To R.F.M.

- A Cherished Friend

(i)

MARTIN GERHARDT BANWELL

STUDIES OF SOME STRAINED-RING
SYSTEMS: TRICYCLO-OCTANES

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ABSTRACT

The present study has been directed towards the synthesis and base promoted rearrangements of some saturated and unsaturated halogenotricyclo-octanes. The preparation of a number of previously unknown 4,4,8-tri- and 4,4,8,8-tetra-halogeno-*anti*-tricyclo[5,1,0,0^{3,5}]-octanes and the corresponding 3,3,8-tri- and 3,3,8,8-tetra-halogeno-*anti*-tricyclo[5,1,0,0^{2,4}]-octanes has been accomplished and the stereochemistries of their ring systems established. The former tricyclo-octanes are base sensitive and on treatment with potassium *t*-butoxide give rise to mixtures of (*E*)- and (*Z*)- β -*t*-butoxystyrenes. However, the *anti*-tricyclo[5,1,0,0^{2,4}]-octanes give no characterisable products on treatment with base. The mechanistic implications of the tricyclo-octane - styrene conversion have been studied in some detail and halogenocyclo-octatetraenes and phenylacetylenes have been eliminated as intermediates.

The behaviour of several methoxy-substituted 4,4,8,8-tetrahalogeno-*anti*-tricyclo[5,1,0,0^{3,5}]-octanes with the same base has been studied, and it has been found that homotropilidenes are formed regiospecifically by 1,4-elimination. These conversions constitute the first known examples of such elimination experienced by ring-fused halogenocyclopropanes. From these studies, evidence is presented which implicates homotropilidenes and bicyclo[4,2,0]octa-2,4-dienes as intermediates in the production of styrenes, and a mechanism for the tricyclo-octane - styrene rearrangement has been proposed.

A new and potentially versatile synthesis of 3,3-dihalogeno-*anti*-tricyclo[5,1,0,0^{2,4}]-oct-5-enes (*anti*-bishomobenzenes) has been developed.

The new route employs readily available starting materials, involves sequential introduction of the cyclopropyl, *gem*-dihalogenocyclopropyl, and olefinic moieties and proceeds in an overall yield of about 14%. This represents a five-fold increase over the previously reported yields.

CHAPTER ONE

INTRODUCTION

The synthesis and reactions of organic molecules which incorporate a small strained-ring have provoked considerable attention among organic chemists in recent years. In particular, the properties of halogenated ring-fused cyclopropanes have been of considerable synthetic utility in the generation of many unusual, and often highly strained, molecules.¹ There now exists a considerable volume of literature dealing with the dehydrohalogenation reactions of dihalocarbene adducts of medium and large ring cycloalkenes. Such species are believed to undergo initial 1,2-elimination to give an ω -chlorobicyclo[n,1,0]alk-1(ω)ene, e.g. (2) (Scheme 1), which does not survive the reaction conditions. Subsequent dehydrohalogenation and rearrangement affords product(s) by a pathway which is dependent upon the magnitude of n in the bicyclo[n,1,0] moiety.² In the absence of a nucleophile, and when the base employed in effecting the dehydrohalogenation is itself a poor nucleophile, the product is generally that resulting from migration of the double bond to a new position of greater stability outside of the three-membered ring. This is followed in some cases by skeletal rearrangement. For example, Billups and co-workers³ have found that reaction of 9,9-dichlorobicyclo[6,1,0]nonane (1) with potassium t-butoxide in dimethyl sulphoxide gives the diene (3), (Scheme 1a). However, the lower homologue, 8,8-dichlorobicyclo[5,1,0]octane (4), undergoes ring contraction to the norcarene (7) under identical conditions (Scheme 1b). The formation of (7) is believed to involve a facile methylene-cyclopropane rearrangement of the diene (6), which is the lower homologue of the isolable diene (3). The *gem*-dibromo derivative (5)

has also been reported⁴ to give rise to the same diene (7).

Scheme 1(a)

Scheme 1(b)

Ransom and Reese⁵ have reported that 7,7-dichlorobicyclo[4,1,0]heptane (8) undergoes reaction with potassium t-butoxide (t-BuOK) in dimethyl sulphoxide (DMSO) at 20° to give a mixture of volatile hydrocarbons containing toluene (10) (c. 2.5%), cyclohepta-1,3,5-triene (11) (c. 1%), ethylbenzene (12) (c. 12%), the *Z*- and *E*-ethylidenecyclohexenes (13) and (14) (c. 7.5%), and *o*-ethyltoluene (15) (c. 25%) (Scheme 2).

Scheme 2

Dehydrobromination of 7,7-dibromobicyclo[4,1,0]heptane (9) under similar conditions, gives volatile products which consist of *o*-ethyltoluene (15) (c. 18%), ethylbenzene (12) (c. 6%) and several unidentified minor products.

The authors⁵ have suggested that the formation of ethylbenzene involves methylation of the initially formed 7-halogenobicyclo[4,1,0]hept-1(7)-ene (16) at C7 by DMSO to give the halogenomethylnorcarene (17) (Scheme 3). The loss of a further mole of hydrogen halide would give the cyclohexa-1,3-diene (18), and finally base catalysed isomerism accounts for the product. Both of the proposed intermediates (17) and (18) could undergo further methylation at C1 thus accounting for *o*-ethyltoluene.

Scheme 3

Scheme 4

In contrast to the above, Shields and Gardner⁶ have found that the dichlorobicycloheptane (8) affords a mixture of two adducts on treatment with potassium isopropoxide in DMSO. The composition of the product mixture is dependent on the mole ratio of the reagents and the compounds were identified as *cis*-1-isopropoxy-7-chlorobicyclo[4,1,0]heptane (20) and *cis*-1,6-di-isopropoxybicyclo[4,1,0]heptane (21a). In each case the latter compound was the major component. The most reasonable rationale for the formation of these products is by way of the elimination-addition sequence shown in Scheme 4; the isopropoxide anion plays the role of base and nucleophile. When a mixture of potassium *t*-butoxide and potassium thiomethide (a good base-nucleophile combination) was employed *cis*-7-chloro-1-methylthiobicyclo[4,1,0]heptane (22) (69%) was the sole product and it was resistant to further dehydrochlorination under the conditions.

An extension of the work with norcarane (8) has involved the use of several weaker bases in DMSO.⁷ Thus sodium methoxide and potassium *p*-methylphenoxide give the corresponding *cis*-1,6-dialkoxynorcaranes (21b,c). Reaction of the *gem*-dichloronorcarane (8) with potassium isopropoxide in DMSO- d_6 gives rise to the *cis*-1,6-di-isopropoxynorcarene (23) with deuterium incorporation at C7 (Scheme 4). The deuterium source in this reaction is unclear (*i*-PrOD or DMSO- d_6) because of the possible⁸ equilibrium between the dimethyl and isopropoxide anions under these conditions.

In the examples thus far discussed involving addition to the 1,(7) double bond, the regiospecificity of addition of the nucleophile to the 7-halobicyclo[4,1,0]hept-1(7)-ene (16), is consistent with the formation of the more stable carbanion e.g. (19) (Scheme 4).

The reactions of some mono-bromo ring-fused cyclopropanes have also been investigated.⁹ Once again dehydrobromination predominantly occurs

in the 1,2-mode within the three-membered ring, to give a bicyclo[n,1,0]-alk-1(ω)-ene which suffers a fate comparable to the earlier examples. The generation of a cyclopropylidene by α -elimination does not appear to be a competitive process in these systems. For example, treatment of *endo*-7-bromobicyclo[4,1,0]heptane† (24) with an excess of *t*-BuOK in DMSO at room temperature affords the Δ^2 -norcarene (25) in 24% yield.

A more efficient dehydrobromination was observed⁹ with *endo*-9-bromobicyclo[6,1,0]nonane (26) which gave a mixture of two olefins (95:5) in 80% yield. The major component was found to be bicyclo[6,1,0]non-1-ene (27) and the minor component bicyclo[6,1,0]non-2-ene (28). Resubjection of either compound to the reaction conditions established that the Δ^2 -olefin (28) is formed from its Δ^1 -counterpart (27). However, olefin (28) was further transformed into bicyclo[6,1,0]non-3-ene (29) (Scheme 5).

†The usage of "endo" and "exo" is based on the popular concept of treating the molecule as a 'sloping roof' from which everything that points downward is termed *endo*.

Scheme 5

The presence of unsaturation in the six-membered ring component of a 7,7-dihalogenobicyclo[4,1,0]heptane, dramatically alters the fate of the 7-halobicyclo[4,1,0]alk-1(7),x-diene, e.g. (32) (Scheme 6), which is initially generated. Thus reaction of the Δ^3 -olefins (30) and (31) with *t*-BuOK in DMSO gives rise to cyclopropabenzene (33) in *c.* 40% yield.¹⁰ The mode of formation of the arene (33) has come under scrutiny.¹⁰ The route generally accepted involves 1,2-elimination, and prototropic shift (Scheme 6) and is consistent with ^{12}C -labelling studies.

Scheme 6

It has recently been shown¹¹ that 7,7-dichlorobicyclo[4,1,0]hept-2-ene (34), the Δ^2 -isomer of (30) also affords cyclopropabenzene (33) under analogous conditions. However, elimination from the Δ^2 -norcarene (34) proceeds less readily and the available experimental evidence implies that partial isomerization of (34) to (30) occurs during the course of the reaction. Consequently, the route from 7,7-dichlorobicyclo[4,1,0]hept-2-ene (34) to cyclopropabenzene (33) is uncertain, since it is not possible to differentiate between 1,2-elimination and a [1,5]H shift [to give the diene (32a) in the same manifold as from the Δ^3 -olefin (30)], isomerization of (34) to (30) followed by elimination, or a combination of the two processes (Scheme 7).

Scheme 7

However, these results do exclude the route from olefin (30) to cyclopropabenzene (33) proceeding via the Δ^2 -isomer (34).

As a result of the studies described above, a variety of 7,7-dihalobicyclo[4,1,0]heptenes have proved to be particularly valuable precursors to other cyclopropa-arenes by the Billups¹² method. The syntheses so far devised are attractive in that the steps involved are generally few, and the product yields satisfactory. For example, replacement of the Δ^3 -double bond of compound (30) by an annelated benzene ring, *viz.* (35), leads to cyclopropa[b]naphthalene (36) in moderate yield.^{13,14,15}

Similarly, the tricyclo[6,1,0,0^{3,6}]non-3(6)-ene (37) gives cyclopropa[a]cyclobuta[d]benzene (38) in 30-40% yield.¹⁶

Vogel and co-workers¹⁷ have synthesised bis-cyclopropa[b,g]naphthalene (40) (*c.* 30%) from both the *cis-cisoid-cis*- and *cis-transoid-cis*-tetracyclo-[5,5,0,0^{3,5,9,11}]dodec-1(7)-enes (39a,b) with a tenfold excess of *t*-BuOK in tetrahydrofuran (THF) at room temperature. These authors suggest that the instability exhibited by (40) (explosive decomposition on melting) could indicate that the unknown bis-cyclopropabenzene (41) may not be capable of existence at room temperature.

The homologue of (40), cyclopropa[e]cyclobuta[b]naphthalene (43) has been prepared by reaction of the benzobicyclo[4,1,0]hept-3-ene (42) with base in THF.¹⁸

Cyclopropa[a]cyclobuta[c]benzene (46) is produced in only 4% yield by dehydrochlorination of the tricycle (44),¹⁹ and attempts to prepare it from the tetra substituted olefin (45) failed. It has been suggested that the presence of a tetra substituted double bond, as in (45), could be critical, particularly if prior rearrangement to the 5,6-position has to occur (Scheme 8).

Scheme 8

Vogel and Sombrock²⁰ have extended the Billups method to the synthesis of 1H-3,8-methanocyclopropa[10]annulene (48). Thus treatment of the bridged cycloheptatriene (47) with a six-fold excess of *t*-BuOK in THF at ambient temperature gave the cyclopropa-annulene (48) in *c.* 80% yield. This system remains the only known non-benzenoid cyclopropa-arene at the present time. However, attempts to synthesise the non-aromatic cyclopropacyclo-octatetraene (50) by dehydrochlorination of the bicyclic diene (49) are currently under investigation in these laboratories.²¹

Treatment of the bicycloheptane (51), the product of chlorination of compound (30), with strong base also gives rise to a cyclopropabenzene. Originally, the structure was assigned as 2-chlorocyclopropabenzene (53)²² and not the 3-chlorocyclopropabenzene (56) as would have been expected on the basis of the Billups-Gunther mechanism.¹⁰ However, further work by both Billups²³ and Garratt²⁴ and their respective co-workers has led to a revision of the assignment as 3-chlorocyclopropabenzene (56). Furthermore, treatment of the tetrabromobicycloheptane (52) in either THF or DMSO also gives rise to the corresponding 3-bromocyclopropabenzene (57).²³

Scheme 9

Initial dehydrohalogenation of the bicyclo[4,1,0]heptanes (51) and (52) could occur more readily in the six-membered ring component of the molecules to yield the corresponding Δ^2 - or Δ^3 -olefins (54) or (55) (Scheme 9). These could then suffer the loss of a further two molar equivalents of hydrogen halide in an analogous manner to the corresponding *gem*-dihalonorcaradienes (34) or (30), respectively (Scheme 7, p. 10).

Recent work in these laboratories²⁵ has demonstrated that treatment of the 2,3-dibromo-7,7-dichlorobicyclo[4,1,0]heptane (58) with *t*-BuOK gives rise to a *c.* 2:1 mixture of 2- and 3-bromocyclopropabenzenes (59) and (57).

The exclusive formation of the bromocyclopropabenzenes (57 and 59) from the mixed halogen precursor (58) argues strongly in favour of a route in which skeletal integrity is preserved.

Despite the successes recorded above, the dehydrohalogenation of a number of other ring-fused *gem*-dihalogenobicyclo[4,1,0]heptyl derivatives has demonstrated a resistance to aromatization and retention of the three-membered ring. For example, Davalian and Garratt²⁶ have attempted to

Scheme 10

prepare cyclopropa[b]anthracene (61) from the dichlorotetrahydroanthracene (60). The only product isolated with a ten-fold excess of *t*-BuOK was the ether (64). However, when the substrate (60) was treated with the stoichiometric amount of base required for cyclopropa-arene formation, the chloride (63) was isolated in 40% yield. In an alternative approach to the cyclopropa-arene (61) *via* the dihydro-derivative (66), the bicyclo[4,1,0]hept-3-ene (65) was treated with 2.5 molar equivalents of *t*-BuOK in DMSO, but only 2-methylantracene (68) was obtained. Whereas the aryl halide (63) and the ether (64) (by subsequent solvolysis of (63) with *t*-BuOK) are probably derived from the anion (62) (Scheme 10), the methyl derivative may come from the dehydroanthracene species (66), which is then converted to (68) by ring opening *via* the anion intermediate (67) shown in Scheme 10.

Halton and Browne^{14,15} have found that competing pathways are involved in the dehydrochlorination of 7,7-dichlorobicyclo[4,1,0]hept-3-ene (30) and its benzannelated derivative (35) (Scheme 11). Thus the Δ^3 -norcarene (30) yields the *t*-butyl ether (73) in *c.* 8% yield in addition to cyclopropabenzene (33). These workers have demonstrated that the ether (73) cannot arise solely from solvolysis of the cyclopropa-arene (33), because of its reluctance to undergo ring cleavage under the reaction conditions. Similar reaction of the analogue (35) with 4, 8, and 16 molar equivalents of base (in THF) gives rise to cyclopropa[b]naphthalene (36) in yields of 11, 22, and 38%, respectively. However, the major product at low _{base} concentration has been assigned as 1-(chloromethyl)naphthalene (72). At higher base concentrations the major by-product is 1-(*t*-butoxymethyl)-naphthalene (74) resulting from solvolysis of the naphthyl halide (72) (Scheme 11).

Independent subjection of the cyclopropa-arene (36) to the reaction conditions produces only 2-(*t*-butoxymethyl)naphthalene (75). This latter observation requires that the route by which the halide (72) and its solvolysis product (74) are produced from (35) involves skeletal rearrangement. It has been suggested¹⁵ that the production of the 1-substituted naphthalenes (72) and (74) involves initial 1,3-elimination (Scheme 11) to give the corresponding bicyclobutanes (69) and (70), which suffer base catalysed rearrangements to give the ring cleaved aromatics (71) and (72).

In an attempt to prepare cyclopropa[a]naphthalene (79) by dehydrochlorination of 7,7-dichlorobenzobicyclo[4,1,0]hept-2-ene (76), Halton *et al.*¹¹ obtained only 1-(chloromethyl)naphthalene (72), 1-(*t*-butoxymethyl)-naphthalene (74) and the elimination-addition product (1-(chloromethylene)-1,2,3,4-tetrahydro-2-*t*-butoxynaphthalene (80). No evidence for the desired cyclopropa[a]naphthalene (79) was obtained. Abstraction of the C-1 benzylic proton of (76) followed by chloride ion loss would give the chlorocyclopropene (77) (Scheme 12). Subsequent [1,5]H shift leads to the high energy *o*-quinodimethane (78) which can aromatize directly to the chloromethynaphthalene (72) by hydrogen migration. This latter compound is known to undergo nucleophilic substitution by *t*-butoxide under the reaction conditions thereby accounting for the ether (74). The formation of the exocyclic olefin (80) is more difficult to rationalize despite its formal derivation from compound (77) by addition of *t*-butanol to the 1,7a-bond.

Billups and Reed²⁷ have investigated the dehydrochlorination of 1-methyl-7,7-dichlorobenzobicyclo[4,1,0]hept-2-ene (81), a species clearly blocked to direct aromatization. Treatment of this compound with t-BuOK (15 molar equiv.) in THF at 15° for 23 hours gave unreacted starting

material (38%) and the t-butylethers (86) and (90) (43%) in a ratio of 1:2 respectively. The formation of (86) and (90) has been rationalized in terms of the mechanism shown in Scheme 13. The formation of the methylenecyclopropane (83) parallels many other systems, e.g. Scheme 1a (p. 2). Further dehydrochlorination could lead to the

Scheme 13

bicycloheptatriene (84) which can rearrange either by cleavage of bond *a* [to give the aryl carbene (85)] or by cleavage of bond *b* [to give the aromatic carbene (87)]. Reaction of carbene (85) with the elements of *t*-butanol results in the ether (86), whereas the isomeric (87) does not react with nucleophile but closes to give a new bicycloheptatriene (88) which leads to the ether (90) *via* (89). This behaviour of carbene (87) is consistent with the nucleophilicity of cycloheptatrienylikenes.

Billups and co-workers²⁸ have also obtained evidence for the bis-annelated bicycloheptatriene (92). Thus treatment of the dehydrophenanthrene (91) with *t*-BuOK (THF, 0°) gives a yellow viscous oil which has been identified as the substituted phenanthrene (94) (mixture of diastereoisomers) in 72% yield. This observation is readily understood in terms of the dibenzobicycloheptatriene (92) (Scheme 14) undergoing ring

Scheme 14

cleavage to the aryl carbene (93) which inserts into the solvent (THF). In an attempt to trap the cyclopropene (92), the bicycloheptane (91) was treated with *t*-BuOK in the presence of methanethiol. The only product isolated was the bis-sulphide (97) which almost certainly arises by addition of the thiol to the cyclopropenes (92) and (96) (Scheme 14).

In contrast to the detailed studies of *gem*-dihalogenobicyclo[4,1,0]-heptyl derivatives discussed above, there have been very few investigations of larger ring systems. There appear to have been no studies of bicyclo[5,1,0] analogues and only one in the bicyclo[6,1,0] series. Thus Shields and Gardner⁹ have investigated the dehydrobromination of the unsaturated bicyclononenes (98) and (99).

(98)

(99)

The monobromo compound (98) gives the cyclopropene (100) which undergoes the expected base promoted olefin migration to give the conjugated diene (101) in 57-70% yield.

The dehydrobromination of the dibromo analogue (99) is more complex and gives the four products (102)-(105).

The authors suggest that the origin of (102) and (103) involves a sequence of dehydrobromination-double bond migrations culminating in bicyclo[6,1,0]nona-2,4,6-triene (106). Indeed, subjection of an authentic sample of this triene to the reaction conditions gave (102) (47%), (103) (23%), and (105) (6.8%). However the bicyclic triene (104) could not be detected in the reaction mixture.

The formation of members of the bicyclo[4,3,0] family (104) and (105) from the dehydrobromination of (99) indicates that a competitive mechanism is operative. Katz and Garratt²⁹ have shown that the cyclononatetraenide ion (107) is relatively stable but that its conjugate acid (108) undergoes rapid electrocyclic ring closure to the triene (104). This fact, coupled with the observation that (104) undergoes an essentially instantaneous isomerization to indan (105) when submitted to the conditions used in its formation, leaves little doubt that the triene (104) isolated from the dibromide (99) exists in solution as the cyclononatetraenide anion (107); the generation of the triene (104) must therefore occur at the moment of quenching (Scheme 15).

Scheme 15

From all of the examples discussed, one may conclude that the dehydrohalogenation of ring-fused cyclopropanes is dominated by an initial 1,2-elimination to give the corresponding cyclopropene. The final products resulting from further reaction of this bridgehead olefin are highly

dependent on the electronic and geometrical constraints imposed by the fused-ring system, on the residual cyclopropene substituents, and on the medium employed.

In contrast to this well defined chemistry, little is known about the behaviour of bis-halogenocarbene adducts of corresponding medium and large ring cycloalkadienes under comparable conditions. Iskander³⁰ has found that the bromomethoxytricyclo[5,1,0,0^{3,5}]octanes (109) and (110) give rise to the styrenes (111) when subjected to mild thermolysis in ionizing media. However the monomethoxy compound (109) affords the cyclobutabenzene (112) in refluxing pyridine,³¹ while the dimethoxy counterpart (110) behaves in the same manner as it does in dimethylformamide.³⁰ The parent tetrabromide is inert under both conditions. The products (111) and (112) have been accounted for on the basis of initial cyclopropyl-allyl opening of one of the three-membered rings to give a bicyclo[5,1,0]heptadiene (Scheme 16).

Scheme 16

The rearrangements displayed by the bis-dihalogenocarbene adducts (109) and (110) are unusual, and the chemistry displayed by their mono-adduct counterparts (30) and (34) is fascinating. Because of this, an investigation into the reactions of tricyclo-octanes such as (112)-(119) in basic media appeared particularly interesting.

