and the receivers were cooled in ice water. All joints were greased with silicone grease. The apparatus had been rinsed with dilute ammonia solution, followed by water and distilled water, before being dried, to remove traces of acid. However, polymerisation of the  $\gamma$ -isomer in the still pot occurred during the collection of this isomer.

Physical constants for the pure isomers were as follows:

$\alpha$ -methylallyl chloride		$\gamma$ -methylallyl chloride	
b.p.	= 31.6-31.8°C/28mm.	b.p.	= 43.0-43.2°C/164mm.
$n_D^{25}$	= 1.4120	$n_D^{25}$	= 1.4320
(lit. b.p. = 24.2-24.6°C/178mm.)		(lit. b.p. = 43.7-44.0°C/177mm.)	
(lit. $n_D^{25}$ = 1.4120-24)		(lit. $n_D^{25}$ = 1.4326-30)	
(198, 81b, 120)		( <u>trans</u> isomer)	
		(120, 198, 81b, 199)	

The fractions were analysed by gas chromatography for isomeric purity and the presence of other impurities. Each isomer was at least 99.8% pure with respect to the presence of the other isomer and no other impurities were detected. The pure isomers were stored at 0°C.

The commercial products were not found to be as stable during fractionation as is reported by other workers.<sup>200</sup> Both isomerisation of the  $\alpha$ -isomer and polymerisation of the  $\gamma$ -isomer tended to occur in the still pot.

(ii) Allyl Chloride

B.D.H. allyl chloride was dried with anhydrous calcium chloride or potassium carbonate, filtered through dry glass wool and distilled through a 4 foot column packed with glass helices. The middle fraction was collected. b.p. =  $43.9-44.0^{\circ}\text{C}/737\text{mm.}$ ,  $n_D^{25} = 1.4103$  (lit. b.p. =  $44.7-44.8^{\circ}\text{C}/760\text{mm.}$ ,  $n_D^{25} = 1.4116$ )<sup>206</sup>

(iii) Tetraethylammonium Chloride

The B.D.H. product ( $\text{Et}_4\text{NCl} \cdot \text{H}_2\text{O}$ ) was recrystallised from acetonitrile and stored in a desiccator in the presence of anhydrous calcium chloride.

Analyses for the chlorine content of anhydrous  $\text{Et}_4\text{NCl}$  were carried out as follows: a suitable weight of  $\text{Et}_4\text{NCl}$  was placed in a small glass boat, which had previously been weighed together with a sample bottle and cap. The boat was then placed in a drying pistol and the solid was dried as described in Section VII, Chapter III. The boat and its dry contents were transferred in the dry-box to the sample bottle, which was reweighed to give the weight of anhydrous salt. The salt was then made up with distilled water to a suitable volume in a standard flask and aliquots were titrated with standard silver nitrate solution, by the potentiometric method, to determine the chloride ion concentration of the solution. e.g.

$$\text{wt. of anhydrous salt} = 0.2360 \pm 0.0002 \text{ gm.}$$

This was made up to 100 ml. of solution and 20 ml. aliquots were titrated with silver nitrate solution (0.01518N).

Theoretical titre = 18.79 ml.

Actual titre = 18.91 ml.

$$\therefore \frac{10^2 \Delta \text{ titre}}{\text{theoretical titre}} = 0.6\%$$

(iv) Tetraethylammonium Chloride Labelled with Chlorine-36

Chlorine-36 labelled  $\text{Et}_4\text{NCl}$  was prepared by neutralising a suitable volume of an aqueous solution of  $\text{HCl}^{36}$  with  $\text{Et}_4\text{NOH}$  solution and adding the weight of  $\text{Et}_4\text{NCl}$  needed to give a labelled salt of the required specific activity. The salt was isolated by evaporating off the solvent, at room temperature under reduced pressure ("Hyvac" pump), in a 250 ml. flask fitted with a splash bulb. The distillate was collected in a trap cooled in liquid air. The solid was pumped fairly dry and then dissolved up in acetonitrile, filtered and transferred to a beaker. The solvent was evaporated off by heating the beaker in a water-bath at a temperature below the boiling-point of the solvent, i.e.,  $< 81.6^\circ\text{C}$ . When nearly all the solvent had evaporated, the beaker was covered with a watch glass and transferred to a vacuum desiccator and the remaining solvent was carefully pumped off. A flask containing phosphorus pentoxide was then added to the desiccator, which was evacuated and left for the solid to dry.

The dry radioactive salt was then recrystallised from acetonitrile and analysed for chlorine content, as described for inactive

$$\text{Et}_4\text{NCl} \cdot \frac{10^2 \Delta \text{titre}}{\text{theoretical titre}} = 0.6\%$$

The normal precautions in accord with the regulations were observed in the handling of this long-lived isotope, which has a half-life of  $4.4 \times 10^5$  years.<sup>205</sup>

(v) Tetraethylammonium Perchlorate

Tetraethylammonium hydroxide (B.D.H. 25% solution) was neutralised with "Analar" perchloric acid (75% solution).

The solutions were diluted to suitable concentrations and the end-point was determined by removing drops and adding them to bromothymol blue. The neutral solution was then concentrated by boiling, cooled in ice water and the crystals of  $\text{Et}_4\text{NClO}_4$  were filtered off and washed with ice water. The solid was recrystallised twice from 90% ethanol and dried at  $60^\circ\text{C}$  and 0.04mm. in a drying pistol.<sup>107,197</sup>

(vi) Butadiene

Butadiene was prepared by "cracking" cyclohexene on a red-hot filament.<sup>201</sup>

Cyclohexene (B.D.H.) was distilled and the fraction with b.p. =  $82.8-83.7/760\text{mm.}$  was collected.<sup>201</sup> (lit. b.p. =  $83^\circ\text{C}$ )<sup>207</sup>

The "cracking" apparatus and procedure used were identical to those described in reference 201, except for minor modifications. (See Fig. 11 ).

# BUTADIENE

# GENERATOR

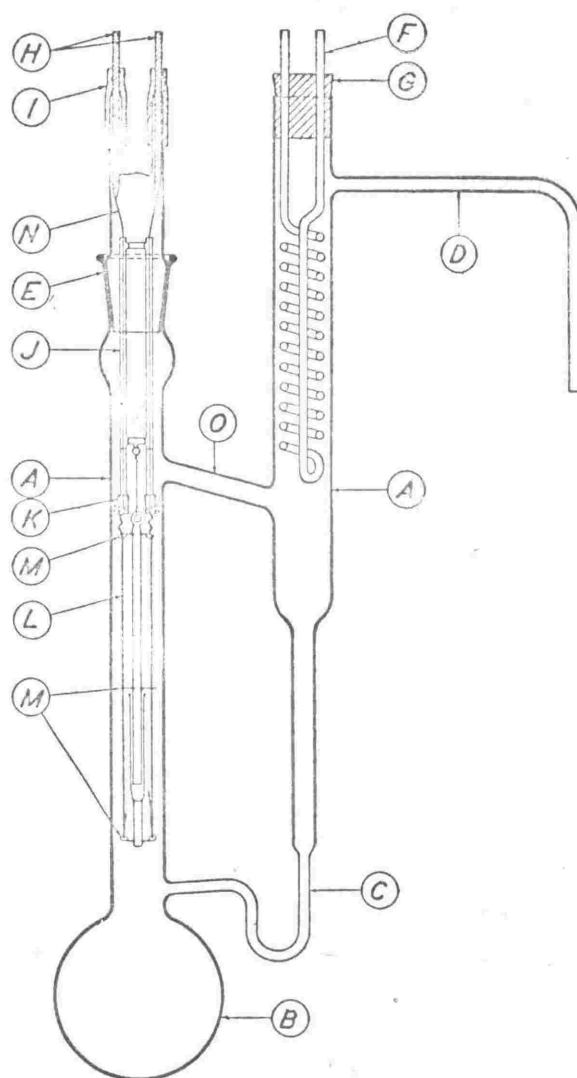


FIG. II.

Cyclohexene was vigorously refluxed in the apparatus and the cracking filament was kept bright red, by adjusting the current through it by means of a "Variac" transformer. The products passed through the copper coil condenser and a trap cooled in ice water into a trap cooled in a Dry Ice-alcohol mixture, which condensed the butadiene (b.p. =  $-4.51^{\circ}\text{C}$ )<sup>169</sup>, but allowed the ethylene (b.p. =  $-105^{\circ}\text{C}$ )<sup>207</sup> saturated with butadiene, to pass through.

The trap containing the liquid butadiene was then connected to a flask containing a solution of bromine in carbon tetrachloride and allowed to warm up, so that the butadiene bubbled slowly through the solution. Crystals of the high melting-point stereoisomer of butadiene tetrabromide separated out. When bromination was complete, the solid was filtered off and recrystallised twice from ethanol, m.p. =  $115-116^{\circ}\text{C}$  (lit. m.p. =  $115-117^{\circ}\text{C}$ )<sup>169,202,203</sup>

The residual solution was then concentrated by removing the solvent under reduced pressure and the low melting-point stereoisomer was isolated and recrystallised twice from ethanol. m.p. =  $35.5-36.0^{\circ}\text{C}$  (lit. m.p. =  $37-39^{\circ}\text{C}$ )<sup>202</sup>

Ethylene and butadiene were detected during the synthesis by absorption in acetonitrile and v.p.c. analysis.

A 55% yield of crude product was obtained. Melting-points were determined using a Fisher-Johns type apparatus.<sup>209</sup>

The high melting-point stereoisomer was used for kinetic work and recrystallised once from ethanol before use.

(vii) 2,6-Iutidine

2,6-Iutidine (K and K Laboratories, Inc.) was dried over potassium hydroxide pellets and distilled through a Vigreux column. b.p. =  $142-143^{\circ}\text{C}/760\text{mm}$ . (lit. b.p. =  $142-143^{\circ}\text{C}$ )<sup>207</sup>  $n_D^{25} = 1.4950$  (lit.  $n_D^{25} = 1.4953$ )<sup>221</sup>

Its purity was checked by v.p.c. analysis.