(112) $X=R=Cl$

(113) $X=Cl, R=H$

(114) $X=R=Br$

(115) $X=Br, R=H$

(116) $X=R=Cl$

(117) $X=Cl, R=H$

(118) $X=R=Br$

(119) $X=Br, R=H$

On the basis of the foregoing, dehydrohalogenation in these latter systems could proceed in one or more of the following ways: (i) in an analogous manner to the bicyclic counterparts (30) and (34) to yield (if skeletal integrity was retained) the as yet unknown biscyclopropabenzene (41) and (120) (Scheme 17). (The highly strained nature of some of the possible intermediates shown in Scheme 17 could make skeletal retention intolerable, and rearrangement(s) could well divert this pathway to give ring cleaved and/or expanded products); (ii) in a manner paralleling the thermal behaviour of the methoxy derivatives (109) and (110); (iii) in an entirely different fashion.

Scheme 17

Consequently, the objectives of the present study were the synthesis and subsequent dehydrohalogenation of the tri- and tetrahalogenotricyclo-[5,1,0,0^{n,n+2}]octanes (112)-(119). It was hoped that the products resulting from elimination in these systems would allow some comparison to be made with the reactions of the corresponding saturated and unsaturated bicyclo[4,1,0]heptyl systems under similar conditions, in order to assess the influence, if any, of the presence of an additional cyclopropane ring.

In addition, because the presence of unsaturation in the bicyclo[4,1,0]heptyl systems so profoundly affects the course of reaction, an investigation of the dehydrohalogenation of the unsaturated tricyclo-octanes (121) and (122) has been another objective of this work.

(121)

(122)

CHAPTER TWO

THE DEHYDROHALOGENATION OF SOME TRI- AND TETRA-HALOGENO-ANTI-TRICYCLO[5,1,0,0^{n,n+2}]OCTANES[†]

As has been discussed in the preceding chapter the synthesis and dehydrohalogenation of tricyclo-octanes (112)-(119) was a primary objective of the present study. The syntheses were readily accomplished by conventional methods and the stereochemistries of the ring systems established by conversion to known compounds. In the case of the "linear" tri- and tetra-halogenotricyclo[5,1,0,0^{3,5}]octanes (112)-(115) the synthetic approach that was employed is outlined in Scheme 18.

Controlled addition of dichlorocarbene (ethyl trichloroacetate - sodium methoxide) to cyclohexa-1,4-diene (123) (readily obtained in 77% yield from Birch reduction of benzene) yields the previously known³² 7,7-dichlorobicyclo[4,1,0]hept-3-ene (30), together with small amounts (c. 6%) of a single bis-adduct which has recently been shown³³ to be 4,4,8,8-tetrachloro-*anti*-tricyclo[5,1,0,0^{3,5}]octane (112) from dipole moment studies. Although a variety of methods are available half-reduction of the *gem*-dichloro moiety was most conveniently effected by treatment of the bicycloheptene (30) with zinc in refluxing ethanolic potassium hydroxide.³⁴ A 12:1 mixture (g.l.c.) of the epimeric 7-chlorobicycloheptenes (124a,b) was obtained. The configuration of the major and minor components

[†]For the sake of brevity the familiar stereochemical descriptors "syn" and "anti" will be used throughout the text of this dissertation in preference to the corresponding I.U.P.A.C. nomenclature of *cis-cisoid-cis* and *cis-transoid-cis*.

Scheme 18

of the mixture can be readily assigned since the C7 chlorine atom is both geminally and vicinally related to protons on the cyclopropane ring:³⁵ the corresponding vicinal coupling constant $J_{7,1(6)}$ is large (*c.* 7 Hz) when the protons are *cis*-related and small (*c.* 3 Hz) when they are *trans*-disposed. The ^1H n.m.r. spectrum of the bicycloheptene mixture (124a,b) exhibits well resolved triplets for the C7 methine proton of the major (3.20 p.p.m., $J_{7,1(6)}$ 7.5 Hz) and minor (2.86 p.p.m., $J_{7,1(6)}$ 2.8 Hz) components and these are assigned, therefore, to the *endo*-isomer (124a) and the *exo*-isomer (124b), respectively.

The stereoselective formation of the *endo*-isomer (124a) in the half-reduction of compound (30) is consistent with the approach of the reagent (zinc) from the direction of least steric interference and abstraction of the *exo*-chlorine atom of (30). Although abstraction of the *endo*-chlorine atom of (30) would give compound (124b) directly, it is believed that this thermodynamically more stable product arises predominantly, if not exclusively by epimerization of the *endo*-isomer *via* the carbanions (126).

Indeed, prolonged treatment of the epimeric mixture under the reducing conditions results in a steady decrease in the *endo:exo* ratio to a value of 10.5:1 after 16 hours.

Subsequent reaction of dichlorocarbene with the bicyclic chloro-olefins (124a,b) (no attempt was made to separate the epimers prior to the

addition of dichlorocarbene as epimerization occurs readily in basic media) results in a product mixture which exhibits a series of triplet resonances in the ^1H n.m.r. spectrum (H8) consistent with the addition having occurred across both faces of the π -bond. However, trituration of the mixture with light petroleum leaves, as the major product, a solid which shows only one pair of triplet resonances at 3.10 ($J = 7.2$ Hz) and 2.51 p.p.m. ($J = 3.0$ Hz) in a ratio of 6.5:1. These are assigned to the C8 methine protons of 4,4,*endo*-8- and 4,4,*exo*-8-trichloro-*anti*-tricyclo[5,5,0,0^{3,5}]octanes (113a,b), respectively and it is noteworthy that the *endo:exo* ratio is reduced compared with that of the starting olefins. In addition to providing analytical and spectroscopic data consistent with the assigned structures, compounds (113a,b) undergo reductive dechlorination (Na/t-BuOH/THF) to a single tricyclic

Scheme 19

hydrocarbon (127), identical to that obtained from both the known tetrabromo- and tetrachloro-*anti*-tricyclo-octanes (114)³⁶ and (112),³³ and in which the stereochemical integrity of the ring junctions is maintained (Scheme 19).³⁷ The stereoselective formation of the *anti*-tricyclo-octanes (113a,b) finds its parallel in the reaction of cyclohexa-1,4-diene (123) with an excess of both the Simmons-Smith reagent and dibromocarbene.

In an analogous sequence of experiments also starting with cyclohexa-1,4-diene (123), controlled addition of dibromocarbene ($\text{CHBr}_3/\text{t-BuOK}/\text{C}_5\text{H}_{12}$) yields the known³⁸ 7,7-dibromobicyclo[4,1,0]hept-3-ene (31) together with very small quantities (<2%) of the bis-adduct³⁶ 4,4,8,8-tetrabromo-tricyclo[5,1,0,0^{3,5}]octane (114). However, this latter compound is best prepared by the addition of an excess of dibromocarbene to diene (123) under phase transfer conditions. Half reduction of the *gem*-dibromo moiety of mono-adduct (31) was effected under the conditions employed for its dichloro-counterpart (30); the progress of the reduction was monitored by g.l.c. and the reaction was found to be complete within half the time (6 hours) of that required for (30). The ^1H n.m.r. spectrum of the product mixture exhibited the anticipated pair of triplet resonances for the C7 methine proton of the major (3.24 p.p.m., $J_{7,1(6)}$ 7.8 Hz) and minor (2.72 p.p.m., $J_{7,1(6)}$ 3.5 Hz) components in a ratio of *c.* 4:1.

On the basis of the magnitude of the coupling constants and chemical shift values these signals are assigned to the *endo*-bromo (125a) and *exo*-bromo (125b) compounds respectively (Scheme 18, p. 32). The formation of the mono-bromo compounds (125a,b) is accompanied by the presence of impurities which have resisted removal by conventional methods. Despite this, addition of dibromocarbene to the Δ^3 -double bonds of the mixture of compounds gave a homogeneous crystalline solid as the major product (41%) of reaction after recrystallization. The ^1H n.m.r. spectrum of this compound reveals the presence of a single triplet resonance at

Scheme 20

at 3.14 p.p.m. ($J = 7.5$ Hz) consistent with an *endo*-bromine atom at C8 of the tricyclo-octane. Reductive debromination (Li/t-BuOH/THF) of this product gives rise to a single tricyclic hydrocarbon identified as tricyclo[5,1,0,0^{3,5}]octane (127) by comparison (¹H n.m.r., g.l.c., and i.r.) with an authentic sample. Thus the crystalline solid resulting from dibromocarbene addition to the olefins (125a,b) is assigned to 4,4,*endo*-8-tribromo-*anti*-tricyclo[5,1,0,0^{3,5}]octane (115a). The ¹H n.m.r. spectrum of the mother liquors from recrystallization of (115a) gave no evidence for the presence of the corresponding *exo*-bromo-*anti*-isomer (115b).

The "angular" tricyclo[5,1,0,0^{2,4}]octanes (116)-(119) have been synthesised by a route (Scheme 20) which parallels that used for their "linear" counterparts outlined above. The addition of one molar equivalent of dichlorocarbene to cyclohexa-1,3-diene (130) yields 7,7-dichlorobicyclo[4,1,0]hept-2-ene (34)³⁹ together with minor amounts of the bis-adduct 3,3,8,8-tetrachloro-*anti*-tricyclo[5,1,0,0^{2,4}]octane (116). This latter tricyclo-octane is again best prepared by bis-dichlorocarbene addition to the cyclohexadiene (130) under phase-transfer catalysis as was reported⁴⁰ by Weyerstahl and co-workers subsequent to these studies. Half reduction of the bicyclohept-2-ene (34) in the manner described earlier affords a 4:1 epimeric mixture of the 7-chlorobicyclo[4,1,0]hept-2-enes (132a,b) which is unaltered on prolonged treatment under the reaction conditions. The addition of dichlorocarbene to this mixture gives rise to the epimeric trichloro-*anti*-tricyclo[5,1,0,0^{2,4}]octanes (117a,b) stereospecifically and with a diminished *endo:exo* ratio of 3:1. As with the tricyclo-octanes (113a,b) the structures of compounds (117a,b) are assigned on the basis of spectroscopic and analytical data and by reductive dechlorination to the same *anti*-tricyclo-octane (134) as is obtained from the known⁴⁰ tetrachloroprecursor (116), (Scheme 21).

Scheme 21

The "angular" tri- and tetrabromo-*anti*-tricyclo-octanes (119) and (118) have been prepared in essentially the same manner. Controlled addition of dibromocarbene ($\text{CHBr}_3/\text{t-BuOK}/\text{t-BuOH}$) to cyclohexa-1,3-diene (130) gives the known⁴¹ 7,7-dibromobicyclo[4,1,0]hept-2-ene (131). Subsequent half-reduction of the *gem*-dibromo moiety gives an epimeric mixture of the monobromonorcarenes (133a,b) (Scheme 20, p. 36) in which the *exo*-isomer predominates over the *endo*-isomer to an extent of two to one. Once again impurities contaminate the reaction mixture. Further addition of dibromocarbene ($\text{CHBr}_3/\text{t-BuOK}/\text{C}_5\text{H}_{12}$) to the Δ^2 -bonds of (133a,b) gives rise to a sweet smelling viscous oil. Fractional distillation and subsequent column chromatography of the distillate on silica gel gives a 1:2 mixture

of 3,3,*endo*-8- and 3,3,*exo*-8-tribromo-*anti*-tricyclo[5,1,0,0^{2,4}]octanes (119a,b) respectively, in 15% combined yield. The orientations of the bromine atom at C8 in this mixture is established from the presence of a pair of triplet resonances in the ¹H n.m.r. spectrum at 3.39 ($J = 7.0$ Hz) and 2.42 p.p.m. ($J = 3.7$ Hz). The lower field resonance is fully consistent with three "all-cis" cyclopropane protons and consequently with the bromine atom in the *endo*-configuration, while the latter resonance is compatible with the epimeric *exo*-configuration for the halogen atom. The *anti* disposition of the ring systems in (119a,b) was established by exclusive reductive debromination to *anti*-tricyclo[5,1,0,0^{2,4}]octane (134), the same product that is obtained from the known⁴² 3,3,8,8-tetrabromo-*anti*-tricyclo[5,1,0,0^{2,4}]octane (118).

In all of the beforementioned syntheses, the addition of dihalocarbene to the double bond of the bicyclo[4,1,0]heptenes (30), (31), (34), (124), (125), (131), (132) and (133) proceeds stereospecifically in an *anti*-fashion except in the case of olefin (124) which reacts stereoselectively in the same fashion; the steric demands of the cyclopropane present in the bicycloheptenes does not allow for the ready synthesis of the corresponding

(135)

(136)

tri- and tetra-halogeno-*syn*-tricyclo-octanes such as (135) and (136).

Because of this the present dehydrohalogenation studies have been confined to the *anti*-tricyclo-octanes (112)-(119).

The medium most commonly employed in effecting dehydrohalogenation in ring-fused halogenocyclopropanes is either tetrahydrofuran (THF) or dimethylsulphoxide (DMSO) containing potassium-*t*-butoxide (*t*-BuOK). In order to allow valid comparisons to be drawn between the dehydrohalogenation reactions of the tricyclo-octanes and their bicyclic counterparts, e.g. (30) and (34), *t*-BuOK was employed in either of the abovementioned solvents throughout this study.

Primarily because of its ready synthesis, the dehydrochlorination of 4,4,8,8-tetrachloro-*anti*-tricyclo[5,1,0,0^{3,5}]octane (112) was studied first. The addition of a solution of the tricycle (112) in THF to a chilled (salt-ice) suspension of *t*-BuOK (9 mol. equiv.) in the same solvent resulted in an immediate blackening of the reaction mixture. After allowing this to stand for *c.* 16 hours, conventional work-up afforded a mixture containing two major and at least six minor u.v. active components as demonstrated by analytical t.l.c. Preparative t.l.c. (p.t.l.c.) resolved four distinct bands (A-D) with R_F values of 0.0, 0.3, 0.5 and 0.8 respectively. Band A ($R_F = 0$) contained immobile material and resubjection of this to p.t.l.c. with a variety of solvents failed to give any satisfactory resolution of the various components. Band D ($R_F = 0.8$) was identified as starting material (112) (2% recovery). Band B ($R_F = 0.3$) and Band C ($R_F = 0.5$) have been identified as (*E*)-4-chloro- β -*t*-butoxystyrene (137) (16%) and (*Z*)-4-chloro- β -*t*-butoxystyrene (138) (15%), respectively on the basis of the following data.

Scheme 22

(*E*)-4-Chloro- β -t-butoxystyrene (137) was isolated as a clear colourless oil with a characteristic pleasant smell. The ^1H n.m.r. spectrum revealed a nine proton singlet (1.35 p.p.m., t-BuO), two one proton doublets (5.87 and 6.94 p.p.m., $J = 12$ Hz), and a broad four proton aromatic singlet (7.10 p.p.m.). The two one-proton doublets are assigned to the vinylic protons at the β - and α -positions of (137) respectively, consistent with the known⁴³ chemical shifts for the α - and β -protons of 4-chlorostyrene (139). The magnitude of the coupling constant indicates a *trans*-substituted double bond. The mass spectrum of (137) showed a molecular ion at m/e 210 ($M^{+\bullet}$) (6%) with a base peak at m/e 154 ($M - \text{C}_4\text{H}_8$) $^{+\bullet}$ and an isotope peak at m/e 156 ($M - \text{C}_4\text{H}_8$) $^{+\bullet}$ (30%) providing evidence for a mono-chloro-containing species. The mass spectral fragmentation pattern can be rationalized as shown in Scheme 22. In particular, the loss of C_4H_8 from the molecular ion is fully consistent with the presence of a t-butyl vinyl ether, the resulting arylacetaldehyde then undergoes normal fragmentation.⁴⁴ The infra-red spectrum exhibits a strong absorption at 1642 cm^{-1} ($\text{C}=\text{C}$), and a band, at 840 cm^{-1} , characteristic of a 4-substituted aromatic nucleus.

(*Z*)-4-chloro- β -t-butoxystyrene (138) was also isolated as a clear colourless oil. The ^1H n.m.r. spectrum again revealed a nine proton singlet (1.32 p.p.m., t-BuO) two one proton vinylic doublets (5.09 and 6.35 p.p.m., $J = 6.5$ Hz) and a four-proton aromatic AA'XX' system (7.06 and 7.40 p.p.m., $J = 9$ Hz). The doublets at 5.09 and 6.35 p.p.m. have been assigned to the vinylic protons at the β - and α -positions of (138) respectively. The significantly smaller coupling constant (6.5 Hz) found in this isomer is clearly indicative of a *cis*-substituted double bond. The mass spectrum of (138) paralleled closely that of (137) (Scheme 22, p. 41) and showed a molecular ion at m/e 210 ($M^{+\bullet}$) (7%) with a base peak at

m/e 154 ($M-C_4H_8$)⁺ and an isotope peak at m/e 154 ($M-C_4H_8$)⁺ again indicating the presence of a mono-chloro- containing species. Like the *trans*-isomer the infra-red spectrum of (138) exhibits a strong absorption at 1640 cm^{-1} , ($C=C$), and a band at 835 cm^{-1} , strong evidence for *para*-substitution in the aromatic ring.

Comparison of the 1H n.m.r. spectra of (137) and (138) with that of 4-chlorostyrene (139) is informative. The styrenes (137) and (139)⁴³ both give rise to broadened aromatic singlets. However, the (*Z*)-isomer (138) exhibits an AA'XX' system for the aromatic protons, presumably due to through space deshielding of the protons at C-2 and C-6 by the proximal oxygen atom at the β -position.

Separate oxidative cleavage³⁰ ($KMnO_4/HO^-$) of the styrenes (137) and (138) yields 4-chlorobenzoic acid (140) exclusively (Experimental),

confirming the presence of a 4-chloro-substituted benzene ring.

There is no evidence (1H n.m.r.) for the presence of any further styrene derivatives in either the crude reaction mixture or the residues after the removal of the arenes (137) and (138). Indeed, the symmetrical g.l.c. peaks for both (137) and (138) confirm their homogeneity. No other products from the dehydrochlorination of (112) have been characterized, and although the combined yields of the styrenes (137) and (138) is low

(31%), it is similar to those obtained in the dehydrohalogenation of their bicyclic counterparts.¹⁰ Consequently the production of (137) and (138) can be taken to represent a major reaction pathway in the dehydrochlorination of the tricycle (112).

On changing the medium for dehydrochlorination of the tricyclo-octane (112) to *t*-BuOK in DMSO, a severely discoloured reaction mixture resulted. This afforded the same (*E*)- and (*Z*)-styrenes (137) and (138) but in yields of 31 and 4% respectively. (*cf.* 16 and 15% respectively in THF). Thus, while the overall yield of styrenes is very similar, the thermodynamically more stable (*E*)-isomer (137) predominates in *t*-BuOK/DMSO which is known to be the more basic medium of the two. While the (*Z*)-isomer (138) undergoes isomerization to the (*E*)-isomer on standing, the rate of rearrangement is such that dehydrochlorination cannot proceed exclusively to yield ^{the} (*Z*)-isomer. Consequently, it is not clear whether the medium influences the rate of (*E*) | (*Z*) isomerization, or the ratio of the initially produced styrenes (137) and (138), or a combination of the two processes.

Dehydrochlorination of the individual epimers of the "linear" trichlorotricyclo octane mixture (113a,b) was not undertaken as epimerization of the mono-chloro-cyclopropyl moiety proceeds readily in basic media (see p. 34). However, the 6.5:1 mixture of (113a,b) was subjected to *t*-BuOK (11 mol.equiv.) in DMSO. The resultant product mixture contained at least six u.v. active components by analytical t.l.c., although only one of these appeared to be present in significant amounts. P.t.l.c. (three successive elutions with light petroleum) afforded one major band ($R_F = 0.26$) together with immobile baseline material. The u.v. active band was extracted to yield a clear colourless oil identified as (*E*)- β -*t*-butoxy-styrene (141) principally from its spectroscopic data.

Fig. 1 60 MHz ^1H n.m.r. Spectrum of
(E)- β -t-Butoxystyrene (141)

(141)

(142)

The ^1H n.m.r. spectrum of styrene (141) (Fig. 1, p. 45) reveals a nine proton singlet (1.33 p.p.m., t-BuO), two one-proton vinylic doublets (5.92 and 6.97 p.p.m., $J = 12$ Hz) and a broad five proton aromatic singlet (7.20 p.p.m.). The doublets at 5.92 and 6.97 p.p.m. have been assigned as due to *trans*-vinylic protons at the β - and α -positions respectively. The infra-red spectrum of styrene (141) exhibits a strong absorption at 1654 cm^{-1} (C=C) and a pair of bands, at 746 and 688 cm^{-1} , characteristic of a mono-substituted aromatic nucleus. The mass spectrum reveals the molecular ion at m/e 176 ($\text{M}^{+\cdot}$) (35%) and the base peak at m/e $(\text{M}-\text{C}_4\text{H}_8)^{+\cdot}$. This fragmentation is again fully consistent with the presence of a *t*-butyl vinyl ether.

In addition to providing satisfactory microanalytical data, compound (141) undergoes oxidative cleavage ($\text{KMnO}_4/\text{HO}^-$) to benzoic acid (48%)

as the sole isolable acid product. Spectroscopic (^1H n.m.r.) examination of the crude reaction mixture from the dehydrochlorination of (113a,b) and the residue remaining after isolation of the (*E*)-styrene (141) provided no evidence for the (*Z*)-isomer (142).

Attempts to effect dehydrochlorination of the epimeric tricyclo-octanes (113a,b) with the base in THF failed, and starting material (57% recovery after recrystallization) was the only species isolated.

The dehydrochlorination of the "linear" tricyclo-octanes (112) and (113a,b) using a variety of base concentrations (6-25 mol. equiv.) in the appropriate solvent leads to the same products with no significant change in the isomer ratio or the yields. Thus competing concentration dependent pathways, a feature in the dehydrohalogenation reactions of a number of bicyclic species discussed in Chapter one,^{14,15} do not operate at the expense of styrene production in these systems at least.

In contrast to the epimeric mixture of trichlorotricyclo-octanes (113a,b) dehydrohalogenation of 4,4-*endo*-8-tribromo-*anti*-tricyclo[5,1,0,0^{3,5}]-octane (115a) proceeds with *t*-BuOK in THF. P.t.l.c. of the crude reaction mixture gave only one major band at $R_F = 0.5$ which yielded a pale green oil tentatively assigned as (*Z*)- β -*t*-butoxystyrene (142) (2%) on the basis of spectroscopic data. This assignment remains tentative, as attempts to obtain additional quantities of (142) for a fuller characterization were thwarted by the non-reproducibility of the reaction.