(viii) Sodium Methoxide in Methanol

Freshly-cut small pieces of sodium were washed successively in two beakers of methanol and quickly transferred to the solvent, which was contained in a flask with a loosely fitted stopper. Solutions of approximately 1M concentration were prepared.

(ix) Lithium Chloride Solutions

Lithium chloride was prepared by adding excess lithium carbonate (B.D.H.) to the required volume of diluted "Analar" hydrochloric acid and boiling. The solution was cooled and filtered, and then boiled down in a silica flask. The solid was finally heated to fusion-point in a stream of dry nitrogen. When cool, the required volume of the appropriate solvent was added to dissolve up the lithium chloride. Precautions were taken to exclude atmospheric moisture. The solution was then filtered and stored in a tightly stoppered flask.

(x) Lithium Chloride- $\gamma$  Solutions

The required volume of chlorine- $\gamma$  labelled hydrochloric acid was transferred to a beaker and excess lithium carbonate (B.D.H.) was added. A suitable volume of "Analar" hydrochloric acid was then added together with excess lithium carbonate. The solution was boiled, cooled and filtered, and then transferred to a silica flask and treated as for the inactive salt. Extra precautions to prevent accidental loss of the salt were, of course, taken in handling this compound.

(xi) Chlorine- $\gamma$  Labelled Hydrochloric Acid

Chlorine- $\gamma$  labelled hydrochloric acid was obtained from "The Radiochemical Centre", Amersham, England, in 40 microcurie lots. The isotope was contained in  $\sim 0.6$  ml. of 2N HCl of specific activity 200-500  $\mu\text{c./gm.}$  of chlorine. This small volume was added to 100 ml. of distilled water and the resultant stock solution was used for preparing radioactive compounds.

$$t_{1/2} = 4.4 \times 10^5 \text{ yr.}, \beta, 0.713 \text{ MeV. } ^{205}$$

(xii) Tetraethylammonium Hydroxide

The B.D.H. product is a 25% aqueous solution. This was diluted before use to a concentration suitable for its purpose.

(xiii) Tritolyl Phosphate (tricresyl phosphate)

B.D.H. for gas chromatography was used.

III Analytical Reagents

(i) Silver Nitrate

Solutions were prepared by dissolving the required weight of the "Analar" salt in distilled water, and were standardised by potentiometric titration using standard solutions of either potassium chloride or sodium chloride. These standard solutions were prepared from the oven-dried "Analar" salts.

The silver nitrate solutions were stored in amber-coloured winchesters.

(ii) Sodium Hydroxide

Carbonate-free sodium hydroxide solutions were prepared from a concentrated solution of the "Analar" pellets in distilled water.<sup>204</sup> They were standardised against portions of oven-dried "Analar" potassium hydrogen phthalate dissolved up in boiled-out water, using phenolphthalein as the indicator.

(iii) Sodium Thiosulphate

Sodium thiosulphate solutions were prepared by dissolving the pentahydrate in boiled-out distilled water and adding 1 ml. of "Analar"

chloroform. They were standardised against standard potassium iodate solutions prepared from the oven-dried "Analar" salt. A freshly-prepared starch solution was used as the indicator.

"Analar" potassium iodide was used at all times.

(iv) Bromine in Methanol

The required volume of bromine (B.D.H.) was added to methanol, which had been dried by the magnesium turnings method and distilled.<sup>208</sup>

(v) Potassium Thiocyanate

The "Analar" salt was dissolved in distilled water and standardised using standard silver nitrate, by the Volhard procedure.<sup>104</sup>

(vi) Water

Distilled water was used at all times.

APPENDIX IDERIVATION OF THE INTEGRATED RATEEQUATION FOR REARRANGEMENT

The rate equation for a reversible first-order or pseudo-first-order reaction is:

$$\frac{dx'}{dt} = k_f(a' - x') - k_b(x_0 + x')$$

where:  $a' - x'$  = the concentration of reactant at time  $t$ .

$x_0 + x'$  = " " " product " " "

$a'$  = the initial concentration of reactant.

$x_0$  = the " " " product.

$k_f$  = the rate constant for the forward reaction.

$k_b$  = " " " " " back "

$x'$  = the concentration of product formed during the reaction time  $t$ .

Now, at equilibrium,  $\frac{dx'}{dt} = 0$ , so that:

$$k_f(a' - x_e') = k_b(x_0 + x_e')$$

where  $x_e'$  is the concentration of product formed during the reaction time  $t_{\infty}$ . Therefore,  $x_e'$ , the concentration of product at equilibrium, is the sum,  $(x_0 + x_e')$ .

$$\text{Now: } \frac{k_f}{k_b} = \frac{(x_0 + x_e')}{(a' - x_e')}$$

$$\begin{aligned} \text{and: } \frac{dx'}{dt} &= k_f(a' - x') - k_f(x_0 + x') \frac{(a' - x_e')}{(x_0 + x_e')} \\ &= k_f \frac{(x_e' - x')(a' + x_0)}{(x_0 + x_e')} \end{aligned}$$

$$\text{and: } \left( \frac{dx'}{x_e' - x'} \right) = k_f \frac{(a' + x_0)}{(x_0 + x_e')} dt$$

Integration from  $t=0$  to  $t=t$  gives:

$$\log_{10} \frac{x_e'}{(x_e' - x')} = \frac{k_f t}{2.303} \frac{(a' + x_0)}{(x_0 + x_e')}$$

Now,  $x$  and  $x_e$ , the total concentrations of product at time  $t=t$  and  $t=\infty$  are given by:

$$x = x' + x_0 \quad \text{and,} \quad x_e = x_e' + x_0$$

Therefore:

$$\log_{10} \frac{(x_e - x_0)}{(x_e - x)} = \frac{k_f t}{2.303} \frac{(a' + x_0)}{x_e}$$

$$\text{Since: } 1 + \frac{k_b}{k_f} = \frac{(a' + x_0)}{x_e}$$

$$\log_{10} \frac{(x_e - x_0)}{(x_e - x)} = \frac{(k_f + k_b)t}{2.303}$$

Putting  $k_1 = k_f + k_b$  and rearranging:

$$k_1 = \frac{2.303}{t} \log_{10} \frac{(x_e - x_0)}{x_e - x}$$

For a pseudo-first-order reaction  $k_1 = k_2 b$ , where  $b$  is the concentration of the catalytic reactant, so that:

$$k_1 = k_2 b = k_2^f b + k_2^b b = X_e k_2 b + (1 - X_e) k_2 b$$

Therefore:

$$k_2^f = \frac{2.303 X_e}{bt} \log_{10} \frac{(x_e - x_0)}{(x_e - x)}$$

where  $X_e = \frac{x_e}{(a + x_0)} = \frac{x_e}{a}$ ,  $a = (a' + x_0)$  being the total substrate concentration.

Or, using the symbols used throughout the text for the rearrangement reaction:

$$k_2'^\alpha = \frac{2.303 X_e}{10^2 bt} \log_{10} \frac{(X_e - X_0)}{(X_e - X)}$$

(for runs starting from the  $\alpha$ -isomer)

where  $X_e$  is now the percentage of substrate converted to the  $\gamma$ -isomer at equilibrium and  $X_0$  and  $X$ , the percentages converted at time  $t=0$  and  $t=t$  respectively.

Similarly when  $k_2^{\gamma}$  is calculated  $X_e$ ,  $X_o$  and  $X$  are now the percentages of substrate converted to the  $\alpha$ -isomer.

$$\text{In conclusion: } k_2' = k_2^{\alpha} + k_2^{\gamma}$$

$$k_1' = k_2'b = k_1^{\alpha} + k_1^{\gamma}$$

where  $k_1'$  and  $k_2'$  are the composite pseudo-first-order and composite second-order rate constants for rearrangement, respectively, and  $b$  is the concentration of  $\text{Et}_4\text{NCl}$ .

APPENDIX IIDERIVATION OF THE INTEGRATED RATEEQUATION FOR ISOTOPE EXCHANGE

Consider the equation:



(which is the only detectable reaction occurring)

and let:  $[\text{RCl}] + [\text{RCl}^{36}] = a$

$[{}^{36}\text{Cl}^-] + [\text{Cl}^-] = b$

Then,  $v = k_2 ab = R$  is the rate of all the possible reactions that can take place between labelled and unlabelled substrate and nucleophile, whether detectable or not.

Now, if  $[\text{RCl}^{36}] = X$  and  $[{}^{36}\text{Cl}^-] = Y$

$$+ \frac{dX}{dt} = R \frac{(a-X)}{a} \frac{Y}{b} \quad \text{and} \quad - \frac{dX}{dt} = R \frac{X}{a} \frac{(b-Y)}{b}$$

$$\text{Therefore, } \frac{dX}{dt} = \frac{R}{ab} (aY - Xb) = \frac{R}{ab} (aZ - aX - bX)$$

as  $Z = X + Y = a$  constant.

$$\text{Therefore, } \frac{dX}{dt} = - \frac{R}{ab} (a+b)X + \frac{RZ}{b}$$

Putting:  $-\frac{(a+b)}{ab}R = \alpha$  and  $\frac{RZ}{b} = \beta$

$$\frac{dX}{dt} = \alpha X + \beta \quad \text{and} \quad \frac{dX}{(X + \frac{\beta}{\alpha})} = \alpha dt$$

Integration between  $t=0$  and  $t=t$  gives:

$$2.303 \log_{10} \frac{(X_t + \frac{\beta}{\alpha})}{(X_0 + \frac{\beta}{\alpha})} = \alpha t$$

or,  $2.303 \log_{10} \frac{(\frac{\alpha}{\beta} X_t + 1)}{(\frac{\alpha}{\beta} X_0 + 1)} = \alpha t$

Substituting for  $\alpha$  and  $\beta$  and then for  $R$  and rearranging:

$$k_2 = -\frac{2.303}{(a+b)t} \log_{10} \frac{[1 - \frac{(a+b)}{a} \frac{X_t}{Z}]}{[1 - \frac{(a+b)}{a} \frac{X_0}{Z}]}$$

but,  $\frac{a}{(a+b)} = \frac{X_{\infty}}{Z}$

so that,

$$k_2 = \frac{2.303}{(a+b)t} \log_{10} \frac{(X_{\infty} - X_0)}{(X_{\infty} - X_t)}$$

In the nomenclature used throughout the book,  $X_{\infty}$  is the final concentration.