The ^1H n.m.r. spectrum of the unstable oil proposed as (*Z*)- β -*t*-butoxystyrene (142) exhibits a nine proton singlet (1.35 p.p.m., *t*-BuO) two single-proton vinylic doublets (5.16 and 6.41 p.p.m., $J = 7.2$ Hz) and two overlapping complex multiplets centred at 7.15 and 7.50 p.p.m. in a ratio of 3:2 respectively. The doublets at 5.16 and 6.41 p.p.m. are assigned to the vinylic protons at the β - and α -positions respectively,

and the magnitude of the coupling constant confirms a *cis*-substituted double bond. The complex multiplets at 7.15 and 7.50 p.p.m. have been assigned to the aromatic protons at positions 3, 4 and 5, and those at positions 2 and 6 respectively. The mass spectrum of compound (142) is very similar to that of the (*E*)-isomer (141) (see p. 46) [m/e 176 (M^{+}) (17%) and 120 ($M-C_4H_8$) $^{+}$ (100%)] and the infra-red spectrum supports an olefinic bond (1640 cm^{-1}) and a mono-substituted aromatic ring (780 and 695 cm^{-1}).

Reaction of 4,4-*endo*-8-tribromo-*anti*-tricyclo[5,1,0,0^{3,5}]octane (115a) with *t*-BuOK (17 mol.equiv.) in DMSO rapidly gave the characteristic pitch black reaction mixture which, after standing at ambient temperature for 17 hours yielded (*E*)- β -*t*-butoxystyrene (141) reproducibly (*c.* 3%) which was identical in all respects to a sample obtained from the reaction of the trichlorotricyclo-octanes (113a,b). In none of these reactions was any evidence for the corresponding (*Z*)-isomer (142) obtained. Indeed the n.m.r. spectrum of the residue after removal of the styrene (141) showed neither vinylic nor aromatic resonances; only *t*-butoxy and alicyclic/aliphatic resonances were present.

Dehydrobromination of 4,4,8,8-tetrabromo-*anti*-tricyclo[5,1,0,0^{3,5}]octane (114) with *t*-BuOK (31 mol.equiv.) in THF (the tetrabromo compound is practically insoluble in DMSO) resulted in the expected pitch black reaction mixture. After the appropriate reaction time, conventional work-up (Experimental) gave rise to two major components as clear colourless, sweet smelling, oils. The ^1H n.m.r. spectrum of the more mobile component ($R_F = 0.6$) revealed resonances characteristic of a *cis*- β -*t*-butoxystyrene. The low resolution mass spectrum displayed molecular ions at m/e 254 (6%) and 256 (6%) (M^{+}) with the base peaks at m/e 198 (100%) and 200 (98%) ($M-C_4H_8$) $^{+}$. The subsequent fragmentation closely paralleled that displayed

Fig. 2 20 MHz ^{13}C n.m.r. Spectrum of the
(Z)-3- and 4-Bromo- β -t-butoxystyrenes (143a,b)

by the 4-chloro- β -t-butoxystyrenes (137) and (138). These data are, clearly, indicative of a nuclear brominated β -t-butoxystyrene. Although satisfactory microanalytical data could not be obtained for this component ($\sim 1.5\%$ error on carbon) because of its slow decomposition on standing, an accurate mass determination of the freshly prepared material was fully in accord with a $C_{12}H_{15}BrO$ species. While the infra-red spectrum of the oil is also fully compatible with this type of structure the aromatic resonances in the 1H n.m.r. spectrum are not consistent with the exclusive presence of the

(143a)

(143b)

4-bromostyrene (143a) as anticipated by analogy with the formation of 4-chlorostyrene (138) from the tetrachloro-system (112). In particular, the presence of a low field aromatic multiplet at 8.01 p.p.m. suggests the 3-bromosubstituted styrene (143b) may well be present; only an aromatic proton straddled by the bromine atom and the *cis*-t-butyl vinyl ether moiety is likely to experience this degree of deshielding. In addition a second vinylic doublet at 6.20 p.p.m. ($J = 7.5$ Hz) lends further support for the presence of a second isomer, to an extent of *c.* 20%.

The ^{13}C n.m.r. of the freshly chromatographed oil (Fig. 2) further supports the presence of two isomers in a ratio of *c.* 80:20 as evidenced by the dual resonances for both the α - (103.7 and 104.8 p.p.m.) and β - (142.4 and 141.6 p.p.m.) carbon atoms. The chemical shifts of the

α -carbons of the bromostyrenes (143a,b) are compatible with the shielding anticipated for C2 of a vinyl ether, e.g. (144),⁴⁵ coupled with the

(143a,b)

(144)

deshielding effect of the aromatic ring. The low field vinylic resonances for the β -carbon atoms in the styrene are in the normal region and reflect the deshielding effect of the adjacent oxygen. The complex pattern for the aromatic carbons also supports the presence of a second isomer. While a *para*-substituted aromatic nucleus would contain only four magnetically non-equivalent carbon atoms, nine distinct aromatic signals are recorded. This is most consistent with the presence of a second (but not a third) and unsymmetrically disubstituted aromatic ring (which would display six

aromatic resonances). On the basis of these data the (Z)-bromo- β -t-butoxystyrenes are assigned as a 4:1 mixture of (Z)-4-bromo- and (Z)-3-bromo- β -t-butoxystyrene (143a,b) respectively.

The second, and less mobile component ($R_F = 0.4$) from the reaction of the tetrabromotricyclo-octane (114) with t-BuOK furnished a ^1H n.m.r. spectrum which displayed vinylic, aromatic and t-butoxy resonances all fully consistent with a β -t-butoxystyrene having a *trans*-configuration about the double bond ($J = 12$ Hz). The low resolution mass spectrum confirmed the presence of a mono-bromo species (M^+ 256, 258) and a t-butyl vinyl ether $[(M-C_4H_8)^+, 198, 200]$. The molecular formula of $C_{12}H_{15}OBr$ was determined by high resolution mass spectrometry, as attempts to obtain microanalytical data were again foiled by the slow decomposition of this oil on standing. The ^1H n.m.r. spectrum of this component displayed a single t-butoxyl resonance at 1.33 p.p.m. and a complex multiplet in the region 6.7-7.45 p.p.m. containing overlapping resonances for the aromatic and α -protons. However, consistent with the asymmetry of the aromatic signals is the presence of two β -proton doublets at 6.15 and 5.88 p.p.m. ($J = 12.0$ Hz) indicating the presence of a second bromo-styrene. The ^{13}C n.m.r. of this component (Fig. 3) once again features dual resonances for the α - (108.6 and 108.4 p.p.m.) and β - (144.2 and 142.8 p.p.m.) carbon atoms in a ratio of 4:1. Furthermore, the presence of ten resonances for the aromatic carbons is consistent with the presence of both a symmetrical and unsymmetrical bromo- β -t-butoxystyrene and these are assigned as

(145a)

(145b)

(*E*)-4-bromo- and (*E*)-3-bromo- β -t-butoxystyrene (145a,b) respectively, by analogy with their geometric counterparts (143a,b). However, this latter assignment must remain tentative.

Separate oxidative cleavage ($\text{KMnO}_4/\text{HO}^-$) of the two bromo-styrene mixtures obtained from the tetrabromotricyclo-octane (114) gave acidic products which were esterified ($\text{CH}_2\text{N}_2/\text{Et}_2\text{O}$) to give the corresponding methyl

benzoates. Small quantities of neutral materials were also obtained but these were too small to allow a full analysis. However, t.l.c. suggests the majority of this material to be unreacted starting material. The ^1H n.m.r. of the purified (p.t.l.c.) methyl benzoates (mixtures of the authentic methyl 2-, 3- and 4-bromobenzoates could not be separated by t.l.c. using the eluents employed in this purification) from both the (*E*)- and (*Z*)-bromostyrene mixtures were identical. An aromatic AA'XX' system (7.62 p.p.m.) characteristic of the methyl 4-bromobenzoate was observed and indeed the spectrum was identical to that of an authentic sample, thereby confirming its presence. However, other very weak aromatic resonances were observed indicating the presence of another bromobenzoate, but because of the low yields involved in the oxidation, an unequivocal assignment of these less intense signals could not be obtained. Indeed, while the ^{13}C n.m.r. spectrum of the product esters also confirms the presence of methyl 4-bromobenzoate, other low intensity signals have remained

unassignable. Attempts to characterise the ester components by g.l.c. methods were also unsuccessful as neither mixtures of the authentic methyl or butyl bromobenzoates could be effectively separated using this technique despite the use of a large number of different stationary phases and columns. (Experimental).

Attempts to establish the sole presence of the bromo- β -t-butoxy-styrene skeleton in the dehydrobromination product mixtures from (114) by chemical methods met with only partial success. Separate hydrogenation/hydrogenolysis of the (143) and (145) (*E*)- and (*Z*)-mixtures gave a complex product mixture after the uptake of two molar equivalents of hydrogen. The major (c. 40%) and only characterized component of this mixture is

identified as 2-phenylethyl t-butyl ether (146), by comparison with an independently prepared sample. Attempts to improve this yield by employing ethanolic sodium hydroxide as the reaction medium, to remove hydrogen bromide, failed. The unsatisfactory yields in these reactions may reflect the lability of the carbon-oxygen bonds in (143) and (145) to the reaction conditions, and the inherent instability of these systems as a whole.

The formation of styrenes from the "linear" tricyclo-octanes (112)-(115) does not appear to be confined to the use of t-BuOK as base. Preliminary studies have shown that treatment of the tetrachloro-*anti*-

tricyclo[5,1,0,0^{3,5}]octane with sodium methoxide in DMSO gives rise to a complex mixture of products from which (*E*)-4-chloro- β -methoxystyrene (147) (1.5%) has been tentatively identified, on the basis of its spectroscopic

(147)

(148)

data. The ¹H n.m.r. spectrum reveals a methoxyl singlet (3.63 p.p.m.), *trans*-disposed α - and β -vinyl proton doublets (6.95 and 5.69 p.p.m., $J = 12$ Hz) and a slightly broadened four proton aromatic singlet (7.10 p.p.m.). The mass spectrum of (147) confirms the presence of a mono-chloro species with molecular ions at m/e 168 (5.7), 170 (1.68%). Limited evidence for the presence of the corresponding (*Z*)-4-chloro- β -methoxystyrene (148) in the reaction mixture was also obtained, but the yield is very low. In fact the low conversion to the β -methoxystyrenes (147) and (148) is consistent with the presence of a more nucleophilic base intercepting reaction intermediates (*cf.* p. 6) as evidenced by a predominance of methoxyl resonances in the ¹H n.m.r. spectrum of the crude reaction mixture.

In contrast to their "linear" counterparts, the "angular" tricyclo-octanes (116)-(119) gave only highly complex product mixtures when subjected to the dehydrohalogenation conditions employed in the preceding sections.

- (116) $X=R=Cl$
 (117) $X=Cl$, $R=H$
 (118) $X=R=Br$
 (119) $X=Br$, $R=H$

Despite many variations in the reaction conditions, the separation procedures (t.l.c.) found to be effective for the linear analogues (112)-(115) are without effect on the severely discoloured tars obtained from the "angular" tricyclo-octanes. No evidence for the presence of the types of styrene derivatives produced in the dehydrohalogenation of compounds (112)-(115) was obtained and the product mixtures contained only traces of olefinic and aromatic materials (1H n.m.r.). Quenching the black solution from compound (116) (t-BuOK/THF) after c. 30 minutes at 0° leads to a 70% recovery of starting material as the only identifiable species. Because of these results comparative dehydrohalogenation studies with these systems was not possible and consequently this aspect of the study was terminated.

In none of the dehydrohalogenation studies described above was any evidence (1H n.m.r. and malodour⁴⁶) for the presence of the bis-cyclopropa-benzenes, (41) and (120), obtained. The formation of styrenes from the "linear" tricyclo-octanes (112)-(115) appears to represent an entirely different reaction course to those followed by ω,ω -dihalogenobicyclo[n,1,0]-alkanes, e.g. (8), and their unsaturated counterparts, e.g. (30), as discussed in Chapter one.

The production of styrenes from their tricyclic precursors, must involve deep-seated skeletal rearrangement and parallels the gross trans-

formations featured in the mild thermolysis of the bromomethoxy-tricyclo[5,1,0,0^{3,5}]octanes (109) and (110).

Iskander³⁰ has adequately rationalized the formation of 3-bromostyrenes (111) (Scheme 23) by sequential cyclopropyl-allyl ring cleavage to give the 1,5-dibromocyclo-octatetraenes (149) which subsequently undergoes valence bond isomerization to the corresponding bicyclic tautomers (150). Ionization, with concomitant homocyclopropenium ion (151) formation is followed by nucleophilic capture (Br^-) from either face of the four-membered ring, to give an epimeric mixture of the bicyclo[4,2,0]-octa-2,4,6(7)-trienes (152). Finally, conrotatory electrocyclic ring cleavage yields the 3-bromostyrenes (111). There is ample literature

Scheme 23

precedent for this type of thermolytic cyclo-octatetraene-styrene conversion.⁴⁷ However, this pathway cannot be in operation for the tetrachloro-compound (112) nor can it be the major pathway in the rearrangement of the tetrabromo-compound (113), *since 3-chlorostyrenes and not the observed 4-isomers* (137), (138), (143a) and (145a) are predicted. However, the route described in Scheme 23 could account for the production of the unsubstituted styrene (141) from its trihalogeno-precursors (113) and (115). Despite this, the analogy with the behaviour of the tetrahalogenotricyclo[5,1,0,0^{3,5}]octanes (112) and (114) argues for a common mechanism in all cases.

It was suspected that the 4-halogenostyrenes (137), (138), (143a), (145a) and presumably the parent styrene (141) could be formed by the route depicted in Scheme 24. Initial 1,3-elimination is stereoelectronically feasible (from molecular models) and would give the trihalogenotetracyclo[5,1,0,0^{2,4},0^{3,5}]octane (153). Since Paquette and Taylor⁴⁸ have demonstrated that cleavage of the bicyclobutane component in derivatives of this ring system occurs in preference to rupture of the three-membered ring, compound (153) could be expected to yield the 1,4-dihalogenocyclo-octatetraenes (155c,d) *via* rearrangement of the semibullvalenes (154).⁴⁹ Application of the Iskander route to these annulenes (155c,d) with nucleophilic capture of the homocyclopropenium ion (157) by the excess *t*-butoxide would complete the sequence.

The formation of the proposed 3-bromostyrenes (143b) and (145b) may arise from the 4-bromo-isomers (143a) and (145a) by so-called "halogen dancing", *via* the bromophenyl anions (159) (Scheme 24). Such scrambling of bromobenzene derivatives with *t*-BuOK has been recorded by Bunnett and co-workers, but the less labile chloro-analogues remain unchanged under these conditions.⁵⁰ Alternatively, the *m*-bromostyrenes and the unsubstituted

Scheme 24

compound (141) may arise directly by the Iskander route (Scheme 24).

The 1,4- and 1,5-dihalogenocyclo-octatetraenes, proposed as intermediates in the formation of the β -t-butoxystyrenes have recently been synthesized⁵¹ by Paquette and co-workers by controlled addition-elimination sequences from the appropriate monohalogenocyclo-octatetraenes (155a,b). However, the procedure employed produces a mixture of the 1,4- and 1,5-derivatives which is only separable with great difficulty. Consequently, in order to determine whether halogenocyclo-octatetraenes are intermediates in the tricyclo-octane - styrene conversion, the more accessible monohalogenocyclo-octatetraenes (155a,b) have been investigated. However, it should be noted that styrene formation would not allow a distinction to be made between the two proposed pathways (Scheme 24).

The preparation of chloro- and bromo-cyclo-octatetraene (155a,b) involved controlled halogenation of cyclo-octatetraene (162) [available

Scheme 25

in two steps from *cis,cis*-cyclo-octa-1,5-diene (Experimental)] and dehydrohalogenation in situ, using *t*-BuOK as base (Scheme 25) as described recently by Huisgen and co-workers.⁵² Dehydrobromination of the bicyclo-octadiene intermediate (163b) proceeded smoothly to give bromocyclo-octatetraene (155b) in 80% yield. However, dehydrochlorination of the dichlorobicyclo-octadiene (163b) proceeded less readily and a mixture of unreacted bicyclo-octadiene (163b) and the desired chlorocyclo-octatetraene (155a) (*c.* 1:4) was obtained. This was readily separated by column chromatographic methods.

Subjection of bromocyclo-octatetraene (155b) to the same dehydrobromination conditions employed throughout this study led to a severely discoloured reaction mixture. The only isolable products (p.t.l.c.) have been identified as cyclo-octa-1,3,5-trieno[b]naphthalene (2.1%), and *t*-butoxycyclo-octatetraene (166) (15%) (Scheme 26) by comparison of their data with those

Scheme 26

previously recorded.⁵³ No evidence (^1H n.m.r. and t.l.c.) was obtained for the presence of the (*E*)- or (*Z*)- β -t-butoxystyrenes (141) and (142) in either the crude reaction mixture or the product residues. Chlorocyclo-octatetraene (155a) behaves in a similar fashion, yielding t-butoxycyclo-octatetraene (166) (16%) but no dimeric product. Once again there was no evidence (^1H n.m.r. or t.l.c.) for the presence of (*E*)- or (*Z*)- β -t-butoxystyrenes.

The behaviour of both of the halogenocyclo-octatetraenes (155a,b) described above is fully consistent with the reaction of bromocyclo-octatetraene under very similar conditions (t-BuOK/ether),^{54,55} where t-butoxycyclo-octatetraene (166) and cyclo-octa-1,3,5-trieno[b]naphthalene (168) are also isolated. The formation of the annulenes (166) and (168) has been rationalized⁵⁴ as depicted in Scheme 26, and involving 1,2-elimination to give the highly reactive 1,2-dehydrocyclo-octatetraene (165). Subsequent addition of t-butanol yields t-butoxycyclo-octatetraene (166). While dimerization and rearrangement (Scheme 26) furnishes cyclo-octa-1,3,5-trieno[b]naphthalene (168), its low yield presumably reflects the high nucleophile concentration in the reaction mixture, and thus the interception of the dehydroannulene (165) before significant dimerization can occur. Since bis-dehydrocyclo-octatetraene (169) is thought⁵⁶ to be more stable than its mono-dehydro-

Scheme 27

counterpart (165), reactions of 1,4- and 1,5-dihalogenocyclo-octatetraenes appear unlikely to differ dramatically from those of the monohalogeno counterparts.

The results described above argue strongly against the involvement of halogenocyclo-octatetraenes as intermediates in the formation of β -t-butoxystyrenes by dehydrohalogenation of the tricyclo-octanes (112)-(115). Indeed, a re-examination of the product mixtures resulting from reaction of the tricyclo-octanes (112)-(115), in the light of the above findings, revealed no evidence for species such as t-butoxycyclo-octatetraenes. Consequently cyclo-octatetraene formation does not represent a detectable reaction pathway in the base promoted rearrangements of the linear tricyclo-octanes (112)-(115).

An alternative mechanistic rationalization of the tricyclo-octane - β -t-butoxystyrene conversion is illustrated in Scheme 27. Conventional 1,2-elimination and formation of the cyclopropene (171) followed by prototropic shift (Chapter 1) would give olefin (172) (Path a, Scheme 27). Further reaction of this highly strained species (172) could proceed either by methylene-cyclopropane rearrangement (m.c.p.) to give the ring-contracted tricycloheptane (173) or by 1,4-elimination to give the cyclopropacycloheptatriene (174). Methylene cyclopropane rearrangement (m.c.p.) of this latter compound would yield the norcaradiene (176), which can also arise by 1,4-elimination in the tricycloheptane (173). Another route to the key intermediate (176) could involve initial 1,4-elimination to give the homotropilidene (175), 1,2-elimination and prototropic shift to give the cyclopropacycloheptatriene (174), and methylene cyclopropane rearrangement (Path b, Scheme 27). Although electrocyclic ring opening of the norcaradiene (176) would give the thermodynamically more stable heptafulvene (177), removal of the norcaradiene tautomer (176) from the equilibrium

mixture by aromatization can occur in two ways. Base abstraction of H1 (Path c, Scheme 27) would yield the 4-substituted phenylacetylenes (179) and (180). Alternatively, base removal of H6 (Path d, Scheme 27) would furnish the 3-substituted acetylenes (181) and (182). Finally, nucleophilic attack at the terminal position of acetylenes (179)-(182) would yield an (*E*)/(*Z*) mixture of the appropriate β -t-butoxystyrenes.

The observed preference for 4-halogenated styrene formation necessarily requires selective ring cleavage of the norcaradiene (176) by abstraction of H6 (Path d, Scheme 27). Indeed, the alternative route involving abstraction of H1 may be less favourable, because mesomerically, the halogen atom at C3 decreases the acidity of this proton relative to H6. Such distinction is not possible in the unsubstituted case.

Of the large number of possible intermediates described in Scheme 37, the most readily obtainable are the arylacetylenes (178)-(180). Consequently, to test the validity of the mechanistic hypothesis outlined above, an investigation of these arenes was undertaken. While phenylacetylene (178) is commercially available, the 4-halogeno derivatives (179) and (180) were prepared by literature methods,⁵⁷ as summarized in Scheme 28.

Scheme 28

Subjection of phenylacetylene (178) to the reaction conditions employed for the trihalogenotricyclo-octanes (113) and (115) ($t\text{-BuOK/DMSO}$) resulted in a characteristically charred reaction mixture which contained traces of the acetylene (g.l.c.) and a single major chromophoric product. This was isolated as a white crystalline solid and identified as (*E*)-1,4-diphenylbut-2-enyne (190) (26%) from its spectroscopic data and comparison of its melting point with the literature value.⁵⁸

Scheme 29

There is no evidence (^1H n.m.r. and t.l.c.) for the presence of (*E*)- β - t -butoxystyrene (141) or its (*Z*)-isomer (142) in either the crude, or residual, reaction material.

Similar subjection of the 4-halogenophenylacetylenes (179) and (180) to $t\text{-BuOK}$ in either THF or DMSO gave rise to a multitude of chromophoric products. No attempts were made to isolate the small quantities of each

individual component involved. However, no evidence for the presence of halogeno- β -t-butoxystyrenes was obtained from any of these mixtures.