% R = the percentage of the theoretical exchange which has occurred at time t.

$$= 10^2 \frac{X}{X_{\infty}}$$

In the case of the exchange runs with allyl chloride Z is the initial activity of the  $\text{LiCl}^{36}$ .

APPENDIX IIIDETERMINATION OF RATE CONSTANTS FOR THE  
ELIMINATION REACTION

The integrated rate equation for a first-order reaction is:

$$k_1 = \frac{2.303}{t} \log_{10} \frac{a}{(a-x)}$$

where  $a$  is the initial concentration of the reactant and  $(a-x)$  is the concentration at time  $t$ . For a pseudo-first-order reaction, which is really concurrent first- and second-order:

$$k_1(\text{obs.}) = k_1 + k_2 b$$

where  $b$  is the concentration of the nucleophilic reagent. (See page 152).

Attempts by four different methods were made, to estimate the pseudo-first-order rate constant for the overall elimination reaction accompanying the much faster  $\text{Et}_4\text{NCl}$  catalysed rearrangement reaction of  $\alpha$ -methylallyl chloride, using the simple equation above and the experimental data for Runs 26 and 27.

Method A:- Rate constants for the elimination reaction were calculated assuming the only reaction to be elimination, so that  $a$  in the above equation was the initial concentration of  $\alpha$ -methylallyl chloride and

(a-x) the initial concentration - the concentration of hydrogen chloride produced by the elimination reaction during the time t. The rate "constants" ( $k_1^E(\text{obs.})$ ) shown in Tables XXV and XXVI were calculated by this method. The mean of values calculated during the formation of 20-40% of the  $\gamma$ -isomer was taken as the rate constant.

Method B:- The elimination rate constants for Runs 26 and 27 were also estimated from a plot of  $\log_{10}(a-x)$  versus t, where (a-x) was the same as defined above. The slope of the graph over the time interval during which 20-40% of the rearranged isomer was formed, was determined and used to estimate the rate constant.

Both of these methods give values which could be up to 30% lower than the true value, for estimations over the range of 20-40%  $\gamma$ -isomer formation, due to the rearrangement reaction removing reactant. (It was assumed before the work described in Section IX, Chapter III was carried out that the  $\gamma$ -isomer does not eliminate hydrogen chloride at a significant rate). Therefore, correction of the rate constants for an assumed depression of 20% was made.

Method C:- The actual concentration of the  $\alpha$ -isomer in the reaction mixture at approximately 20%  $\gamma$ -isomer formation was calculated from the data and used as the initial concentration of  $\alpha$ -methylallyl chloride. The concentrations of the elimination products, produced during the time interval during which 30-40% of the  $\gamma$ -isomer was formed, were then used to calculate values of the rate constant.

Effectively this means the equation:

$$k_1 = \frac{2.303}{(t-t_0)} \log_{10} \frac{a}{(a-(x-x_0))}$$

was used, with  $a$  being corrected for elimination and rearrangement up to 20%  $\gamma$ -isomer formation, or time  $t_0$ . The concentration of elimination products at time  $t$  was  $x$  and at time  $t_0$  was  $x_0$ .

Method D:- A plot of  $\log_{10}(a-(x-x_0))$  versus  $t$  for each run, enabled the rate constant to be evaluated from the slope of the graph.

Both of these methods correct for rearrangement up to time  $t_0$ , i.e., up to  $\sim 20\%$   $\gamma$ -isomer formation. The effect of the rearrangement reaction on the elimination reaction over 20-40%  $\gamma$ -isomer formation was neglected.

The rate constants ( $k_1^E(\text{obs.})$ ) given by the four methods are shown below.

<u>Run 26</u>	<u>Run 27</u>	<u>Mean of Runs 26 and 27</u>
$10^7 k_1^E(\text{obs.})$ ( $\text{sec.}^{-1}$ )	$10^7 k_1^E(\text{obs.})$ ( $\text{sec.}^{-1}$ )	$10^7 k_1^E(\text{obs.})$ ( $\text{sec.}^{-1}$ )
1.36 $\rightarrow$ 1.70	1.63 $\rightarrow$ 2.04	1.50 $\rightarrow$ 1.87
(Method B $\rightarrow 1.36 \times \frac{10}{8}$ )	(Method B $\rightarrow 1.63 \times \frac{10}{8}$ )	
1.66	1.96	1.81
(Method D)	(Method D)	
1.58 $\rightarrow$ 1.98	1.57 $\rightarrow$ 1.96	1.58 $\rightarrow$ 1.97
(Method A $\rightarrow 1.58 \times \frac{10}{8}$ )	(Method A $\rightarrow 1.57 \times \frac{10}{8}$ )	
1.56	1.93	1.74
(Method C)	(Method C)	

It may be seen that the graphical method neglecting rearrangement (Method B) gives values which, when corrected for an assumed 20% depression due to the rearrangement reaction removing substrate, are in reasonable agreement with those for which attempts to correct for rearrangement by other methods have been used.

As the errors in the data and reproducibility of the data give errors in the rate constants of the order of the error due to neglecting the rearrangement reaction, the above method appears to give a reasonable estimate of the rate constant and it was therefore adopted.

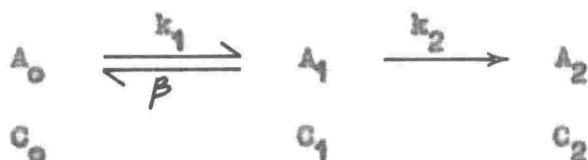
Further difficulties involved in the estimation of the rate constant for elimination were as follows:- (a) by analogy with the results for allyl chloride in Section I, Chapter III, it was probable that all the allylic chlorides would interact with acetonitrile to form  $1 \times 10^{-3} M$  chloride ions and a cation, which is, or reacts with water to form, a hydrogen ion, during the time interval over which the rearrangement and elimination reactions were being studied. As this concentration was not negligible by comparison with the concentration of acid produced by the elimination reaction, it was an added source of ambiguity and error; (b) as the elimination reaction is only the minor contributor to the overall reactions of the substrate, estimations of the rate constant during the formation of the first 20% of the  $\gamma$ -isomer were avoided, because of the low concentrations of acid produced and consequently the large analysis errors in determining these small amounts. However, in determining the rate constant over 20-40%  $\gamma$ -isomer formation, the effect of  $HCl_2^-$  ion formation on the

chloride ion catalysed component of the elimination reaction, had to be neglected.

Therefore, it was considered that the preliminary data for the elimination reaction, obtained from these runs, did not warrant attempts at a more sophisticated analysis for the rate constant,<sup>152</sup> since its main value was as the experimental data. (i.e., in the form of hydrogen chloride concentration).

However, some of the data for Runs 26 and 27 was compared with data obtained from calculations using equations for a reversible-consecutive two-stage reaction.

Rodiguin and Rodiguina have derived equations for a reversible-consecutive two-stage reaction with a reversible first stage and a single initial substance, which relate the concentration of each product and the initial reactant at time  $t$ , to the rate constants for the various stages.<sup>152</sup>



If the concentration of  $A_0$  at time  $t=0$  is 0 and the concentration of  $A_1$  is  $C_1^0$ , then:

$$C_0 = \beta C_1^0 \left| \frac{1}{\delta_2 - \delta_1} e^{-\delta_1 t} + \frac{1}{\delta_1 - \delta_2} e^{-\delta_2 t} \right|$$

$$C_1 = C_1^0 \left| \frac{k_1 - \delta_1}{\delta_2 - \delta_1} e^{-\delta_1 t} + \frac{k_1 - \delta_2}{\delta_1 - \delta_2} e^{-\delta_2 t} \right|$$

$$C_2 = C_1^0 \left| 1 - \frac{k_2 (k_1 - \delta_1)}{\delta_1 (\delta_2 - \delta_1)} e^{-\delta_1 t} - \frac{k_2 (k_1 - \delta_2)}{\delta_2 (\delta_1 - \delta_2)} e^{-\delta_2 t} \right|$$

where  $\delta_1, \delta_2$  are the roots taken with opposite sign of the quadratic equation:

$$(\delta^2 + (\beta + k_1 + k_2)\delta + k_1 k_2) = 0$$

$\beta, k_1$  and  $k_2$  being the pseudo-first-order rate constants for the reactions.

The mean experimental composite rate constant for the rearrangement reaction, calculated from the simple rate equation (see Section VI, Chapter III), was dissected into its pseudo-first-order components and these, together with values for  $k_1^E$  and  $k_2^E$  of  $3.45 \times 10^{-8} \text{ sec.}^{-1}$  and  $3.15 \times 10^{-6} \times 0.0485 \text{ sec.}^{-1}$  respectively, calculated as described in Section VI and above, were used in the equations above, to calculate values for  $C_0, C_1$  and  $C_2$  at various times for Runs 26 and 27.  $C_0, C_1$  and  $C_2$  correspond to the concentrations of  $\gamma$ -methylallyl chloride,  $\alpha$ -methylallyl chloride and elimination products present in the reaction mixture at time  $t$ . The small amount of the  $\gamma$ -isomer present at time  $t=0$  was neglected and the reaction times chosen were the experimental

times during which 20-40% of the  $\gamma$ -isomer was formed.