The dimeric product (190) formed from phenylacetylene (178) can be rationalized by base abstraction of the acetylenic proton and subsequent attack by this species at the terminal position of an unionized molecule of substrate (178) (Scheme 29). The production of the thermodynamically more stable (*E*)-isomer (190) may arise *via* the intermediacy of the vinyl carbanion (189) with the bulky substituents in a favoured antiperiplanar conformation. The absence of the corresponding 4-halogeno-substituted dimers (*vide supra*) may reflect the lower acidity of the acetylenic proton and/or the less nucleophilic nature of the 4-halogeno-acetylides.

On the basis of the results described above phenylacetylenes are highly unlikely to be intermediates in the formation of β -t-butoxystyrenes from the tricyclo-octanes (112)-(115) and halogenocyclo-octatetraenes have already been eliminated. While labelling studies using isotopically enriched carbene (^{12}C or ^{13}C) could be employed to considerable advantage (Scheme 30)

Scheme 30

for following at least two of the carbon atoms in this skeletal rearrangement, financial restrictions have prevented this type of investigation from being carried out.

An alternative form of labelling would involve suitably substituted tricyclo-octanes. Ideal candidates for this type of study were considered to be the tetrachloro mono- and di-methoxytricyclo[5,1,0,0^{3,5}]octanes (191)-(194). These are the chloro-analogues of the bromomethoxytricyclo-

- (191) $R^1 = \text{OCH}_3, R^2 = R^3 = \text{H}$
 (192) $R^1 = R^3 = \text{OCH}_3, R^2 = \text{H}$
 (193) $R^1 = \text{H}, R^2 = R^3 = \text{OCH}_3$
 (194) $R^1 = R^2 = \text{OCH}_3, R^3 = \text{H}$

octanes (109) and (110) which furnish 3-bromostyrenes on mild thermolysis. Consequently, an examination of the base promoted rearrangements of compounds (191)-(194) was undertaken, and the results from this study form the basis of the following chapter.

CHAPTER THREE

SUBSTITUENT EFFECTS IN THE DEHYDROHALOGENATION
OF SOME TETRAHALOGENOTRICYCLO-OCTANES

The synthesis and dehydrohalogenation of the mono- and di-methoxytetrahalogenotricyclo-octanes (191)-(194) has been undertaken because of the possibility of gaining further information on the tricyclo-octane/styrene reactions by virtue of the presence of methoxy labelled carbon atoms. In addition, it would also allow for comparing and contrasting the thermolytic behaviour of the bromomethoxytricyclo-octanes (109)-(110) with the base promoted rearrangements of their chloro-counterparts.

The previously known⁵⁹ 1- and 1,5-di-methoxy-4,4,8,8-tetrachloro-*anti*-tricyclo[5,1,0,0^{3,5}]octanes (191) and (192) and their unknown analogues (193) and (194) were prepared in excellent yields by the route illustrated in Scheme 31. Thus Birch reduction of the appropriate aromatic

Scheme 31

ether (readily prepared by methylation of the corresponding phenol) gives the cyclohexadienes (199)-(202). Subsequent bis-addition of dichlorocarbene (ethyl trichloroacetate/sodium methoxide) furnishes the required mono- and di-methoxy-4,4,8,8-tetrachloro-*anti*-tricyclo-octanes (191)-(194) in overall yields of *c.* 75%. This represents a two-fold increase in the previously reported⁵⁹ yields and results from a prolonged reaction time (22 vs 0.5 h) in the carbene addition step.

The ^{13}C and ^1H n.m.r. spectra of compounds (191)-(194) are particularly informative and the asymmetry conferred upon the "linear" tricyclo-octane skeleton by methoxyl substitution in some of these compounds is clearly evident from these data. The more symmetrical 1,3- and 1,5-dimethoxytricyclo-octanes (193) and (192) display only five carbon resonances as expected, while the asymmetrical 1-methoxy derivative (191) (Fig. 4, p. 73) exhibits nine well resolved resonances all of which have been assigned. (Table 1). The ^1H n.m.r. spectrum of the 1,5-dimethoxytricyclo-octane (192) (Fig. 5) in addition to displaying a six-proton singlet (3.40 p.p.m., $2\times\text{OCH}_3$) exhibits

(192)

three, two-proton, doublets of doublets characteristic of an AMX system,⁶⁰ in which the A and M protons are geminally related. The coupling constants (J_{AM} 15 Hz; J_{AX} 7.8 Hz; J_{MX} 2.0 Hz) reflect the smaller dihedral angle

Fig. 4 20 MHz ^{13}C n.m.r. Spectrum of
4,4,8,8-Tetrachloro-1-methoxy-*anti*-
tricyclo[5,1,0,0^{3,5}]octane (191)

TABLE I

Chemical Shifts and Assignments of ^{13}C N.M.R. Resonances
of the Methoxytricyclo-octanes (191), (192) and (193)

COMPOUND CARBON ATOM	 (191)	 (192)	 (193)
C1	62.29	62.25	63.61
C2	17.22	18.90	22.51
C3	24.88	31.77	63.61
C4	64.31	65.29	65.37
C5	23.16	62.25	30.74
C6	14.58	18.90	15.52
C7	30.62	31.77	30.74
C8	64.90	65.29	65.37
OCH ₃	54.52	54.76	54.67

Fig. 5 60 MHz ^1H n.m.r. Spectrum of 4,4,8,8-Tetrachloro-1,5-dimethoxy-*anti*-tricyclo[5,1,0,0^{3,5}]octane

between H_A and H_X (c. 5° from Drieding molecular models) than between H_M and H_X (c. 120°). The 1H n.m.r. spectrum of the isomeric 1,3-dimethoxytricyclo-octane (193) features a six-proton singlet (3.45 p.p.m., $2 \times OCH_3$) and a two-proton singlet (2.62 p.p.m.) which has been assigned to the isolated methylene group protons at C2. The remaining protons are characterized by a pair of two-proton doublet of doublets (2.23 and 1.64 p.p.m.) which have been assigned to the methylene protons at C6 and the cyclopropyl protons at C5 and C7, respectively. In contrast the 1,7-dimethoxy- and 1-methoxytricyclo-octanes (194) and (191) do not contain "insulating" methoxyl substitution patterns and consequently the 1H n.m.r. spectra of these compounds display more extensively coupled (and unresolvable) multiplets for the ring protons.

The dehydrochlorination of the methoxytricyclo-octanes (191)-(194) under the conditions described in the preceding Chapter (addition of the substrate to base) results in severe decomposition and, ^{in each case} a multitude of products are formed (t.l.c.). The sole isolable product (4%) results from compound (192), and microanalytical, together with mass spectral, data identify this clear colourless oil as a $C_{10}H_{11}Cl_3O_2$ species. However further discussion as to the nature of this species is postponed until later in the text (see p.85) in light of the following.

In direct contrast to the above, addition of a filtered THF solution of t-BuOK (1.25 molar equiv.) to a solution of the same 1,5-dimethoxytricyclo-octane (192) in THF yields an entirely different chromophoric $C_{10}H_{11}Cl_3O_2$ species (54%). This is identified as 4,8,8-trichloro-3,7-dimethoxybicyclo[5,1,0]octa-2,4-diene (203) (a homotropilidene) on the basis of its spectroscopic data. The 1H n.m.r. spectrum reveals two distinct methoxyl resonances at 3.42 and 3.54 p.p.m. - the latter chemical shift suggests a vinyl ether. In addition, the presence of a one-proton

vinyllic triplet (6.47 p.p.m., $J = 3$ Hz) argues for the presence of a tetra-substituted dienic moiety. The remaining higher resonances reveal a one-proton doublet of doublets at 3.29 p.p.m. ($J = 18$ and 3 Hz), a second doublet of doublets (2.90 p.p.m., $J = 18$ and 3 Hz), and finally a high field doublet (2.23 p.p.m., $J = 6$ Hz). The multiplets at 6.47, 3.29 and 2.90 p.p.m. are reminiscent of an AMX system in which $J_{AX} \approx J_{MX}$, and the large coupling constant implicates a geminal relationship between the A and M protons. This type of coupling system is fully consistent with the coupling anticipated between the vicinally related H5 vinyllic and H6 methylene protons in (203). The remaining pair of doublets (4.88 and 2.23 p.p.m.) reflect a single two-spin (AB) system and is again fully consistent with the coupling anticipated between H2 (vinyllic) and H1 (cyclopropyl). This coupling allows a ready distinction between compound (203) and its [1,5]H shift isomer (204) which would display vicinal coupling between the adjacent vinyl protons. The ^{13}C n.m.r. spectrum of (203) reveals ten carbon resonances testifying to the complete asymmetry of the species. These resonances have been assigned as indicated in Table II. The presence of four sp^2 -hybridized carbon atoms, two of which constitute a vinyl ether moiety [shielding and deshielding of C2 and C3 respectively (see p. 51)], is evident from this data. Indeed, the

remaining two carbon atoms have resonances consistent with a vinyl chloride⁴⁵ moiety. The remaining higher field resonances are compatible

with the presence of the residual *gem*-dichloromethoxycyclopropyl unit.

The diene (203) is unstable and decomposes inside 3 hours with the evolution of hydrogen chloride when exposed to air at room temperature and this has prevented the collection of accurate microanalytical data. However, the mass spectrum of (203) at low ionization energy (12 eV) displays molecular ions at 268 (2.2%) and 270 (2.2%) and base peaks at m/e 233 (100%), 235 (64%), $(\text{M}-\text{Cl})^+$ fully in accord with a $\text{C}_{10}\text{H}_{11}\text{Cl}_3\text{O}_2$ species. An accurate mass determination (70 eV) of the $(\text{M}-\text{Cl})^+$ peak confirms a $\text{C}_{10}\text{H}_{11}\text{Cl}_3\text{O}_2$ species. The infra-red spectrum of the compound reveals bands at 1630 ($\text{C}=\text{C}$) and 3080 ($\text{C}-\text{H}$ cyclopropane stretch) cm^{-1} and is fully consistent in all respects with the proposed structure (203).

Treatment of both the 1- and 1,3-di-methoxytricyclo-octanes (191) and (193) in THF with a solution of the filtered base gave rise to the corresponding homotropilidenes (205) and (206) in 59 and 18% yields respectively.

The ^1H n.m.r. spectrum of the monomethoxyhomotropilidene (205) displays a one-proton vinylic doublet (4.94 p.p.m., $J = 6$ Hz) and a one-proton vinylic triplet (6.44 p.p.m., $J = 3$ Hz) reminiscent of the

Fig. 6 20 MHz ^{13}C n.m.r. Spectrum of
the Monomethoxyhomotropilidene (205)

TABLE II

Chemical Shifts and Assignments of ^{13}C N.M.R. Resonances
of the Homotropilidenes (203), (205) and (206)

COMPOUND CARBON ATOM

	(203)	(205)	(206)
C1	35.36	28.78	67.23
C2	91.82	91.91	92.39
C3	153.29	153.21	154.56
C4	128.48	128.02	127.77
C5	118.18	117.79	118.78
C6	26.87	22.40	22.81
C7	64.82	25.77	31.14
C8	69.19	66.63	69.52
OCH ₃ (VINYLIC)	54.97	54.69	55.36
OCH ₃ (CYCLOPR.)	54.78	-	54.96

multiplicities of the vinylic resonances for the dimethoxyhomotropilidene (203). Once again these multiplicities confirm the presence of (205) and not its [1,5]H shift isomer (207). The ^{13}C n.m.r. spectrum of (205) (Fig. 6) displays nine carbon resonances, all of which are readily assigned (Table II), and are fully in accord with the proposed structure.

Whereas the reactions of (191) and (192) proceed readily, that of (193) is markedly slower and the product homotropilidene (206) is contaminated with inseparable starting material. The 1H n.m.r. spectrum of the mixture allows for full assignment of the resonances due to the homotropilidene (206). Whereas the low field vinyl proton appears as a triplet (6.56 p.p.m., $J = 3$ Hz) as in (203) and (205), the higher field vinylic resonance (5.02 p.p.m.) is a singlet due to the absence of an adjacent (cyclopropyl) proton. Nonetheless, these multiplicities eliminate the [1,5]H shift-isomer (208) as the product of reaction. The ^{13}C data are also fully compatible with the structure ^{for (206)} (Table II) with ten distinct carbon resonances being observed. The high and low resolution mass spectra of (205) and (206) confirm the species as $C_9H_8Cl_3O$ and $C_{10}H_{11}Cl_3O_2$ respectively (Experimental). Surprisingly, the 1,7-dimethoxytricyclo-octane (194) is resistant to reaction and is recovered (81%) unchanged.

Attempts to characterize the homotropilidenes (203), (205) and (206) through their Diels-Alder adducts with 4-phenyl-4H-1,2,4-triazoline-3,5-dione (PTAD), the most potent dienophile known, have been unsuccessful.

Attempts to isolate other products from the reaction of the methoxytricyclo-octanes with filtered base have failed. In fact, 1,4-elimination in the monomethoxytricyclo-octane (191) can proceed in four distinct ways to give four different products (205), (207), (209),

Scheme 32

or (210). Remarkably the only one of these paths observed is that involving abstraction of an H₂ proton and concomitant cleavage of the Cl-C₇ cyclopropane ring bond to give, with chloride ion loss from C₈, product (205). The ¹H n.m.r. spectra of the residues left after the removal of starting

materials and products reveal a very low proportion of vinylic- or aromatic-containing products.

The formation of homotropilidenes does not appear to be confined to the tetrachloromethoxytricyclo-octanes (191)-(193). Preliminary studies with the previously known⁵⁹ tetrabromo-1,5-dimethoxytricyclo-octane (109) have led to a single major chromophoric product (43%) tentatively identified

as 4,8,8-tribromo-3,7-dimethoxybicyclo[5,1,0]octa-2,4-diene (211) on the basis of its ^1H n.m.r. and mass spectral data. The multiplicities of the resonances in the ^1H n.m.r. spectrum of (211) are identical with those of its trichloro-analogue (203) and the mass spectrum of (211) while not displaying a molecular ion exhibits an $(\text{M}-\text{Br})^+$ peak (100%). The absence of a parent ion, even at low (12 eV) ionizing voltages presumably reflects the higher lability of this compound (211) compared to its chloro-counterpart (203). Indeed, discolouration of the initially isolated clear colourless oil commences almost immediately at room temperature.

The regiospecific formation (vide supra) of the homotropilidenes (203), (205), (206), and (211) must involve initial 1,4-elimination. Although abstraction of H_2 (path a, Scheme 33a), as has been invoked in the mild thermolysis of analogues in weakly basic media (Scheme 33b),⁶¹ and is consistent with the increased steric demand of (193), it is not possible to

Scheme 33a

Scheme 33b

distinguish between this and removal of H6 (Path b, Scheme 33a) followed by rapid [1,5]H shift. On this basis it is hard to rationalize the resistance of the 1,7-dimethoxytricyclo-octane to 1,4-elimination, although the presence of a second cyclopropyl-methoxyl group may affect the lability

of the bridgehead σ -bond in basic media. The failure of (191), (192), (193), and (109) to suffer 1,2-elimination and yield a tricyclo-oct-1(8)-ene, by analogy with all other ring-fused *gem*-dihalogenocyclopropanes in the presence of strong base, is unusual and the results constitute the first examples of *t*-BuOK promoted 1,4-elimination in ring-fused cyclopropane systems.

Re-subjection of the homotropilidenes (203), (205), and (206) to base under either mode of addition shows the compounds to be remarkably resistant to further dehydrochlorination. For example, the 1,7-dimethoxybicyclo-octane (203) suffers some decomposition but the homotropilidene is recovered in yields of 62 (base to substrate) and 23 % (substrate to base) as the sole identifiable component. Similarly treatment of the monomethoxyhomotropilidene (205) (base to substrate) leads to 65% recovery of starting material. Surprisingly there was no evidence for cyclo-octatetraene formation, by further 1,4-elimination despite the increased acidity of the methylene protons in these systems.

It will be recalled that the addition of the 1,5-dimethoxytricyclo-octane (192) to a suspension of *t*-BuOK in THF gave rise to a $C_{10}H_{11}Cl_3O_2$ species. The 60 MHz 1H n.m.r. spectrum of this compound (Fig. 7, p. 86)

Fig. 7 60 MHz ^1H n.m.r. Spectrum of the
Unknown $\text{C}_{10}\text{H}_{11}\text{Cl}_3\text{O}_2$ Species
Obtained from (192)

displays two distinct methoxyl resonances at 3.55 and 3.71 p.p.m., the latter suggestive of a vinyl ether. In addition, the presence of a one-proton vinylic singlet (6.02 p.p.m.) and a one-proton vinylic doublet (5.63 p.p.m., $J = 3.0$ Hz) argues for the presence of a dienic moiety. The u.v. spectrum [λ_{max} 260 nm ($\log \epsilon$ 4.15)] and the chromophoric nature of the compound on t.l.c. support this. The remaining higher field resonances reveal a one-proton doublet of doublets (3.16 p.p.m., $J = 3$ and 6 Hz), a one-proton overlapping doublet of doublets (2.81 p.p.m., $J = 6$ and 8 Hz) and a one-proton doublet (2.2 p.p.m., $J = 8$ Hz). The absence of coupling of the order of 15 Hz (*c.f.* starting material, p. 75) suggests that geminal coupling is not involved in this case. The data clearly eliminate the homotropilidene (203) and its [1,5]H shift isomer (204) as structures for

(203)

(204)

for this compound because of the absence of appropriate vicinal coupling in the vinylic resonances. The 100 MHz ^1H n.m.r. spectrum of this unknown species further reveals that the lower field vinylic resonance is a one-proton doublet ($J = 1.0$ Hz), rather than a singlet. However, it is not clear as to which of the higher field resonances the coupling is associated with.

The ^{13}C n.m.r. spectrum of the compound (Fig. 7a, p.85) exhibits ten discrete resonances. The multiplicities obtained by ^{13}C - ^1H coupling experiments

Fig. 7a 25 MHz ^{13}C n.m.r. Spectrum of the Unknown
 $\text{C}_{10}\text{H}_{11}\text{Cl}_3\text{O}_2$ Species obtained from (192)

TABLE III

Comparison of Chemical Shifts of ^{13}C N.M.R. Resonances
of Unknown $\text{C}_{10}\text{H}_{11}\text{Cl}_3\text{O}_2$ Species and the Homotropilidenes
(203), (205) and (206)

UNKNOWN $\text{C}_{10}\text{H}_{11}\text{Cl}_3\text{O}_2$ SPECIES			$\sim\Delta\delta^a$	HOMOTROPILIDENES
δ	MULTIPLICITY	ASSIGNMENT		δ RANGE
164.9	s	$=\text{C}-\text{OCH}_3$	10-11	153.2-154.6
135.7	s	$=\text{C}-\text{Cl}$	7-8	127.8-128.4
108.7	d	$\text{HC}=\text{C}-\text{Cl}$	-(9-10)	117.8-118.8
92.4	d	$\text{HC}=\text{C}-\text{OCH}_3$	0	91.8-92.4
89.7	s	$\text{R}_3\text{C}-\text{OCH}_3$	23-26	64-67
88.1	s	R_2CCl_2	19	69
56.3	q	$\text{CH}_3\text{O}-\text{C}=\text{C}$	1	54.7-55.4
53.7	q	CH_3OCR_3	-1	54.7-55.4
50.4	d	RCHR_2	15-22	28-35
39.3	d,d	R_2CH_2	14-17	22-26

^a A negative sign represents shielding of resonances in left-hand column with respect to those in right-hand column.

as well as the tentative assignments are indicated in Table III. Significantly, the resonance at highest field (39.3 p.p.m.) is a doublet of doublets ($J = 142.9$ and 150.1 Hz) indicative of a methylene moiety with two non-equivalent protons attached. No long range C-H coupling is recorded. A comparison of the chemical shifts of these resonances with those for the homotropilidenes (203), (205), and (206) reveals dramatic differences (Table III). For example, the lowest field resonance has been assigned to C1 of a methyl vinyl ether, but is *c.* 10-11 p.p.m. more deshielded than the equivalent carbon resonances in the homotropilidenes. Indeed, almost without exception the chemical shifts of the resonances of the unknown species are at variance with their homotropilidene counterparts. In particular, the chemical shifts of higher field (non-methoxyl) resonances (39.3-89.7 p.p.m.) are all significantly deshielded (*c.* 14-26 p.p.m.) with respect to the homotropilidenes.

A comparison of the ^1H n.m.r. spectrum of the unknown species with those of compounds (203), (205), and (206) reveals that the vinylic proton resonances at 6.02 and 5.03 p.p.m. are shielded ($\Delta\delta$ 0.4-0.5) and deshielded ($\Delta\delta$ 0.1-0.2) respectively. Furthermore, as the higher field signal is a doublet (and not a triplet), it cannot be in a seven-membered ring adjacent to a $-\text{CH}_2-$ unless the conformation is markedly different from those of (203), (205), and (206). Finally, the low field proton exhibits small (1 Hz) long range coupling.

In light of the above, it is suggested that the doublet at 5.63 p.p.m. is due to a vinylic proton located as shown in (213) below, and coupled to a pseudo-axial allylic proton, H_b ($\theta \approx 90^\circ$) and not to the pseudo-equatorial allylic proton, H_c ($\theta \approx 0^\circ$) *viz.*

(213)

(214)

Furthermore, it is H_c and not H_b that is coupled to the remaining R_3CH proton (δ 1H 2.2; ^{13}C , 50.4). This is fully compatible with a molecular model of the homotropilidene (214) in which the H_c-H_d dihedral angle is *c.* 15° while that between H_b and H_d is *c.* 95° . The 1 Hz long range coupling exhibited by H_e in (214) is also accounted for in this structure. However, structure (214) suffers from the following deficiencies: (i) the deshielding of H_d by 0.1-0.2 p.p.m. relative to its counterparts in (203) and (205); (ii) the shielding of H_e by 0.4-0.5 p.p.m. relative to (203) and (205); and (iii) the dramatic deshielding of Cl, C6, C7 and C8. While the infra-red spectrum is very similar to that of homotropilidene (203) and the u.v. also compatible with the substituted diene, its formation from (192) is not easy to rationalize. In addition, the shielding and deshielding effects tend to argue for a completely different carbon skeleton than that depicted by (214).