By comparing the experimental concentrations of the products and initial reactant at time  $t$  with the calculated values, an indication could be obtained of how well the rate constants for the various stages, calculated as outlined above from the simple rate equations, neglecting or making somewhat arbitrary corrections for possible perturbing effects, represent the experimental data and the true rate constants.

The calculated and experimental values are compared in Table LXXI. A and C compare the data for Run 26 at reaction times 1935, 3111, 4727 min. respectively and B and D compare the data for Run 27 at reaction times 1727, 2622, 4650, 5852 min. respectively.

The experimental values for the concentration of  $\alpha$ - and  $\gamma$ -methylallyl chloride given in A and B were calculated from the isomer ratios neglecting the elimination reaction. For example, at 20%  $\gamma$ -isomer formation, the concentration of  $\gamma$ -methylallyl chloride was taken to be  $0.20a$ , where  $a$  was the initial concentration of  $\alpha$ -methylallyl chloride, approximated to the initial substrate concentration. The experimental values for C and D were calculated from the isomer ratios allowing for the elimination reaction. For example, at 20%  $\gamma$ -isomer formation, the concentration of  $\gamma$ -methylallyl chloride was taken to be  $0.2(a - [H^+])$ .

The experimental and calculated values of  $C_0$ ,  $C_1$  and  $C_2$  may be seen to be in reasonably good agreement and  $C_0$  values would be in even better agreement if the small amount of rearrangement at zero time were allowed for.

TABLE LXXI

	[ $\alpha$ -MAC] (expt'l.)	[ $\alpha$ -MAC] (calc.)	[ $\gamma$ -MAC] (expt'l.)	[ $\gamma$ -MAC] (calc.)	[H <sup>+</sup> ] (expt'l.)	[H <sup>+</sup> ] (calc.)
A	0.0983	0.0976	0.0250	0.0233	$2.4 \times 10^{-3}$	$2.4 \times 10^{-3}$
	0.0872	0.0857	0.0361	0.0340	3.4 "	3.6 "
	0.0748	0.0727	0.0485	0.0455	5.0 "	5.0 "
B	0.0963	0.0958	0.0211	0.0195	1.9 "	2.1 "
	0.0895	0.0868	0.0279	0.0276	2.7 "	3.0 "
	0.0733	0.0707	0.0441	0.0419	5.0 "	4.8 "
	0.0677	0.0634	0.0497	0.0484	6.4 "	5.7 "
C	0.0964	0.0976	0.0245	0.0233		
	0.0848	0.0857	0.0351	0.0340		
	0.0718	0.0727	0.0465	0.0455		
D	0.0947	0.0958	0.0208	0.0195		
	0.0874	0.0868	0.0273	0.0276		
	0.0701	0.0707	0.0423	0.0419		
	0.0640	0.0634	0.0470	0.0484		

Therefore, it may be concluded that the simple rate equations used for calculating the rate constants give a reasonably accurate estimate of the true rate constant and that the pseudo-first-order rate constant for the overall elimination reaction derived and corrected in the way discussed in Section VI and above in this appendix, and taken as being the mean of the values obtained for Runs 26 and 27, gives a reasonably accurate estimate of the true rate constant for the reaction. (See, however, Section XIII).

Unfortunately, time was not available before the termination of this project to investigate the possibility of a more precise study of the elimination reaction, using v.p.c. analysis for butadiene production and more refined analyses for acid production and preferably of the rate of elimination from a substrate initially at the isomer ratio of an equilibrium mixture, so as to minimize the complications of the rearrangement reaction.

APPENDIX IVDENSITY VERSUS TEMPERATURE DATA  
FOR ACETONITRILE

DENSITY (gm./ml.)	TEMP. (°C)
0.665	126.0
0.682	111.0
0.699	96.0
0.716	81.0
0.7234	75.0
0.7394	60.0
0.7554	45.0
0.7714	30.0
0.7821 (std.)	20.0
0.7847	17.6
0.8034	0.0

## APPENDIX V

V.P.C. DATA FOR REPRESENTATIVE REARRANGEMENT RUNS (RUNS 30 & 35)

<u>Run 30</u>				
$\frac{[\alpha]}{[\delta]}$	$\left  \frac{\alpha}{\delta} \right $	$\left  \frac{\alpha}{\delta} \right _{av.}$	$K_{(cal.)}$	$\delta^{\circ}$ $\delta$ -MAC
17.56	3.64, 3.48, 3.48	3.53	4.97	
unknown	30.1, 38.1, 31.5	33.2	(4.97)	0.60
17.56	3.57, 3.47	3.52	4.99	
8.19	1.73, 1.61	1.67	4.90	
unknown	5.04, 5.04, 5.07	5.05	(4.95)	3.85
17.56	3.34, 3.41	3.37	5.21	
8.19	1.59, 1.60, 1.62	1.60	5.12	
unknown	3.02, 3.01, 2.92	2.98	(5.16)	6.11
17.56	3.41	3.41	5.15	
8.19	1.63, 1.67	1.65	4.96	
unknown	1.70, 1.62, 1.67	1.66	(5.06)	10.64
8.19	1.60, 1.61, 1.65	1.62	5.06	
3.94	0.787, 0.822	0.804	4.90	
unknown	1.04, 1.08, 1.11, 1.08	1.08	(4.98)	15.7
8.19	1.64, 1.62	1.63	5.02	
3.94	0.788, 0.791	0.790	4.99	
unknown	0.823, 0.819, 0.824	0.822	(5.00)	19.6
3.94	2.92, 2.79	2.85	1.382	
2.69	1.79, 1.84	1.82	1.478	
unknown	1.98, 2.00, 2.00	1.99	(1.430)	26.0