In an attempt to obtain a crystalline adduct of the unknown compound for a crystallographic study, it was treated with a solution of PTAD in chloroform. While the fading of the crimson colour of the dienophile was markedly slower (16 h vs. 2 h) than for the homotropilidenes no characteristic adduct was obtained. Consequently, and despite the volume of data collected, the structure of this $C_{10}H_{11}Cl_3O_2$ species remains in considerable doubt.

When the non-methoxylated tricyclo-octanes (112) and (114) (Chapter 2) are subjected to the same conditions (filtered base to substrate), the styrenes (137), (138), (143), and (145) are produced, and while the yields are low

(95% and 86% recovery of (112) and (114) respectively), no evidence was obtained for homotropilidene formation.

In order to determine the effect of substituents other than methoxyl on the base promoted reactions of halogenated tricyclo-octanes, the analogous mono- and di-methyltricyclo-octanes (215)-(217), have been studied. These were prepared by conventional methods as shown in Scheme 34,

Scheme 34

Scheme 35a

but on treatment with *t*-BuOK in THF (substrate to base) the severely discoloured reaction mixtures gave no characterizable materials. When filtered base was added to the substrates, starting materials were recovered in *c.* 96% yields.

The unusual and unexpected 1,4-eliminations experienced by the methoxytricyclo-octanes in strongly basic media could have serious implications on the mechanism of the tricyclo-octane/styrene conversion (Chapter 2). Specifically, such elimination within the unsubstituted derivatives (112)-(115) would give the homotropilidenes (221)-(224) (Scheme 35). Should these compounds be more reactive towards base than their methoxylated counterparts, nucleophilic attack by *t*-BuO⁻ at C1 of the homotropilidene with concomitant ring cleavage would furnish the cyclo-octa-1,3,6-trienes (225) (Scheme 35a). Conjugation by abstraction of one of the doubly allylic C5 protons and reprotonation at C7 would give an epimeric mixture of the conjugated trienes (226). Disrotatory electrocyclic ring closure in both modes would deliver the bicyclo[4,2,0]octa-2,4-dienes (227) and (228) with *endo*- and *exo*-*t*-butoxy substituents respectively, and presumably in equilibrium as illustrated. Elimination of hydrogen chloride from each of these dienes would yield the trienes (229) and (230), which necessarily undergo conrotatory electrocyclic ring cleavage stereospecifically to give the appropriate (*E*)- or (*Z*)-styrene as has been discussed (Chapter 2). On this basis the proportion of (*E*)- and (*Z*)-styrenes is governed by the equilibrium between (226) and its ring-closed isomers (227) and (228). Although regiospecific ring-cleavage of the 2-oxa-bicyclo[4,1,0]heptane (231) to give (232) occurs by *t*-butoxide attack at C1,⁶² the formation of 4-halogenated styrenes does not of necessity require nucleophilic attack

Scheme 35b

at this centre (Scheme 35a). The incorporation of *t*-butoxyl at C7 of the homotropilidenes could also be operative as illustrated in Scheme 35b.

In contrast to the "linear" tetrahalogeno-*anti*-tricyclo-octanes, initial 1,4-elimination in the corresponding trihalogeno-systems can proceed by two modes, to give different products. Only when initial cleavage of the mono-halogenocyclopropane moiety occurs (Scheme 36) can the styrenes (141)

Scheme 36

and (142) be produced. This may well account for the lower yield of styrenes (141) and (142) (>5%) by comparison with their 4-halogenated derivatives (c. 28%).

A suitable test for the mechanistic hypothesis outlined above involves the homotropilidenes (223)⁶³ and (224)⁶⁴ resulting from 1,4-elimination in the "linear" trihalogeno-*anti*-tricyclo-octanes (113) and (115). These

compounds have been obtained from controlled dihalogenocarbene addition to

cycloheptatriene, itself available in two steps from cyclohexene.⁶⁵ Addition of 7,7-dichlorobicyclo[5,1,0]octa-2,4-diene (223) to a suspension of *t*-BuOK in DMSO resulted in the usual highly discoloured reaction mixture. Work-up yielded both (*E*)- and (*Z*)- β -*t*-butoxystyrene (141) and (142) reproducibly in 5.5 and 2.0% yields respectively, and identified by comparison with the samples previously obtained. Similar treatment of the bromo-analogue (224) again gave the (*E*)- and (*Z*)-styrenes in comparable yields. While the chloro-derivative is unreactive in THF (58% recovery), 7,7-dibromobicyclo[5,1,0]octa-2,4-diene (224) yields the (*E*)-styrene (141) (5%) exclusively.

The appearance of the (*Z*)-styrene (142) in the dehydrohalogenation of the homotropilidenes (223) and (224) in DMSO contrasts markedly with its absence in the dehydrohalogenation of the tricyclic precursors (113) and (114). Similarly, the appearance of the (*E*)-styrene (141), but not the (*Z*)-isomer (142), on treating the dibromohomotropilidene (224) with *t*-BuOK in THF also seems anomalous. If the rate determining step in the tricyclo-octane-styrene conversion involves 1,4-elimination delivering the appropriate homotropilidene, then subsection of the authentic homotropilidenes to the reaction conditions would result in a higher steady state concentration of all the subsequent

intermediates. Consequently, these factors may affect the equilibrium between the bicyclic intermediates (227) and (228) (Scheme 35a, p. 93) which independently yield the appropriate (*E*)- and (*Z*)-styrene. Alternatively, and perhaps more likely, other pathways circumventing homotropilidenes, and yielding higher (*E*)/(*Z*) ratios could be in operation in the tricyclo-octane - styrene conversion.

Some support for the intermediacy of the bicyclo[4,2,0]octa-2,4-dienes, *e.g.* (227) and (228), stems from subjection of (*E*)-7,8-dichlorobicyclo[4,2,0]-octa-2,4-diene (163a) to the reaction conditions for styrene formation. Both

Scheme 37

the (*E*)-styrene (141) (0.5%) and the (*Z*)-isomer (142) (1.0%) are produced as minor products from this bicyclo-octane. Their formation can be rationalized as shown in Scheme 37, with nucleophilic attack by $t\text{-BuO}^-$ occurring from either face of the four-membered ring in (163a). Subsequent elimination of hydrogen halide would yield the bicyclic trienes (230) and (229) which on conrotatory ring-opening would give the appropriate styrene. Surprisingly perhaps, there is little evidence for cyclo-octatetraene formation in this reaction, and in fact subjection of the bicyclo-octane (163a) to $t\text{-BuOK}$ in DMSO results in considerable decomposition.

From these observations it is clear that both homotropilidenes and bicyclo[4,2,0]octadienes do yield *t*-butoxystyrenes. However, because of the difference in the (*E*)/(*Z*) ratios recorded from the homotropilidenes and the trihalogenotricyclo-octanes, compounds (223) and (224) are presumed not to be the sole precursors to the styrenes.

From the results outlined in this and the preceding chapter it can be seen that replacing the 3,4- π bond of a bicyclo[4,1,0]hept-3-ene by a three-membered ring or fusing a three-membered ring across the sp^3 -centres at C3 and C4 of a bicyclo[4,1,0]heptane has a profound effect not only on the initial mode of elimination in the ring-fused halogenated cyclopropane, but also on the fate of the intermediates. Furthermore, these base promoted reactions have allowed for synthetic entry into specifically substituted styrenes and homotropilidenes, which would not be easily accessible by other more conventional methods.

CHAPTER FOUR

THE SYNTHESIS OF GEM-DIHALOGENO-ANTI-BISHOMOBENZENES

From the commentary in the Introduction it will be recalled that the presence of unsaturation within the larger carbocycle of a ring-fused *gem*-dihalogenocyclopropane has a dramatic effect on the fate of the ring system in strongly basic media. In order to assess the combined effects of unsaturation and a second cyclopropane moiety within this framework, the synthesis of the *gem*-dihalogeno-*anti*-bishomobenzenes[†] (121) and (122) was a further objective of this study. However, although

(121)

(122)

a new and viable synthesis of the *anti*-bishomobenzenes (121) and (122) has been achieved, it has not been possible to investigate fully the properties of these compounds at the time of writing. While alternative "linear" tricyclo-octanes such as (234) and (235) also contain the desired functionality for this type of study, devising synthetic approaches

[†]The more rigorous nomenclature for compounds (121) and (122) is 3,3-dichloro- and 3,3-dibromo-*cis-transoid-cis*-tricyclo[5,1,0,0^{2,4}]-oct-5-ene respectively.

to such species is by no means straightforward. For example, while bicyclo[4,2,0]octa-3,6(1)-diene (231) is readily available⁶⁶ and is a possible precursor to (232), Birch reduction of cyclopropabenzene

does not furnish the diene (233), the required precursor for (234) and (235); ring cleaved products are formed instead.⁶⁷

Immediately prior to the commencement of this study, Paquette and Taylor reported⁴⁸ a nine step and low yielding (2-3% overall) synthesis of the *gem*-dibromo-*anti*-bishomobenzene (122), which involved intractable bicyclobutane intermediates (Scheme 38). While this route furnishes the desired *gem*-dibromo compound (122) by unusual thermolytic rearrangement of the tetracyclo-octane (236), there is no evidence that the less labile *gem*-dichloro analogue would undergo the same rearrangement. Because of the length of this route, its low overall yield and its possible lack of generality, it was considered highly desirable to seek alternative and more applicable routes to *gem*-dihalogeno-*anti*-bishomobenzenes.

Perhaps the most elegant synthesis of the parent *anti*-bishomobenzene (238) is that developed recently by de Meijere and co-workers.⁶⁸ This approach involves ozonolysis of the readily available "angular" tricyclo-octane (134) to yield the ketone (237). Methyl lithium promoted

Scheme 38

Bamford-Stevens rearrangement of the derived tosylhydrazone yields the desired tricyclo-octene (238) in *c.* 30% overall yield. However, in view of the ease of formation of cyclopropylidenes from *gem*-dihalogenocyclopropanes and methyl lithium,⁴⁸ a modification of this route to utilize

the dihalogenotricyclo-octanone (239), as depicted above was considered too dubious to justify investigation.

An alternative approach to *anti*-bishomobenzene (238) has involved bis-cyclopropanation of readily available dimethyl 1,2-dihydrophthalate (240).

Subsequent hydrolysis of the resultant tricyclic diester (241) and electrolytic bis-decarboxylation of the diacid affords the hydrocarbon (238) in unspecified yield.⁶⁹ Attempts to extend this route to the *gem*-dihalogeno derivatives (121) and (122) by sequential introduction of dihalogenocarbene and methylene to the diene (240) failed. The only

products isolated were the phthalates (242) and (243), (Experimental), which presumably reflects the high base and thermal labilities⁷⁰ of the diene (240). Consequently, it was concluded that any approach to *gem*-dihalogeno-*anti*-bishomobenzenes required completely new strategies.

The initial synthetic plan is illustrated in Scheme 39. Epoxidation of the readily available Δ^3 norcarene (30) under the appropriate conditions⁷¹ would result in the *anti*-product (244) exclusively. Lithium

Scheme 39

dialkylamide promoted opening of the epoxide moiety was expected⁷² to furnish the *anti*-bicyclo[4.1.0]hept-2-en-4-ol (245) which on Simmons-Smith cyclopropanation would deliver the *anti*-tricyclo-octanol (246b) because of participation by the hydroxyl group.⁷³ Finally, elimination of the elements of water from (246b) would yield the desired *anti*-bishomobenzene (121).

Reaction of the dichloronorcarene (30) with the sterically demanding *m*-chloroperbenzoic acid/chloroform epoxidation system resulted in a single (t.l.c.) oxygenated product, proposed as the desired *anti*-oxirane (244) principally on the basis of its spectroscopic and microanalytical data. The homogeneity of the epoxidation product was verified by g.l.c. where a single symmetrical peak was observed on a variety of columns. While conclusive proof of the *anti*-stereochemistry of (244) has not been obtained, the mode of formation almost certainly precludes this product from being the *syn*-isomer. Indeed, it has been shown recently⁷⁴ that epoxidation of 7,7-dibromobicyclo[4,1,0]hept-3-ene (31) under similar conditions gives only the *anti*-derivative (247) as

demonstrated by X-ray methods. Treatment of the epoxide (244) with lithium diethylamide (2.5 molar equiv.), as detailed by Rickhorn and Thummel⁷² for the ring cleavage of various cyclohexene oxides, leads to a complex mixture of products (8 by t.l.c.) containing olefinic and hydroxyl moieties (i.r., ¹H n.m.r.). No evidence (mass spectral, Lassaigne sodium test) was obtained for the presence of halogenated material in this mixture. Despite a large number of variations in the reaction conditions, epoxide cleavage with simultaneous preservation of the *gem*-dichlorocyclo-

propane could not be achieved. In an attempt to circumvent this problem dye-sensitized photo-oxygenation⁷⁵ of the olefin (30) was undertaken, but

unreacted starting material (~95% recovery) was consistently returned. Variations in the dye (Rose Bengal, Methylene Blue) and solvent systems were ineffective. However, this lack of reactivity may reflect the non-availability of the most appropriate light source, rather than the inherent properties of the substrate (30).

During the course of this work a report on the regiospecific synthesis of bromoketones from epoxides appeared.⁷⁶ The applicability of such a reaction to the synthesis of the tricyclo-octene (121) is illustrated in Scheme 40. It was envisaged that reaction of the epoxide would give the bromoketone (248) which on elimination of the elements of hydrogen bromide could yield the bicycloheptenone (249), a valuable synthon for the preparation of annelated bicyclo[4,1,0]hept-2-enes. In particular, treatment of the ene-one (249) with a dimethylsulphonium ylide⁷⁷ should yield the tricyclo-octanone (251, n=1) and ultimately the *anti*-bishomobenzene (121). Photolysis of a solution of (244) in carbon tetrachloride containing bromine led to a mixture of products containing

Scheme 40

the desired bromoketone (248) albeit in low yields (*c.* 6%). The orientation of the bromine substituent at C4 is tentatively assigned as *anti* with respect to the three-numbered ring (*vide infra*). The low yield of the ketone and the presence of other products could well be the result

of radical rearrangements and participation of the three-membered ring.

A modification of the route (Scheme 40) has led to a higher yield of the bromoketone. Thus treatment of the olefin (30) with N-bromosuccinimide in moist dimethyl sulphoxide according to the method of Dalton and Datta⁷⁸ yields the crystalline bromohydrin (250) (81%). The ¹H n.m.r. spectrum of the bromohydrin reveals a low field multiplet (3.75 p.p.m., 2H) assigned to H3 and H4, and a somewhat broader and complex multiplet (2.15 p.p.m., 7H) assigned to the remaining protons. While the infra-red⁷ spectrum and microanalysis are fully compatible with the structure (250), the data do not allow for a distinction to be made between the proposed isomer and its doubly epimeric counterpart. However, bromonium ion formation is expected to proceed from the direction of least steric interference and give the isomer *anti* with respect to the three-membered ring. Nucleophilic attack by water would then occur from the syn-face to give the trans-diaxial bromohydrin (250). Oxidation of the bromohydrin

using Jones reagent⁷⁹ (CrO₃/H₂SO₄) gave the bromoketone (248) in 99.5% yield, identical in all respects to the sample obtained from the epoxide (244). The ¹H n.m.r. spectrum of the ketone displays a one-proton

Scheme 41

triplet (4.04 p.p.m., $J = 3.0$ Hz) assigned to the methine proton at C4. The remaining resonances are present as unresolvable complex multiplets. Nonetheless, the infra-red spectrum of the bromoketone (248) as well as the microanalytical data are fully consistent with the assigned structure.

Attempts to dehydrobrominate the bromoketone (248) under a wide variety of conditions either returned unreacted starting material or gave uncharacterisable decomposition products. For example, treatment with dry distilled pyridine at room temperature for 48 hours yields starting material (60% recovery), and treatment with sodium iodide/triethyl amine in acetone⁸⁰ led to severe decomposition. Despite a large number of attempts under various conditions the ene-one (249) could not be prepared by dehydrobromination of the bromoketone (248). Consequently, attempts to prepare this α,β -unsaturated ketone and ultimately the *gem*-dichloro-*anti*-bishomobenzene (121) by this approach were abandoned.

An alternative route to the *anti*-bishomobenzenes (121) and (122) which allows for sequential introduction and survival of the cyclopropyl and olefinic moieties is illustrated in Scheme 41. Controlled Simmons-Smith cyclopropanation of cyclohexa-1,4-diene⁸¹ gave bicyclo[4,1,0]hept-3-ene (252) in 28% yield, contaminated⁸¹ (c. 15%) with the corresponding *syn*- and *anti*-bisadducts (127) and (262). Epoxidation of the olefin (252)

with *m*-chloroperbenzoic acid gave rise to a mixture of two oxygenated products (90%) in a ratio of *c.* 2:1 by g.l.c. (the two components could not be completely resolved by g.l.c.). After fractional distillation the epoxides were not contaminated with the tricyclo-octanes (127) and (262). The major and minor oxidation products of this mixture have been assigned as 4-oxa-*anti*-tricyclo[5,1,0,0^{3,5}]octane (253a) and 4-oxa-*syn*-tricyclo[5,0,0^{3,5}]octane (253b) respectively, by comparison of their ¹H n.m.r. spectral data with those recently communicated⁷⁴ for the separated epoxides. The ¹H n.m.r. spectrum of the mixture reveals a shielded multiplet at -0.4 p.p.m. (two-thirds of a unit integral) which has been assigned to the H8_{endo}-cyclopropyl proton in the *anti*-isomer (253a). It has been suggested⁷⁴ that this shielding reflects an enhanced diamagnetic contribution from the (transannular) carbon atoms of the epoxide ring. The remaining resonances reveal a broad two-proton singlet at 2.95 p.p.m. assigned to H3 and 5, and a four-proton methylene envelope (1.50-2.61 p.p.m., H2 and 6) and a higher field complex multiplet (-0.1-1.00 p.p.m.) assigned to the remaining (3 $\frac{1}{3}$) cyclopropyl protons of (253a) and (253b). No attempt was made to separate the isomeric epoxides as stereochemical integrity is lost in the proposed generation of the olefinic moiety in the *anti*-bishomobenzenes (121) and (122) (Scheme 41).

The key step in this synthetic approach to compounds (121) and (122) is the conversion of the epimeric epoxides into the allylic alcohols (254). The net result of this rearrangement is the production of a trifunctional molecule from a difunctional one, which allows for the further introduction of the *gem*-dihalogenocyclopropyl and olefinic moieties that constitute the bishomobenzenes (121) and (122). Attempts to effect the rearrangement of the epoxides to the allylic alcohols,

using conditions identical to those employed⁸² in the conversion of the homologous oxirane (263) to the bicyclo-octenol (264) (LiNEt_2 , 20 h.,

35.5°), led to a product which, while containing the desired allylic alcohols (254) (c. 60%), was contaminated with a large quantity of a carbonyl-containing (infra-red) species. The contaminant is presumed to be bicyclo[4,1,0]hept-3-one (265) which may arise by isomerization of the

Δ^2 -double bond in (254) to the thermodynamically favoured Δ^3 -position giving the intermediate enol, which tautomerizes to the ketone (265). Consistent with this is the known⁸³ interconversion of 2- and 3-norcarene with $t\text{-BuOK}$ as catalyst where the Δ^2 -isomer undergoes isomerization three times faster than its Δ^3 -counterpart. Paquette and co-workers appear to have overcome these difficulties by employing lithium diethylamide

(c. 5 molar equiv.) at room temperature for 48 hours.⁷⁴ However, the yields involved are low (40%) and the dye-sensitized photo-oxygenation of the norcarene (252) gives the alcohols in the same yield. Kissel and Rickborn⁷² have investigated the efficiency of various lithium dialkylamides, at differing concentrations in effecting rearrangement of cyclohexene oxide to cyclohexene-3-ol. These workers have found that the best conditions involve c. 2.5 molar equivalents of lithium dipropylamide in ether at reflux to give the alcohol in >99% yield. Consequently the epoxide mixture was subjected to these conditions and the progress of reaction monitored by g.l.c. methods. After c. 7.5 hours essentially no starting material remained. G.l.c. revealed two major and more polar products, and two minor components, these latter capable of removal by fractional distillation. The purified colourless viscous oil (61%) is identified as a 1:2 mixture of the *syn*- and *anti*-bicyclo[4,1,0]hept-2-ene-4-ols (254b) and (254a) corresponding to stereospecific ring cleavage of each of the epoxides (253a) and (253b). As a result of the improved yield in this step, the epoxidation of bicyclo[4,1,0]hept-3-ene (252) and subsequent base-promoted rearrangement gives the allylic alcohols in higher yield than by direct photo-oxygenation of the olefin (252).

The ¹H n.m.r. spectrum of the mixture of allylic alcohols is complex, but several of the multiplets are well separated and assignable. Thus the lowest field one-proton multiplet at 6.10 p.p.m. is assigned to the vinylic proton at C3 while a second one-proton multiplet at 5.48 p.p.m. is assigned to the adjacent vinylic proton at C2. The ordering of these assignments reflects the probable deshielding of H3 by the adjacent -OH moiety. A one-proton, complex multiplet at 4.10 p.p.m. is assigned to the epimeric protons at C4 and the chemical shift of this resonance results from the combined deshielding effects of adjacent -OH and olefinic

residues. In addition, a fourth one-proton multiplet at 2.40 p.p.m. is assigned to the allylic cyclopropyl proton at C1. The hydroxyl proton resonance (3.10 p.p.m.) is identified by conventional (D_2O) methods. The remaining higher field resonances constitute a broad methylene - methine envelope (5H, 0.2-2.1 p.p.m.) and are assigned to the protons at C5, 6 and 7. The infra-red spectrum of the mixture confirms the presence of the olefinic (1630 cm^{-1}), hydroxyl (3320 cm^{-1}), and cyclopropyl (3040 cm^{-1}) moieties. Furthermore, the mass spectrum (14 eV) reveals a parent ion at m/e 110 (47%) and ions at m/e (109 (18%) $(M-H)^+$; 95 (100%) $(M-CH_3)^+$; 92 (82%) $(M-H_2O)^+$ and 91 (34%) $(C_7H_7)^+$, all fully in accord with the assigned structure.

The two minor reaction products resulting from cleavage of the epoxide (253) are believed to be the ketone (265) (c. 2%) and the hydroxyamines (266) (c. 7%) by analogy with the minor products from ring cleavage

of cyclohexene oxide.⁷² No attempt has been made to characterize these compounds.

The acetylation of the allylic alcohols (254) is necessary for protection of the hydroxy-function during the subsequent dihalogenocarbene addition step (Scheme 41). Acetylation of the alcohols yielded a sweet

smelling product oil containing a major and more mobile, reaction product and several other minor and unidentified slower moving components.

Column chromatography afforded a mixture of the acetates (255) as a clear colourless oil (70%). The ^1H n.m.r. spectrum of the mixture reveals a

(255a)

(255b)

highly deshielded one-proton doublet of multiplets at 6.08 p.p.m. and is assigned to the vinylic proton at C3. A two-proton complex multiplet at higher field (4.80-5.20 p.p.m.) is assigned to H2 and H4. This represents a deshielding of ≈ 0.9 p.p.m. for the H4 proton in (255) with respect to its counterpart in (254) and is fully consistent with the change in chemical shift expected upon introduction of an acetyl moiety. The H1 resonance of (255), like that of (254), appears as a complex multiplet at 2.40 p.p.m. A three-proton singlet at 2.01 p.p.m. is assigned to the methyl protons of the acetate and remains unresolvable even on treatment of the n.m.r. sample with lanthanide shift reagent $\text{Eu}(\text{fod})_3$. The protons at C5-7 appear as a broad methylene-methine envelope (5H, 0.25-1.80 p.p.m.). The infra-red spectrum of the purified acetylation product confirms the presence of the olefinic (1630 cm^{-1}), acetoxy (1730 cm^{-1}) and cyclopropyl (3040 cm^{-1}) moieties and the mass spectrum (17 eV) reveals a parent ion at m/e 152 (3.5%) and ions at m/e 93 (100%) ($\text{M}-\text{CH}_3\text{CO}_2^+$) and 91 (14%) (C_7H_7^+), all in full agreement with the

norcar-2-ene acetate structure (255). Unfortunately neither g.l.c. nor t.l.c. analysis has permitted a determination of the relative ratios of the *syn*- and *anti*-acetates (255a) and (255b) in the purified product. A further attempt to determine the ratio of the acetate mixture involved hydrolysis of the esters (255) back to the allylic alcohols (254). G.l.c. analysis of the crude reaction product after six hours revealed a four component mixture containing unreacted acetate(s) (255) (10.6%), the allylic alcohols (254a) (78.6%) and (255b) (9.2%) and the bicyclo[4,1,0]hept-3-one (265) (1.5%). While extending the reaction period resulted in a decrease in the amount of acetate (255) (*c.* 3%) and an increased proportion of the major alcohol (254a), the yield of the minor alcohol was essentially unchanged, and the amount of ketone (265) had increased marginally. This study suggests that while the *anti*-acetate (255a) is hydrolyzed directly

Scheme 42

to the corresponding alcohol (254a), the more sterically hindered *syn*-acetate (255b) could undergo normal hydrolysis or suffer epimerization and/or prototropic shift delivering either the epimeric Δ^2 -acetate (255a) or the Δ^3 -vinyl acetate (266) (Scheme 42). Hydrolysis of the less sterically crowded acetates (255a) and (266) would yield the allylic alcohol (254) or the ketone (265). As a result it has not been possible to ascertain the *syn:anti* ratios for the acetates, although it is assumed that acetylation of the alcohols (254) proceeds stereospecifically under the conditions employed.

Addition of dihalogenocarbene to the mixture of allylic acetates was effected using the appropriate haloform and 50% aqueous sodium hydroxide with triethylbenzylammonium bromide as phase transfer catalyst. After *c.* 40 hours at room temperature, work-up and column chromatography yielded an epimeric mixture of the corresponding 5-acetoxy-3,3-dihalogeno-*anti*-tricyclo[5,1,0,0^{2,4}]octanes (256) (80%) and (257) (53%) respectively.

(256) X=Cl

(257) X=Br

(258) X=Cl

(259) X=Br

(267) X=Cl

(268) X=Br

The less mobile minor components from the reaction mixtures have been identified as the corresponding 3,3-dihalogeno-*anti*-tricyclo[5,1,0,0^{2,4}]octan-5-ols (258) and (259). Although no other components have been identified from these reaction mixtures, the presence of the tricyclo-

octanols (258) and (259) tends to suggest that other less polar products may be derived from carbene addition/insertion to these species giving, for example, the ethers (267) and (268).

The ^1H n.m.r. spectrum of the acetylated products (256), (Fig. 8) derived from dichlorocarbene addition to the allylic acetates (255), displays a low field one-proton multiplet at 5.20 p.p.m. assigned to the H5 adjacent to the acetate group, and a sharp singlet at 2.10 p.p.m. attributed to the acetoxy methyl protons. The remaining alicyclic resonances are present as complex envelopes except for two high field multiplets at -0.1-0.3 and 0.4-0.85 p.p.m. which indicates the presence of a cyclopropanated product. The mass spectrum of the acetates (256) reveals molecular ions at m/e 234, 236 and 238 in a ratio of 100:68:10 indicative of a dichloro-containing species. Peaks at m/e 175, 177, and 179 correspond to the loss of $\text{CH}_3\text{CO}_2\cdot$ from the parent ions. The remaining ions are also consistent with the fragmentation of structures (256).

G.l.c. analysis of the dichloro-acetates (256) has not permitted a determination of the epimer ratio, and in fact these traces display single symmetrical peaks. However, satisfactory microanalytical data have been obtained for the product mixture, and the major and minor components are assigned as 5β -acetoxy- and 5α -acetoxy-3,3-dichloro-tricyclo[5,1,0,0^{2,4}]octane[†] (256b) and (256a) (c. 3.5:1) respectively.

[†]The naming of 5-substituted *anti*-tricyclo[5,1,0,0^{2,4}]octanes such as (256)-(261) and (270) is based on the Chemical Abstracts method of using α and β , with the cyclohexane 'plane' as the plane of reference. Thus compound (256b) would be named (1 α ,2 β ,4 β ,5 α ,7 α)-5-acetoxy-3,3-dichloro-*cis-transoid-cis*-tricyclo[5,1,0,0^{2,4}]octane.

Fig. 8 60 MHz ^1H n.m.r. Spectrum of
 (1 α ,2 β ,4 β ,5 α ,7 α)- and
 (1 α ,2 β ,4 β ,5 β ,7 α)-5-Acetoxy-3,3-
 Dichloro-*anti*-tricyclo[5,1,0, $0^{2,4}$]-
 octane (256a,b)

Fig. 9 60 MHz ^1H n.m.r. Spectrum of (1 α ,2 β ,4 β ,5 β ,7 α)-3,3-Dichloro-*anti*-tricyclo[5,1,0,0^{2,4}]octan-5-ol (258a)

approach was considered too dubious to pursue.

Hydrolysis of the tricyclo-octanol acetates (256) gave an oily solid (98%) which on recrystallization from pentane afforded a white crystalline solid identified as 3,3-dichloro-*anti*-tricyclo[5,1,0,0^{2,4}]octan-5 β -ol (258a) on the basis of its spectroscopic and microanalytical data. The ¹H n.m.r. spectrum of the alcohol (258a) (Fig. 9) revealed a one-proton

doublet of doublet of doublets ($J = 5.5, 8.5$ and 10.0 Hz) which is assigned to H5- α .

A Drieding molecular model of (258a) reveals that because of strong steric interactions between the *endo*-chlorine atom at C3 and H6- β , the preferred conformation is most likely to be that depicted below:

in which C5 is "up" and C6 is "down" with respect to the *gem*-dichlorocyclopropyl moiety. In this favoured conformation the dihedral angles between H5 and H4 is *c.* 0°, H5 and H6- α *c.* 40°, and H5 and H6- β *c.* 70°. On this basis and the Karplus relationship,⁸⁵ the observed coupling constants are fully consistent with expectations. An exchangeable hydroxyl resonance is recorded at 3.10 p.p.m., and the remaining four resonances appears as multiplets (Fig. 9). The broad four-proton multiplet at 1.60-2.40 p.p.m. is assigned to the nuclei at C2, 4 and 6 and is consistent with the chemical shifts of the cyclopropyl protons in (116) and the methylene protons in

(116)

(134)

the parent system (134). The two-proton complex multiplet at 1.25 p.p.m. is assigned to the C1 and C7 bridgehead cyclopropyl protons, consistent with the chemical shift of the corresponding resonances for H1, 2, 4 and 7 in (134). The multiplets at 0.6 and 0.08 p.p.m. are assigned to the *endo*- and *exo*-cyclopropyl protons at C8 respectively. The mass spectrum of the alcohol (258a) does not display molecular ions even at low ionizing voltages. However, the presence of peaks at *m/e* 148, 150 and 152 in a ratio of 100:64:12 indicates a C₆H₆Cl₂ species which corresponds to loss of the elements of acetaldehyde (C₂H₄O) from the tricyclo-octanol (258a). A molecular formula of C₈H₁₀Cl₂O for this solid is substantiated by satisfactory microanalytical data.

The ^1H n.m.r. spectrum of the mother liquors obtained from the recrystallization of the 5β -ol (258a) shows, in addition to the resonances for the crystalline material, the presence of a low field multiplet at 3.75 p.p.m. together with additional higher field envelopes. This argues strongly for the presence of the epimeric 5α -tricyclo-octanol (258b). In fact subsequent investigations have confirmed the presence of this epimer (vide infra). The higher chemical shift for the C5- β proton in this (5α -ol) epimer ($\Delta\delta$ 0.35) is not easy to rationalize, particularly since other 5β -substituents (e.g. AcO-) are at lower field than their epimeric counterparts. However, this phenomenon may reflect conformational effects.

Hydrolysis of the dibromo-acetates (257) also yields an oily solid (98%) which furnishes, on recrystallization a white crystalline solid (c. 75%) assigned as 3,3-dibromo-*anti*-tricyclo[5,1,0,0^{2,4}]octan-5 β -ol (259a). The ^1H n.m.r. spectrum of (259a) is almost identical to that of its dichloro-counterpart (258a), and the infra-red, mass spectral, and microanalytical data are fully in accord with the assigned structure. Similarly, the ^1H n.m.r. spectrum of the mother liquors obtained from the recrystallization support the presence of the epimeric 5α -tricyclo-octanol (259b) (22%).

Elimination of the elements of water from the alcohols would yield the highly desirable and sought after *anti*-bishomobenzenes (121) and (122). However, all attempts to dehydrate the alcohols directly have been unsuccessful. For example, *p*-toluenesulphonic acid catalysed dehydration of (258a) gave rise to a complex product mixture, the ^1H n.m.r. spectrum of which revealed aromatic and benzylic resonances. These observations suggest formation and rearrangement of the carbonium ion intermediate (269) involving

cyclopropyl participation. Treatment of the tricyclo-octanols (258) with phosphorous oxychloride or thionyl chloride in pyridine, strong dehydrating media,⁸⁶ both gave rise to product mixtures containing the

same three major components (g.l.c.). The ^1H n.m.r. spectrum of the crude reaction mixture revealed no olefinic resonances, but did display a complex multiplet at 3.90 p.p.m. and a characteristic methylene-methine envelope suggesting the presence of the epimeric trichlorotricyclo-octanes (270). Preparative t.l.c. has led to the isolation of an epimeric mixture of these trichloro-compounds (270). In addition to displaying ^1H n.m.r. and infra-red spectra fully consistent with the assigned structures, the mass spectrum reveals peaks at m/e 210, 212 and 214 (100:62:11) $(\text{M})^{+}$, and

microanalytical data confirm a $C_8H_9Cl_3$ species. The third component evident by g.l.c. is of unknown composition and structure.

On the basis of the foregoing, it appears that leaving groups at C5 in the "angular" tricyclo-octane system are quite susceptible to nucleophilic attack. Similarly, the development of too much carbonium ion character at this site leads to skeletal rearrangement, presumably by neighbouring cyclopropyl participation. In order to achieve the elimination of the elements of water from the alcohols (258) and (259) an E2 or concerted-type elimination appears necessary. To these ends the mesylates of (258) and (259) have been prepared by standard methods.⁸⁷ However, it is worthy of

mention that attempts to prepare the corresponding tosylates have not been completely successful, as full esterification could not be effected, presumably because of the steric demands of the derivative.

The 1H n.m.r. spectrum of the crude mesylate product mixture from the *gem*-dichloro-alcohols (258) reveals a pair of sharp resonances at 3.05 and 2.95 p.p.m. in a ratio of *c.* 3.5:1 respectively. These have been assigned to the mesylate methyl protons of the 5 α - and 5 β -derivatives respectively. The deshielding of the methyl resonance in the β -epimer is again consistent with this configuration (*vide supra*). In addition, the

Fig.10 60 MHz ^1H n.m.r. Spectrum
of (1 α ,2 β ,4 β ,5 β ,7 α)-3,3-
Dichloro-5-mesyloxy-*anti*-
tricyclo[5,1,0,0^{2,4}]-
octane (260a)

spectrum of this mixture displays a deshielded multiplet at 5.07 p.p.m. which has been assigned to the C5 methine protons. In all other respects this spectrum is very similar to those of the alcohols (258) and the acetates (256). Mesylation of the solid 3,3-dichloro-*anti*-tricyclo[5,1,0,0^{2,4}]octan-5 β -ol (258a) gave a pure crystalline product (90%), the ¹H n.m.r. spectrum of which is shown in Fig. 10. Significantly, the 5 β -mesylate methyl resonance at 3.05 p.p.m. is present in this spectrum. On the basis that mesylation is stereospecific, then the ratio of the 5 β -ol (258a) to 5 α -ol (258b) is *c.* 3.5:1. Although extrapolation of this ratio to the inseparable acetate precursors (256) may be spurious, it is interesting to note that essentially the same ratio is recorded for the spectroscopically distinguishable dibromo-acetates (257).

Analogous mesylation of the *gem*-dibromo-alcohols (259) gives rise to a *c.* 3.5:1 mixture of the 5 β - and 5 α -derivatives as evidenced by the ¹H n.m.r. spectrum of the crude product. Similarly, mesylation of the pure *gem*-dibromo-5 β -alcohol (259a) gives rise to a crystalline derivative, with a ¹H n.m.r. spectrum indicative of the β -derivative.

The non-nucleophilic base, 1,8-diazabicyclo[5,4,0]undec-7-ene (DBU)⁸⁸ has been successfully employed by a number of researchers in the generation of olefins from mesylates.⁸⁹ Thus treatment of the mesylate (260a) in DMSO at 70° with dried DBU gave after 72 hours two major products (t.l.c.). These have been identified as 3,3-dichloro-*anti*-tricyclo[5,1,0,0^{2,4}]octan-5 α -ol (258b) (14%) and 3,3-dichloro-*anti*-tricyclo[5,1,0,0^{2,4}]oct-5-ene (121) (the dichloro-*anti*-bishomobenzene) (51%) on the basis of their respective spectroscopic data. The ¹H n.m.r. spectrum of the pure 5 α -alcohol (a clear colourless oil) (Fig. 11) displays a one-proton multiplet at 3.75 p.p.m. which is assigned to H5- β , and an exchangeable

Fig.11 60 MHz ^1H n.m.r. Spectrum of (1 α ,2 β ,4 β ,5 α ,7 α)-3,3-Dichloro-*anti*-tricyclo[5,1,0,0^{2,4}]octan-5-ol (258b)

hydroxyl resonance is recorded at 2.92 p.p.m. The remaining resonances appear as a series of complex multiplets over the range 0-2.50 p.p.m. These higher field envelopes are identical to those observed in the ^1H n.m.r. spectrum of the crude product from hydrolysis of the acetates (256) which were not assigned to the epimeric 5β -alcohol (258a). The infra-red and mass spectral data are also in accord with this structure. Satisfactory microanalytical data were obtained for the 5α -ol as its crystalline 3,5-dinitrobenzoyl-derivative.

The ^1H n.m.r. spectrum of 3,3-dichloro-*anti*-tricyclo[5,1,0,0^{2,4}]oct-5-ene (121) displays a low field one-proton doublet of multiplets (5.96 p.p.m., $J = 10.0$ Hz) and a higher field one-proton doublet of doublets (5.49 p.p.m., $J = 10.0$ and 4.8 Hz). These resonances have been assigned to the vinylic protons H5 and H6 of (121) respectively, with the magnitude of the common coupling constant (10 Hz) indicative of two vicinally and *cis*-related vinylic protons. The lowest field resonance of a rather complex methylene/methine envelope is a one-proton doublet (2.21 p.p.m., $J = 10.2$ Hz) and this is assigned to H2. A one-proton doublet of doublets at 1.75 p.p.m. ($J = 10.2$ and 4.8 Hz) is assigned to H4 and, from the coupling constants, this proton appears to be vicinally coupled to H2 and allylically coupled to

H6. A narrow one-proton doublet at 1.40 p.p.m. ($J = c. 2.8$ Hz) is assigned to H7 and this nucleus is presumably allylically coupled to H5. The only remaining discernable resonance is the highest field one-proton multiplet at 0.56 p.p.m. which is assigned to the *exo*-proton at C8. The resonances for the remaining protons at C1 and C8 (*endo*-proton) are within the high field envelope and appear as complex multiplets in the region 0.90-1.60 p.p.m. Perhaps rather anomalously, the lowest field non-vinylic proton is H2 in spite of the fact that H4 is both allylic to the olefinic moiety and adjacent to, and in the same plane as, the *exo*-chlorine atom at C3 and thus might well have been expected to be more deshielded than H2. Nonetheless, the coupling relationships described above have been confirmed by decoupling experiments.

A minor impurity in the isolated *anti*-bishomobenzene (121) is evident from its ^1H n.m.r. spectrum and this has prevented the acquisition of accurate microanalytical data. However, the mass spectrum of (121) reveals parent ions at m/e 174, 176 and 178 in a ratio of 100:65:10 indicative of a two chlorine containing species. The high resolution mass data on the ion at 174 mass units confirms a molecular formula of $\text{C}_8\text{H}_8\text{Cl}_2$. The fragmentation of the parent ion is consistent with structure (121) revealing ions at m/e 159, 3.2%, 161, 2.4% ($\text{M}-\text{CH}_3$) $^+$; m/e 139, 12%, 141, 4% ($\text{M}-\text{Cl}$) $^+$; and m/e 83, 100%, 85, 65%, 87, 10% (CHCl_2) $^+$. The infra-red spectrum of this olefinic product is also fully consistent with the *anti*-bishomobenzene structure (121) revealing diagnostic bands at 3050 (cyclopropyl C-H), 1640 (C=C) and 820 (C-Cl) cm^{-1} . G.l.c. analysis of the oil reveals a major product with a minor and unidentified contaminant at higher retention time.

Definitive confirmation of the structure of the *gem*-dichloro-*anti*-bishomobenzene (121) has been established by reductive dechlorination ($\text{Na}/t\text{-BuOH}/\text{THF}$) to the parent *anti*-bishomobenzene (238).^{68,69,90} The ^1H

n.m.r. spectrum of the crude reduction product is identical to the spectrum

of authentic (238).⁷⁴ Significantly the pair of multiplets assigned to the vinylic protons in (121) is collapsed to a broad singlet in the more symmetric reduction product (238). Similarly, the methylene/methine envelope in (121) is collapsed to a less complex pattern. G.l.c. analysis of the reduction product reveals a single major component with a significantly shorter retention time than the *gem*-dichloro-precursor (121).

The absolute yield of the olefin (121) from the mesylates (260) has been increased to *c.* 59% by rigorously excluding moisture from the reagents and reaction vessel and with the result that hydrolysis of sulphonyl esters (260) is no longer a competing process. However, the yield of the olefin (121) is sensitive to the scale of the reaction and appears to be maximized (59%) when employing *c.* 0.74 mmol (200 mg) of mesylate. A six-fold increase in the reaction bulk results in a decrease in the yield of the olefin (121) to 26%. Nonetheless, the higher yield of olefin can be preserved by conducting the elimination in batches on the appropriate scale. Thus the overall yield of the *anti*-bishomobenzene (121) from the readily available bicyclo[4.1.0]hept-3-ene (252) is *c.* 14%; this represents a 500% increase in the anticipated yield for (121) by thermolytic rearrangement of the appropriate tetracyclo-octane.⁴⁸ Studies are currently being undertaken to

Fig.12 60 MHz ^1H n.m.r. Spectrum
of 3,3-Dibromo-*anti*-
tricyclo[5,1,0, $0^{2,4}$]oct-5-
ene (122)

effect the dehydromesylation of (260) under milder conditions and in higher yields.

Treatment of the dibromomesylate (261a) with DBU in DMSO at 70° under the same conditions employed for its dichloro-counterpart (260a) afforded two major products (t.l.c.) which have been identified as the 3,3-dibromo-*anti*-tricyclo[5,1,0,0^{2,4}]octan-5 α -ol (259b) (14%) and 3,3-dibromo-*anti*-tricyclo[5,1,0,0^{2,4}]oct-5-ene (122) (the dibromo-*anti*-bishomobenzene) (59% based on recovered alcohol).

The ¹H n.m.r. and i.r. spectra of the 5 α -alcohol (259b) obtained from this reaction are fully consistent with the assigned structure and are almost identical to the spectra of the dichloro-counterpart (258b).

The ¹H n.m.r. spectrum of the olefin (122) (Fig. 12) displays identical multiplicities and similar chemical shifts to those of its *gem*-dichloro-counterpart. Consequently, the analysis of the coupling in this spectrum is the same as that for its dichloro-counterpart (vide supra) and has received confirmation from decoupling experiments. Once again a minor and unidentified impurity in the isolated *anti*-bishomobenzene (122) is evident from its ¹H n.m.r. spectrum (see Fig. 12) and this has again prevented the acquisition of accurate microanalytical data.

The mass spectrum of (122) reveals parent ions at m/e 262, 264 and 266 in a ratio of c. 1:2:1 indicative of a dibromo species and high

resolution mass data on the ion at 264 mass units confirms a molecular formula of $C_8H_8Br_2$. The fragmentation of the parent ion is consistent with the assigned structure as is the infra-red spectrum. Similarly g.l.c. analysis reveals a single major product together with a minor contaminant at higher retention time.

Confirmation of the structure of the *gem*-dibromo-*anti*-bishomobenzene (122) has been established by reductive debromination (Li/t -BuOH/THF). The parent *anti*-bishomobenzene (238) obtained from the dibromobishomobenzene is identical (1H n.m.r. and g.l.c.) to the material obtained from reductive dechlorination of (121).