Run 30 (cont.)

$\frac{[\alpha]}{[\delta]}$	$\left  \frac{\alpha}{\delta} \right $	$\left  \frac{\alpha}{\delta} \right _{av.}$	$K_{(cal.)}$	$\% \delta\text{-MAC}$
1.50	1.11, 1.08	1.10	1.364	
2.01	1.40, 1.36, 1.37	1.38	1.456	
1.50	1.06, 1.02, 1.04	1.04	1.442	
unknown	1.33, 1.34, 1.32	1.33	(1.449)	34.2
2.01	1.37, 1.46	1.41	1.429	
1.50	1.04, 1.08	1.06	1.415	
unknown	1.00, 0.997, 1.01	1.00	(1.420)	41.3
1.50	1.05, 1.06	1.05	1.429	
0.966	0.688, 0.684	0.686	1.408	
unknown	0.775, 0.733, 0.764	0.757	(1.418)	48.2
2.59	1.81, 1.90	1.85	1.454	
2.01	1.38, 1.45	1.41	1.426	
unknown	1.94, 1.96, 1.96	1.95	(1.440)	26.3

Run 35 (cont. from p. 336)

2.21	0.871, 0.908	0.890	2.48	
unknown	1.36, 1.31, 1.36	1.34	(2.44)	23.4

Run 35

$\frac{[\gamma]}{[\alpha]}$	$\left  \frac{\gamma}{\alpha} \right $	$\left  \frac{\gamma}{\alpha} \right _{av.}$	$K_{(cal.)}$	% $\alpha$ -MAC
9.53	4.10,4.02,3.92	4.01	2.38	
unknown	74.0,69.1,59.4	67.5	(2.38)	0.62
9.53	3.92,4.03	3.97	2.40	
3.96	1.63,1.64	1.63	2.43	
unknown	10.1,10.4,10.4	10.3	(2.41)	3.86
9.53	3.98,3.98,4.04	4.01	2.38	
3.96	1.63,1.58	1.60	2.48	
unknown	5.27,5.16,5.15	5.19	(2.43)	7.35
9.53	4.04,3.86	3.95	2.41	
3.96	1.58,1.58	1.58	2.51	
unknown	3.35,3.28,3.45,3.31	3.35	(2.46)	10.82
9.53	3.91,3.97	3.94	2.42	
3.96	1.61,1.65	1.63	2.43	
unknown	2.44,2.45,2.55,2.52	2.49	(2.42)	14.2
9.53	3.97,3.91	3.94	2.42	
3.96	1.65,1.57	1.61	2.46	
unknown	1.96,1.92,1.90	1.93	(2.44)	17.5
3.96	1.57,1.58	1.58	2.51	
2.21	0.858,0.876	0.867	2.55	
unknown	1.53,1.52,1.52	1.52	(2.53)	20.6
3.96	1.67,1.63	1.65	2.40	

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SUGGESTIONS FOR FURTHER WORK

1. A more precise study of the  $\text{Et}_4\text{NCl}$  catalysed elimination reaction could be carried out, possibly using an equilibrium mixture of the two isomers as the initial reactant to minimize the complications due to the faster rearrangement reaction. An extension of the study to include various temperatures, which would enable the activation parameters to be determined, would also be of value. By developing a method for accurately determining the concentration of a solution of butadiene in acetonitrile, quantitative v.p.c. analyses for butadiene could be carried out using an internal standard. More precise acid analyses by the potentiometric titration method could also be used.

2. Further investigation of the surface-catalysed elimination reaction at various temperatures and initial concentrations of reactant would enable the activation parameters and the type of adsorption isotherm obeyed to be determined. By varying reaction conditions and the concentrations of the reactants to make trends conclusive and by increasing the accuracy of product ratio analyses by gas chromatography, information about the contribution of this mechanism to the elimination reaction observed in the presence of  $\text{Et}_4\text{NCl}$  could be obtained.

3. A determination of the rates of rearrangement and elimination in the presence of (a) added hydrogen chloride and (b) 2,6-lutidine would also be worthwhile.

4. An investigation of the rate constants for the isotope exchange ( $S_N2$ ) reactions of the cis and trans isomers of  $\gamma$ -methylallyl chloride, to see if there is any difference in their reactivity when a chloride ion is the nucleophile, would be valuable.

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