The yield of the olefin (122) from dehydromesylation of (261a) is equally dependent upon the scale of reaction and the best yields are also obtained at the 0.74 mmol level. Thus the overall yield of the *anti*-bishomobenzene (122) from bicyclo[4,1,0]hept-3-ene (252) is c. 12% and this represents a four-to-five fold increase over the published route employed by Paquette and Taylor.⁴⁸

In order to establish the applicability or otherwise of this type of reaction sequence to the construction of other *anti*-bishomobenzenes attempts to synthesise the *gem*-halogeno-dimethyl-*anti*-bishomobenzenes (271) and (272) (Scheme 43) are currently underway in these laboratories.⁹¹

Scheme 43

Only preliminary investigations on the behaviour of the *gem*-dichloro-*anti*-bishomobenzene (121) with strong base have thus far been achieved. The use of potassium *t*-butoxide in DMSO (substrate to base) leads to a severely discoloured reaction mixture which affords a yellow oil on work-up. The ^1H n.m.r. spectrum of this shows only traces of olefinic and aromatic materials and t.l.c. reveals only minor quantities of discrete reaction products. There is no evidence (^1H n.m.r. and malodour⁴⁶) for the presence of the bis-cyclopropabenzene (120), a product which might have been expected on the basis of the successful aromatization of the tricyclononene (44) under similar conditions.

On this admittedly preliminary basis then, the *gem*-dichloro-*anti*-bishomobenzene (121) appears to behave in a similar fashion to its saturated counterparts (116)-(119) affording only highly complex product mixtures.

As a result of the increased availability of the *anti*-bishomobenzenes (121) and (122), detailed investigations of their base promoted and thermal rearrangements are envisaged in the near future.

CHAPTER FIVEEXPERIMENTALGeneral Methods

Microanalyses were performed by Professor A.D. Campbell and associates, University of Otago. High resolution mass spectra were recorded by Dr G.J. Wright, University of Canterbury, on an AEI MS902 spectrometer, while low resolution mass spectra were recorded on a Micromass 12F instrument. Infra-red spectra were recorded as Nujol and hexachlorobutadiene (hcbd) mulls or as thin films on Unicam SP200 and SP1000 spectrophotometers. Ultraviolet spectra were recorded on a Shimadzu UV200 instrument and extinction coefficients are expressed, in parentheses, as $\log_{10}\epsilon$. ^1H and ^{13}C n.m.r. data were recorded in deuteriochloroform solution on a Hitachi-Perkin Elmer R20 60-MHz and a Varian Associates CFT 20 20-MHz instrument respectively, with tetramethylsilane as internal standard. N.m.r. resonance multiplicities are defined by the usual notation. Analytical g.l.c. was performed on a Pye Series 105 chromatograph equipped with an Autolab Minigrator. Merck Kieselgel GF₂₅₄ was used for t.l.c.: analytical plates being made to a thickness of 0.25 mm and preparative plates to a thickness of 0.75 mm. Components were detected under an ultraviolet lamp at 254 nm and/or by spraying the plates with ethanol-concentrated sulphuric acid-anisaldehyde 93:5:2 (v/v) followed by heating on a hot plate (for oxygenated species) or with iodine spray (for unsaturated species). Merck silica gel type 60 was used as packing material for column chromatography, and the loadings were 1 g of mixture to 50-100 g. Solvents were purified according to Perrin, Armarego and Perrin,⁹² and the petroleum

Addendum to Experimental

The stationary phases employed in gas-liquid-chromatographic analyses were: (i) 5% SE-30; (ii) 25% SE-30; (iii) 5% C-20M; (iv) 3% OV-1; (v) 25% Apiezon L. The solid support in all columns used was 80-100 mesh Gas-Chrom Q.

ether used throughout the work is the fraction b.p. 60-80°, unless otherwise stated. Moisture sensitive reagents were dispensed under nitrogen in a Gallenkamp dry box and prolonged reagent additions were performed at a constant rate with a Hershberg dropping funnel. Melting and boiling points are uncorrected and the former were determined using a Reichert hot stage melting point apparatus.

Alkali metal alkoxides were prepared by reacting the clean metal, usually c. 15 g, in a large excess of the dry alcohol. Reflux was maintained until the metal had completely reacted, whereupon the excess alcohol was removed by careful distillation, and the remainder removed by prolonged pumping in vacuum at c. 100°. The resulting white cakes were pulverised to fine powders and stored, tightly stoppered, in a dry box. Potassium t-butoxide was stored for a maximum period of three weeks under these conditions.

Cyclohexa-1,4-diene (123).

Cyclohexa-1,4-diene was prepared by Birch reduction of benzene, essentially according to the method employed by Paquette and Barrett⁹³ in the reduction of o-xylene. A five litre three-necked flask, cooled on a dry-ice/isopropanol bath was fitted with a mechanical stirrer and a dry-ice condenser. The flask was charged with liquid ammonia (c. 2.5 l), the stirrer started, and anhydrous diethyl ether (450 g, 630 cm³), absolute ethanol (460 g, 581 cm³, 10 moles), and dry distilled benzene (235 g, 267 cm³, 3.0 moles) were added slowly in that order. Freshly cut sodium (207 g, 9.0 g atoms) was then added in small pieces over a five hour period. The reaction mixture was removed from the cold bath and the ammonia allowed to evaporate over eight hours. The reaction flask was then equipped with a reflux condenser, and the reactants maintained under an oxygen-free nitrogen blanket while

ice-water (800 cm³) was added slowly with stirring to dissolve the salts. The resultant upper organic layer was removed and washed with water (3×800 cm³), dried (Na₂SO₄), and concentrated in vacuo on an ice-bath. Distillation of the residue through a 55 cm Vigreux column gave cyclohexa-1,4-diene (123) (185 g, 77%) (99% pure by g.l.c.) as a clear colourless liquid, b.p. 85–86° at 760 mm (lit.⁹⁶ 85.6° at 760 mm). $\nu_{\max}$ 3020, 2855, 2815, 1640, 1435, 1410, 966 and 892 cm⁻¹. δ 2.63, broad s, methylene protons; 5.59, broad s, vinylic protons. G.l.c. {5% SE-30 glass column [6 mm (od.) by 1.5 m], 52°, N₂ at 32 cm³ min⁻¹} 72 s.

trans-1,2-Dibromocyclohexane (129)

trans-1,2-Dibromocyclohexane (95%), b.p. 110–112° at c. 30 mm Hg (lit.⁹⁴ 95%, 108–112° at 25 mm Hg) was prepared from cyclohexene (128) by the method Synder and Brooks.⁹⁴ $\nu_{\max}$ 2950, 2865, 1452, 1439, 1184, 1002, 868 and 676 cm⁻¹. δ 1.18–2.75, complex m, 8H, methylene protons; 4.41, m, 2H, methine protons.

Cyclohexa-1,3-diene (130)

Cyclohexa-1,3-diene (130) was prepared from *trans*-1,2-dibromocyclohexane by a modification of the method of Schaefer and Endres.⁹⁵ *trans*-1,2-dibromocyclohexane (168 g, 0.69 mol) was added in a dropwise fashion to a suspension of externally prepared sodium isopropoxide (127 g, 155 mol) in dry distilled triethylene glycol (350 cm³) maintained under nitrogen at c. 130–170 mm Hg. The rate of addition of the dibromide was adjusted so that the temperature of the reaction mixture was maintained at 100–110° without external heating, and the product diene was allowed to flash distill into a chilled (salt-ice) receiver flask. The distillate was

washed with water ($4 \times 70 \text{ cm}^3$), dried (Na_2SO_4) and filtered. Distillation of the filtrate through a 55 cm Vigreux column gave cyclohexa-1,3-diene (130) (24.9 g, 45%) as a clear colourless liquid b.p. $80-83^\circ$ (lit.⁹⁵ $80-83^\circ$ at 760 mm Hg). δ 2.10, broad s, 4H, methylene protons; 5.75, broad s, 4H, vinylic protons. G.l.c. {5% SE-30 glass column [6 mm (od.) by 1.5 m], 52° , N_2 at 32 cm min^{-1} } 70 s.

Ethyl trichloroacetate

Sulphuric acid (40 cm^3 , 98%) was added cautiously to a solution of trichloroacetic acid (500 g, 3.06 mole) in absolute ethanol (200 cm^3). The resulting mixture was heated under reflux for 1.0 h, cooled and diluted with water (500 cm^3). The lower organic layer was separated, washed with saturated sodium bicarbonate ($1 \times 200 \text{ cm}^3$), water ($2 \times 500 \text{ cm}^3$), and dried (CaCl_2). Distillation gave ethyl trichloroacetate (574 g, 98%) as a clear colourless liquid, b.p. $167-168^\circ$ (lit.⁹⁶ $167.5-168^\circ$).
 ν_{max} 2960, 1760, 1362, 1295, 1245, 1015, 879, 825, 798 and 682 cm^{-1} .

4,4,8,8-Tetrabromo-cis-transoid-cis-tricyclo[5,1,0,0^{3,5}]octane (114)

To a chilled (salt-ice) suspension of benzyltriethylammonium bromide (1.0 g) in bromoform (53 cm^3) containing cyclohexa-1,4-diene (8.0 g, 0.1 mol) was added aqueous sodium hydroxide (50% w/w, 64 cm^3) over 10 min. The light brown reaction mixture was slowly heated until a vigorous exothermic reaction commenced. This was allowed to continue with occasional moderation on a cold water bath and then the mixture maintained under reflux for 40 min with occasional shaking. The product mixture was poured into warm water (200 cm^3) and extracted with hot chloroform ($4 \times 150 \text{ cm}^3$).

The combined organic extracts were filtered through a column (2.5 cm diam.) containing basic alumina (40 g, activity grade I) to give a clear deep red liquid. Concentration in vacuum afforded an oily solid which was recrystallized twice (chloroform) in the presence of activated charcoal to yield 4,4,8,8-tetrabromo-*cis-transoid-cis*-tricyclo[5,1,0,0^{3,5}]octane (114) (18.1 g, 43%) as colourless needles, m.p. 206.5-207.5° (lit.³⁶ 204.2-206.2°) (Found: C, 22.8; H, 1.9; Br, 75.6. Calc. for C₈H₈Br₄: C, 22.7; H, 1.9; Br, 75.4%).

3,3,8,8-Tetrabromo-cis-transoid-cis-tricyclo[5,1,0,0^{2,4}]octane (118)

The tetrabromotricyclo-octane (118) was prepared as described above for compound (114) except that during the addition of carbene to cyclohexa-1,3-diene (130) the reaction mixture was stirred at ambient temperature for 17 h and not heated under reflux. Recrystallization twice (chloroform/ethanol) of the crude reaction product in the presence of activated charcoal gave 3,3,8,8-tetrabromo-*cis-transoid-cis*-tricyclo[5,1,0,0^{2,4}]octane (118)³³ (19.8 g, 47%) as colourless needles, m.p. 70.5-71.5° (Found: C, 23.0; H, 2.0; Br, 75.7. Calc. for C₈H₈Br₄: C, 22.7; H, 1.9; Br, 75.4%). $\nu_{\max}$ 1200, 1035, 1009, 987, 814, 760, 730 and 685 cm⁻¹. δ 1.05, complex m, 2H, 1.75, m, 4H, 2.17, complex m, 2H.

3,3,8,8-Tetrachloro-cis-transoid-cis-tricyclo[5,1,0,0^{2,4}]octane (116)

3,3,8,8-Tetrachloro-*cis-transoid-cis*-tricyclo[5,1,0,0^{2,4}]octane (116) was prepared by essentially the same procedure as has recently been reported.⁴⁰

Yield: 84%, b.p. 121-121.5°/3.5 mm (lit.⁴⁰ 125°/4 mm), m.p. 36-37° (Found: C, 39.1; H, 3.3; Cl, 57.7. Calc. for C₈H₈Cl₄: C, 39.1; H, 3.3; Cl, 57.7%). $\nu_{\max}$ 1212, 1196, 1062, 1031, 969, 927, 846, 823, 777 and 700 cm⁻¹. δ 1.19, complex m, cyclopropyl protons at C4 and C7; 1.75, complex m,

methylene protons; 2.11, complex m, cyclopropyl protons at C1 and C2.

4,4,8,8-Tetrachloro-cis-transoid cis-tricyclo[5,1,0,0^{3,5}]octane
(112), *7,7-Dichlorobicyclo[4,1,0]hept-3-ene* (30) and
7,7-Dichlorobicyclo[4,1,0]hept-2-ene (34)

To a stirred suspension of sodium methoxide (18.8 g, 0.348 mol) in pentane (130 cm³) was added the appropriate cyclohexadiene (10.0 g, 0.126 mol) and the resultant mixture cooled in a salt-ice bath. Ethyl trichloroacetate (48 g, 0.252 mol) was added dropwise over a period of 1 h, the salt-ice bath removed and the stirring continued for a further 6 h. The mixture was poured into water (150 cm³), the organic phase separated, washed with water (2×50 cm³), dried (CaCl₂), filtered and concentrated in vacuum to a brown oil.

(i) The oil resulting from the addition of dichlorocarbene to cyclohexa-1,4-diene was diluted with light petroleum (20 cm³) and the precipitated solid collected by filtration. Recrystallization (benzene/light petroleum, 1:1) gave *4,4,8,8-tetrachloro-cis-transoid-cis-tricyclo[5,1,0,0^{3,5}]octane* (112) (1.9 g, 6%) as a colourless crystalline solid, m.p. 170–172° (lit.³² 178–180°) (Found: C, 39.4; H, 3.3; Cl, 57.6. Calc. for C₈H₈Cl₄: C, 39.1, H, 3.3; Cl, 57.7%). $\nu_{\max}$ 2912, 1438, 1346, 1308, 1223, 1098, 997, 946, 792 and 762 cm⁻¹. δ 1.60, complex m, 4H; 2.10, complex m, 4H, m/e 244 (1.6%), 246 (2.1), 248 (1.1), M⁺⁺; 209 (16.5%), 211 (16.5), 213 (5.7), (M-Cl)⁺; 101 (100%), 103 (35).

(ii) The filtrate from (i) above was concentrated in vacuum and distilled to give *7,7-dichlorobicyclo[4,1,0]hept-3-ene* (30) (14.0 g, 69%) as a clear colourless liquid, b.p. 88–90°/23 mm (lit.¹⁵ 88–90°/23 mm), $\nu_{\max}$ 3020, 2885, 2820, 1429, 1332, 1220, 1118, 1072, 1006, 949, 800, 702 and 670 cm⁻¹. δ 1.80, m, cyclopropyl protons; 2.27, broad s, methylene

protons; 5.45, s, vinylic protons.

(iii) The oil from the addition of dichlorocarbene to cyclohexa-1,3-diene afforded 7,7-dichlorobicyclo[4,1,0]hept-2-ene (34) in the same yield and with the same boiling point (52.5-53°/1.25 mm) as reported previously¹¹ despite the shortened reaction time.

7,7-Dibromobicyclo[4,1,0]hept-3-ene (31) and

7,7-Dibromobicyclo[4,1,0]hept-2-ene (131)

7,7-Dibromobicyclo[4,1,0]hept-3-ene (31) was prepared by the method of Hofmann *et al.*³⁸ Yield: 72%, m.p. 37.0-37.5° (lit.³⁸ 36.8-37.0°).

$\nu_{\max}$ 3025, 2890, 2820, 1428, 1056, 982, 939, 739, and 667 cm^{-1} .

δ 1.90, m, cyclopropyl protons; 2.20, m, methylene protons; 5.45, broad s, vinylic protons.

7,7-Dibromobicyclo[4,1,0]hept-2-ene (131) was prepared essentially according to the method of Lindsay and Reese.⁴¹ A freshly prepared solution of potassium *t*-butoxide (1.0 M, 200 cm^3) in *t*-butanol was added in a dropwise fashion over a period of 4 h to a chilled (ice) solution of cyclohexa-1,3-diene (130) (10-23 g, 0.13 mol) in *t*-butanol (50 cm^3) containing bromoform (33.0 g, 0.13 mol). The resultant mixture was stirred for a further 1 h, poured into petroleum ether (250 cm^3), and quenched with water (250 cm^3). The two phases were separated, and the aqueous phase extracted with petroleum ether (250 cm^3). The combined organic phases were washed with water (3×300 cm^3), dried (Na_2SO_4), filtered and concentrated in vacuum to give a red oil. Distillation gave 7,7-dibromobicyclo[4,1,0]-hept-2-ene (131)⁴¹ (17.91 g, 58%) as a clear colourless liquid b.p. 80-83°/1.4 mm (Found: C, 33.8; H, 3.3; Br, 63.1. Calc. for $\text{C}_7\text{H}_8\text{Br}_2$: C, 33.4; H, 3.2; Br, 63.4%). $\nu_{\max}$ 3020, 2910, 2812, 1445, 1430, 1350, 1040, 840, 766 and 682 cm^{-1} . δ 1.95, complex m, 6H; 5.85, broad s, vinylic

protons. m/e 250, 7%, 252, 17.8%, 254, 4%, M^{+} ; 171, 85.5%, 173, 77%, $(M-Br)^{+}$; 91, 100%, $(C_7H_7)^{+}$. G.l.c. {5% C-20M glass column [6 mm (od.) by 1.5 m], 153°, N_2 at $40\text{ cm}^3\text{ min}^{-1}$] 288 s.

endo- and exo-7-Chlorobicyclo[4,1,0]hept-3-ene (124), and

endo- and exo-7-Chlorobicyclo[4,1,0]hept-2-ene (132)

To a stirred solution of the appropriate 7,7-dichlorobicyclo[4,1,0]heptene (6.90 g, 42.3 mmol) in ethanol (140 cm^3) containing potassium hydroxide (14.0 g, 0.25 mol) was added finely divided zinc (28.0 g, 0.43 mol) and the resulting mixture heated under reflux with continuous stirring for 18 h. Dichloromethane (60 cm^3) was added, the solution filtered, and the filtrate extracted with an excess of hydrochloric acid (2 M). The aqueous phase was re-extracted with dichloromethane ($2 \times 60\text{ cm}^3$) and the combined organic extracts washed with water ($2 \times 100\text{ cm}^3$), dried ($CaCl_2$), filtered and concentrated in vacuum to a pale yellow oil.

(i) Distillation of the oil resulting from treatment of the bicyclohept-3-ene (30) gave a 10.5:1 mixture of *endo- and exo-7-chlorobicyclo[4,1,0]hept-3-ene (124)* (2.10 g, 39%) as a colourless liquid, b.p. $46^\circ/5.5\text{ mm}$ (Found: C, 66.0; H, 6.9; Cl, 25.6; M^{+} 128.0395. C_7H_9Cl requires C, 65.4; H, 7.0; Cl, 27.6%; M^{+} 128.0393). $\nu_{\max}$ 3005, 2870, 2810, 1425, 1275, 1110, 1085, 1002, 731, 695 and 662 cm^{-1} . δ *endo*-isomer (124a): 1.70, complex m, protons at C1, C2, C5 and C6; 3.20, t, J 7.5 Hz, $CHCl$; 5.46, broad s, vinylic protons; *exo*-isomer (124b): 1.70, complex m, protons at C1, C2, C5 and C6; 2.86, t, J 2.8 Hz, $CHCl$; 5.35, broad s, vinylic protons. G.l.c. {25% E-30 glass column [0.95 cm (o.d.) by 2.1 m], 102° , N_2 at $100\text{ cm}^3\text{ min}^{-1}$] *endo*-isomer (124a) 500 s; *exo*-isomer (124b) 370 s (*endo/exo* 10.5:1).

(ii) Distillation of the oil resulting from treatment of the bicyclohept-2-ene (34) gave a 3:1 mixture of *endo*- and *exo*-7-chlorobicyclo[4,1,0]hept-2-ene (132) (1.64 g, 30%) as a colourless liquid, b.p. 48°/5.1 mm (Found: C, 64.8; H, 7.4; Cl, 28.5. C_7H_9Cl requires C, 65.4; H, 7.1; Cl, 27.6%). $\nu_{\max}$ 3040, 2925, 2850, 1440, 1290, 1043, 959, 795, 778, 720 and 686 cm^{-1} . δ *endo*-isomer (132a): 1.80, complex m, protons at C1, C4, C5, and C6; 3.32, t, J 7.5 Hz, $CHCl$; 5.75, complex m, vinylic protons; *exo*-isomer (132b): 1.80, complex m, protons at C1, C4, C5 and C6; 2.90, t, J 2.8 Hz, $CHCl$; 5.75, complex m, vinylic protons. G.l.c. (conditions as above) *endo*-isomer (132a) 480 s; *exo*-isomer (132b) 370 s (*endo/exo* 3:1).

endo- and *exo*-7-Bromobicyclo[4,1,0]hept-3-ene (125) and

endo- and *exo*-7-Bromobicyclo[4,1,0]hept-2-ene (133)

The half-reduction of the 7,7-dibromobicyclo[4,1,0]heptenes (31) and (131) were carried out by the method employed for their chloro analogues above, but with a shorter reaction time (6 vs 18 h).

endo- and *exo*-7-Bromobicyclo[4,1,0]hept-3-ene (125) (34% of a 4:1 mixture), b.p. 46-48°/1.5 mm. $\dagger \nu_{\max}$ 3029, 2975, 2900, 2885, 2835, 1660, 1428, 1286, 1218, 1116, 998, 732, 695, 668 and 625 cm^{-1} . δ *endo*-isomer (125a): 1.75, complex m, 6H; 3.25, t, $J_{7,1(6)}$ 7.8 Hz, H7; 5.46, broad s, H3 and H4; *exo*-isomer (125b): 1.75, complex m, 6H; 2.72, t, $J_{7,1(6)}$ 3.5 Hz, H7; 5.46 broad s, H3 and H4. G.l.c. {5% C-20M glass column [6 mm (od.) by 1.5 m], 120°, N_2 at 40 $cm^3 min^{-1}$ } *endo*-isomer (125a) 217 s; *exo*-isomer (125b) 127 s (*endo/exo* 4:1). m/e (20 eV) 172, 11%, 174, 11%, M^{+} .

endo- and *exo*-7-Bromobicyclo[4,1,0]hept-2-ene (133) (50% of a 1:2 mixture), b.p. 46-48°/1.5 mm. $\dagger \nu_{\max}$ 3020, 2960, 2910, 2845, 1654,

$\dagger$ Satisfactory microanalytical data have not been obtained for these compounds due to slow decomposition on standing. However, they have been converted to compounds for which accurate data have been obtained.

1440, 1090, 1030, 740 and 660 cm^{-1} . δ *endo*-isomer (133a): 1.75, complex m, 6H; 3.42, t $J_{7,1(6)}$ 7.8 Hz, H7; 5.75, broad s, H2 and H3; *exo*-isomer (133b): 1.75, complex m, 6H; 2.81, t $J_{7,1(6)}$ 3.0 Hz, H7; 5.75, broad s, H2 and H3. m/e (20 eV) 172, 13%, 174, 13%, M^{+} ; 91, 100%. G.l.c. (conditions as above) *endo*-isomer (133a) 120 s; *exo*-isomer (133b) 180 s (*endo/exo* 1:2).

4,4,*endo*-8- and 4,4,*exo*-8-Trichloro-cis-transoid-cis-tricyclo[5,1,0, $0^{3,5}$]octane (113), and 3,3,*endo*-8- and 3,3,*exo*-8-Trichloro-cis-transoid-cis-tricyclo[5,1,0, $0^{2,4}$]octane (117)

To a chilled (salt-ice) suspension of sodium methoxide (3.8 g, 70.3 mmol) in pentane (20-25 cm³) containing the appropriate epimeric mixture of 7-chlorobicycloheptenes, was added ethyl trichloroacetate (13.3 g, 70 mmol) over 1 h. The resultant mixture was stirred at ambient temperature for a further 30 h and worked up in the manner described for compounds (30), (34) and (112).

(i) The oily solid resulting from the addition of dichlorocarbene to the bicyclohept-3-enes (124) was removed by filtration, washed with light petroleum (1 cm³) and filtered through a column (2 cm diam.) of alumina (55 g) eluting with carbon tetrachloride. Concentration of the eluate in vacuum afforded a 6.5:1 mixture of 4,4,*endo*-8- and 4,4,*exo*-8-trichloro-cis-transoid-cis-tricyclo[5,1,0, $0^{3,5}$]octane (113) (2.46 g, 50%) as colourless crystalline flakes, m.p. 72.5-74° (Found: C, 45.3; H, 4.4; Cl, 50.3. C₈H₉Cl₃ requires C, 45.4; H, 4.3; Cl, 50.3%). ν_{max} 3002, 2897, 2838, 1445, 1275, 1249, 1083, 1045, 775, 730 and 688 cm^{-1} . δ *endo*-isomer (113a): 0.9-2.2, complex m, 8H; 3.10, t, J 7.2 Hz, CHCl; *exo*-isomer (113b): 0.9-2.2, complex m, 8H; 2.51, t, J 3.0 Hz, CHCl.

(ii) Distillation of the brown oil resulting from the addition of dichlorocarbene to the 7-chloro-bicycloheptenes (132) gave a 3:1 mixture of 3,3,endo-8- and 3,3,exo-8-trichloro-cis-transoid-cis-tricyclo[5,1,0,0^{2,4}]-octane (117) (2.62 g, 53%) as a clear colourless oil, b.p. 210°/8 mm (Found: C, 45.4; H, 4.4; Cl, 49.6. C₈H₉Cl requires C, 45.4; H, 4.3; Cl, 50.3%). $\nu_{\max}$ 3020, 2955, 2876, 1452, 1288, 1228, 1139, 1095, 1049, 967, 925, 828, 797 and 684 cm⁻¹. δ *endo*-isomer (117a): 0.95-2.35, complex m, 8H; 3.37, t, *J* 6.9 Hz, CHCl; *exo*-isomer (117b): 0.95-2.35, complex m, 8H, 2.53, t, *J* 2.8 Hz, CHCl.

4,4,endo-8-Tribromo-cis-transoid-cis-tricyclo[5,1,0,0^{3,5}]-octane (115a) and 3,3,endo-8- and 3,3,exo-8-Tribromo-cis-transoid-cis-tricyclo[5,1,0,0^{2,4}]-octane (119)

To a chilled (salt-ice) and stirred suspension of potassium *t*-butoxide (15.1 g, 135 mmol) in pentane (120 cm³) containing the appropriate epimeric mixture of 7-bromobicycloheptenes (5.0 g, 28.9 mmol), was added a solution of bromoform (21.7 g, 85.5 mmol) in pentane (90 cm³) dropwise over 0.5 h. The resultant mixture was stirred at ambient temperature for a further 16 h and then quenched with water (100 cm³). The organic phase was separated, washed with water (2×100 cm³), dried (Na₂SO₄) and concentrated in vacuum to give an oil.

(i) The oil resulting from the addition of dibromocarbene to the bicyclohept-3-enes (125) slowly solidified. Recrystallization (ethanol/activated charcoal) gave 4,4,endo-8-tribromo-cis-transoid-cis-[5,1,0,0^{3,5}]-octane (115a) (4.21 g, 41%) as lustrous white crystals, m.p. 87-88° (Found: C, 28.1; H, 2.8; Br, 69.4. C₈H₉Br₃ requires C, 27.9; H, 2.6; Br, 69.5%). $\nu_{\max}$ 3002, 2925, 2915, 2852, 1465, 1350, 1305, 1257, 1215, 1190, 1065, 1045, 740 and 720 cm⁻¹. δ 1.15, complex m, H1 and H7; 1.74, complex M, H3 and H5;

2.04, complex m, methylene protons; 3.15, t, $J_{8,1(7)}$ 8.0 Hz, H8. m/e (20 eV) 342, 0.5%, 344, 1%, 346, 1%, 348, 0.5%, M^{+} ; 104, 100%, $(M-Br_2-HBr)^{+}$.

(ii) The oil resulting from the addition of dibromocarbene to the bicyclohept-2-enes (7g,h) was subjected to vacuum distillation and the major fraction (b.p. 126-127°/1.75 mm) collected. The distillate was subjected to column chromatography over silica gel (5 cm diam. column; 120 g) with light petroleum elution to give a 1:2 mixture of 3,3,endo-8- and 3,3,exo-8-tribromocis-transoid-cis-tricyclo[5,1,0,0^{2,4}]octane (119) (1.5 g, 15%) as a clear colourless oil, b.p. 127-128°/1.75 mm (Found: C, 28.7; H, 2.8; Br, 68.4. C₈H₉Br₃ requires C, 27.9; H, 2.6; Br, 69.5%). $\nu_{\max}$ 3020, 2950, 2930, 2870, 1443, 1252, 1229, 743, 732 and 679 cm⁻¹. δ *endo*-isomer (119a): 0.8-1.55, complex m, H1, H2, H4 and H7; 1.6-2.35, complex m, methylene protons, 3.39, t, $J_{8,1(7)}$ 7.0 Hz, H8; *exo*-isomer (119b): 0.8-1.55, complex m, H1, H2, H4 and H7; 1.6-2.35, complex m, methylene protons; 2.42, t, $J_{8,1(7)}$ 3.7 Hz, H8. m/e (12 eV) 342, 32%, 344, 100%, 346, 91%, 348, 23%, M^{+} .

cis-transoid-cis-Tricyclo[5,1,0,0^{3,5}]octane (127)

To a stirred mixture of 4,4,8,8-tetrabromo-cis-transoid-cis-tricyclo[5,1,0,0^{3,5}]octane (114) (1.69 g, 3.99 mmol), dry t-butyl alcohol (3.5 g, 47.3 mmol) and dry, freshly distilled, tetrahydrofuran (40 cm³) under an atmosphere of dry oxygen-free nitrogen was added lithium wire (1.32 g, 0.19 g-atom) cut into small pieces in the neck of the flask. The reaction began almost immediately and stirring was continued for 21 h at ambient temperature. The resultant mixture was poured into ice-water (50 cm³) through a glass-wool plug and the inorganic solids thus retained washed with pentane (30 cm³). The filtrate was extracted with pentane (2×60 cm³) and the combined organic phases were washed with water (2×50 cm³), dried (Na₂SO₄), filtered, and concentrated in vacuum to a pale yellow oil. Microdistillation at slightly

reduced pressure afforded *cis-transoid-cis*-tricyclo[5,1,0,0^{3,5}]octane (127)⁹⁷ (220 mg, 51%) as a colourless liquid (Found: C, 88.7; H, 11.4. Calc. for C₈H₁₂: C, 88.8; H, 11.2%). $\nu_{\max}$ 3065, 3008, 2920, 2855, 1455, 1029, 985, 914, 830 and 801 cm⁻¹. δ 0.53, m, cyclopropyl protons; 1.75, m, methylene protons. G.l.c.: in a 5% SE-30 glass column [6 mm (o.d.) by 1.5 m] at 58° with nitrogen as carrier gas and a flow rate of 38 cm³ min⁻¹ the retention time was 120 s.

Reductive Dechlorination of the Chlorotricyclooctanes (112), (113), (116) and (117)

To sodium sand [prepared by shaking molten sodium (3.8 g, 0.19 g-atom) in hot dry, freshly distilled *o*-xylene and washing the cooled sand with ether (3×25 cm³) and freshly distilled tetrahydrofuran (2×20 cm³)] was added a solution of the appropriate chlorotricyclooctane (1.0 g) and dry *t*-butyl alcohol (1.5 mol.equiv. per chlorine atom) in dry tetrahydrofuran (20 cm³). The ensuing mixture was heated under reflux under an atmosphere of nitrogen for 1 h and filtered through a pad of glass wool into water (100 cm³). The inorganic salts were washed with hexane (40 cm³) and the aqueous phase extracted with hexane (3×50 cm³). The combined organic extracts were dried (Na₂SO₄) and concentrated in vacuum to a pale yellow oil which was distilled at slightly reduced pressure.

(i) 4,4,8,8-Tetrachloro- and the 4,4,8-trichloro-*cis-transoid-cis*-tricyclo[5,1,0,0^{3,5}]octane mixture (112) and (113) respectively, afforded *cis-transoid-cis*-tricyclo[5,1,0,0^{3,5}]octane (127) [70% from (112); 61% from (113)] as the sole hydrocarbon product and with the same retention time as an authentic sample on a 5% SE-30 column. A mixture with authentic material showed a single peak on both 5% SE-30 and 3% OV-1 columns.

(ii) 3,3,8,8-Tetrachloro- and the 3,3,8-trichloro-*cis-transoid-cis*-tricyclo[5,1,0,0^{2,4}]octane mixture (116) and (117), respectively, afforded the same hydrocarbon product *cis-transoid-cis*-tricyclo[5,1,0,0^{2,4}]octane (134) [71% from (116); 62% from (117)] (Found: C, 89.2, H, 11.2. Calc. for C₈H₁₂: C, 88.8; H, 11.2%). $\nu_{\max}$ 3070, 3007, 2920, 2865, 1463, 1395, 1023, 835, 758 and 709 cm⁻¹. δ 0.70, m, cyclopropyl protons; 1.66 broad s, methylene protons. A g.l.c. retention time of 186 s was recorded on a 5% SE-30 column at 62°; an admixture of the two samples gave a single peak on both a 5% SE-30 and a 3% OV-1 column.

Reductive Debromination of the Bromotricyclooctanes (114), (115), (118) and (119)

The reductive debrominations of the bromotricyclooctanes (114), (115), (118) and (119) were performed by employing the method described above for compound (114).

(i) 4,4,8,8-Tetrabromo- and 4,4,endo-8-tribromo-*cis-transoid-cis*-tricyclo[5,1,0,0^{3,5}]octane (114) and (115) respectively, afforded the same hydrocarbon product *cis-transoid-cis*-tricyclo[5,1,0,0^{3,5}]octane (127) [51% from (114); 63% from (115)] with the same retention time as an authentic sample on a 5% SE-30 column. A mixture with an authentic sample showed a single peak on both 5% SE-30 and 3% OV-1 columns.

(ii) 3,3,8,8-Tetrabromo- and the 3,3,8-tribromo-*cis-transoid-cis*-tricyclo[5,1,0,0^{2,4}]octane mixture (118) and (119) respectively, afforded *cis-transoid-cis*-tricyclo[5,1,0,0^{2,4}]octane (134) [53% from (118); 67% from (119)] as the sole isolable hydrocarbon product and with the same retention time as the product previously obtained from the chloro analogues (116) and (117). Admixture of the samples gave a single peak on both 30% SE-30 and 5% OV-1 columns.

Dehydrochlorination of the cis-transoid-cis-Tricyclooctanes

(112), (113), (116) and (117)

A solution of the appropriate tetrachlorotricyclooctane (112), (116) or the epimeric trichlorotricyclooctane mixtures (113), (117) (2.0 g) in either tetrahydrofuran or dimethyl sulfoxide (50 cm³) (see below) was added dropwise over 0.5 h to a chilled (salt-ice) and stirred suspension of potassium *t*-butoxide (8 mol.equiv.; twofold excess) in the same solvent (100 cm³). The resultant black solution was stirred at ambient temperature for 16 h, diluted with water (200 cm³) and extracted with light petroleum (3×200 cm³). The combined organic extracts were washed with water (2×100 cm³) dried (Na₂SO₄) and concentrated in vacuum to brown oil. The product mixture thus obtained was subjected to preparative t.l.c. with light petroleum elution and the bands obtained extracted with chloroform (100 cm³).

(i) The product mixture from 4,4,8,8-tetrachloro-*cis-transoid-cis*-tricyclo[5,1,0,0^{3,5}]octane (112) in tetrahydrofuran resulted in four bands A-D with R_F values of 0.0, 0.3, 0.5 and 0.8 respectively.

Band A (R_F 0.0) was resubjected to preparative t.l.c. (benzene elution) but no satisfactory separation of the components was obtained.

Band B (R_F 0.3) yielded (E)- β -*t*-butoxy-4-chlorostyrene (137) (270 mg, 16%) as a colourless oil (Found: C, 68.4; H, 7.4; Cl, 16.6. C₁₂H₁₅ClO requires C, 68.4; H 7.2; Cl, 16.8%). $\nu_{\max}$ 2960, 2910, 1642, 1490, 1367, 1255, 1185, 1150, 1090, 915 and 840 cm⁻¹. $\lambda_{\max}$ (C₆H₁₂) 270 nm (log ϵ 4.23). δ 1.35, s, (CH₃)₃C; 5.93, d, J 12.0 Hz, ArCH=CHOBu^t; 7.03, d, J 12.0 Hz, ArCH=CHOBu^t; 7.19, s, aromatic, m/e 210, 6%, M⁺; 154, 100%, 156, 33%, (M-C₄H₈)⁺.

Band C (R_F 0.5) yielded (Z)- β -*t*-butoxy-4-chloro-styrene (138) (260 mg, 15%) as a colourless oil (Found: C, 68.4; H, 7.4; Cl, 16.6. C₁₂H₁₅ClO requires C, 68.4; H, 7.2; Cl, 16.8%). $\nu_{\max}$ 2970, 2920, 1640, 1485, 1420, 1368, 1268, 1180, 1085, 1010 and 835 cm⁻¹. $\lambda_{\max}$ (C₆H₁₂) 264 nm

(log ϵ 4.59). δ 1.39, s, $(\text{CH}_3)_3\text{C}$; 5.20, d, J 6.5 Hz, $\text{ArCH}=\text{CHOBu}^t$; 6.50, d, J 6.5 Hz, $\text{ArCH}=\text{CHOBu}^t$; 7.42, AA'XX', 8.1 Hz, aromatic, m/e 210, 7%, M^+ ; 154, 100%, 156, 33%, $(M-\text{C}_4\text{H}_8)^+$.

Band D (R_F 0.8) gave 4,4,8,8-tetrachloro-*cis-transoid-cis*-tricyclo[5,1,0,0^{3,5}]octane (112) (40 mg, 2% recovery) as colourless crystals, m.p. and mixture m.p. 170–172°.

On performing the reaction in dimethyl sulfoxide, compounds (137) and (138) were obtained in yields of 31 and 4%, respectively, but no starting material was recovered. Variations in quantity of base employed from a stoichiometric quantity to a 12.5-fold excess in either solvent gave the same products in essentially the same yields.

(ii) The product mixture from the 6.5:1 epimeric mixture of 4,4,8-trichloro-*cis-transoid-cis*-tricyclo[5,1,0,0^{3,5}]octanes (113) in dimethyl sulfoxide (the base in tetrahydrofuran was without effect) gave two bands A and B with R_F values of 0.0 and 0.26 after three successive elutions with light petroleum.

Band A (R_F 0.0) was resubjected to preparative t.l.c. but elution with a variety of solvents failed to provide any satisfactory separation.

Band B (R_F 0.26) afforded (E)- β -*t*-butoxystyrene (141) (75 mg, 5% as a clear oil (Found: C, 81.0; H, 9.1. $\text{C}_{12}\text{H}_{16}\text{O}$ requires C, 81.8; H, 9.2%). ν_{max} 2975, 1650, 1372, 1262, 1217, 1192, 1145, 925, 752 and 700 cm^{-1} . δ 1.33, s, $(\text{CH}_3)_3\text{C}$; 5.92, d, J 12 Hz, $\text{PhCH}=\text{CHOBu}^t$; 6.97, d, J 12 Hz, $\text{PhCH}=\text{CHOBu}^t$; 7.20, broad s, aromatic, m/e 176, 10%, M^+ ; 120, 100%, $(M-\text{C}_4\text{H}_8)^+$.

Variations in the quantity of base employed failed to increase the yield of styrene (141).

(iii) Treatment of 3,3,8,8-tetrachloro-*cis-transoid-cis*-tricyclo[5,1,0,0^{2,4}]octane (116) as described above and under a variety of alternative

conditions in either solvent afforded only uncharacterizable black tars. Quenching of the reaction in tetrahydrofuran after 30 min gave a 70% recovery of starting material.

(iv) Treatment of the 3:1 epimeric mixture of 3,3,8-trichloro-*cis-transoid-cis*-tricyclo[5,1,0,0^{2,4}]octanes (117) under a variety of conditions in dimethyl sulfoxide (the base was without effect in tetrahydrofuran) failed to yield any characterizable product.

Dehydrobromination of the cis-transoid-cis-Tricyclooctanes
(114), (115), (118) and (119)

To a chilled (salt-ice) and stirred suspension of potassium *t*-butoxide (8 mol. equiv.) in either tetrahydrofuran or dimethyl sulfoxide (100 cm³) (see below) was added dropwise over 0.5 h a solution of the appropriate tetrabromotricyclooctane (114)/(118) (8.02 mmol) or the tribromotricyclooctane (115)/(119) (9.37 mmol) in the same solvent (50 cm³). The resultant black solution was stirred at ambient temperature for 16 h, diluted with water (200 cm³) and extracted with light petroleum (3×200 cm³). The combined organic extracts were washed with water (2×100 cm³), dried (Na₂SO₄), filtered and concentrated in vacuum to a brown oil. The oil was subjected to preparative t.l.c. (light petroleum elution) and the bands obtained extracted with dichloromethane (50 cm³).

(i) The product mixture from 4,4,8,8-tetrabromo-*cis-transoid-cis*-tricyclo[5,1,0,0^{3,5}]octane (114) in tetrahydrofuran resulted in three bands A-C with R_F values of 0.0, 0.4 and 0.6 respectively.

Band A (R_F 0.0) was resubjected to preparative t.l.c. with a variety of eluents but no satisfactory separation of the components was obtained.

Band B (R_F 0.4) yielded an inseparable 4:1 mixture of (E)-4-bromo- β -*t*-butoxystyrene (145a) and (E)-3-bromo- β -*t*-butoxystyrene (145b) (205 mg, 10%) as a colourless oil (Found: M^{+} 254.0286 and 256.0277. $C_{12}H_{15}BrO$ requires M^{+} 254.0307 and 256.0287). ν_{max} 2955, 2910, 1640, 1464, 1368, 1254, 1145, 1016, 920, 908 and 747 cm^{-1} . λ_{max} (C_6H_{12}) 269 nm (log ϵ 4.12). δ 4-bromo-isomer (145a): 1H : 1.33, s, $(CH_3)_3C$; 6.15, d, J 12.0 Hz, $ArCH=CHOBu^t$; 6.90, d, J 12.0 Hz, $ArCH=CHOBu^t$; 6.82-7.50, complex m, aromatic protons; ^{13}C : 28.2 $(CH_3)_3C$; 77.4, $(CH_3)_3C-O$; 108.6, $ArCH=CHOBu^t$; 123-133, aromatic carbon resonances; 136.8, Cl; 144.2, $ArCH=CHOBu^t$; 3-bromo-isomer (145b): 1H : 1.33, s, $(CH_3)_3C$; 5.79, d, J 12.0 Hz, $ArCH=CHOBu^t$; 6.82-7.50 complex m, aromatic protons and $H\alpha$; ^{13}C : 28.2 $(CH_3)_3C$; 77.4 $(CH_3)_3C-O$; 108.4, $ArCH=CHOBu^t$; 123-133 aromatic carbon resonances; 135.5, Cl; 142.8, $ArCH=CHOBu^t$. m/e 254, 24%, 256, 23%, M^{+} ; 198, 98%, 200, 100%, $(M-C_4H_8)^{+}$.

Band C (R_F 0.6) yielded an inseparable 4:1 mixture of (Z)-4-bromo- β -*t*-butoxystyrene (143a) and (Z)-3-bromo- β -*t*-butoxystyrene (143b) (175 mg, 8.5%) as a pale yellow oil (Found: M^{+} 254.0304 and 256.0275. $C_{12}H_{15}BrO$ requires M^{+} 254.0307 and 256.0287). ν_{max} 2955, 2910, 1640, 1480, 1381, 1280, 1190, 1100, 1032 and 781 cm^{-1} . λ_{max} (C_6H_{12}) 271 nm (log ϵ 4.19). δ 4-bromo-isomer (143a): 1H : 1.35, s, $(CH_3)_3C$; 5.52, d, J 7.5 Hz, $ArCH=CHOBu^t$; 6.45, d, J 7.5 Hz, $ArCH=CHOBu^t$; 7.15, AA'XX' system J 10.5 Hz, aromatic protons; ^{13}C : 28.1, $(CH_3)_3C$; 77.8, $(CH_3)_3C-O$; 103.7, $ArCH=CHOBu^t$; 122-133 aromatic carbon resonances; 135.7, Cl; 142.4, $ArCH=CHOBu^t$; 3-bromo-isomer (143b): 1H : 1.35, s, $(CH_3)_3C$; 5.51, d, J 7.5 Hz, $ArCH=CHOBu^t$; 6.33, d, J 7.5 Hz, $ArCH=CHOBu^t$; 6.8-7.5, complex m, $H4$, $H5$ and $H6$; 8.03, m, $H2$; ^{13}C : 28.1 $(CH_3)_3C$; 77.8, $(CH_3)_3C-O$; 104.7, $ArCH=CHOBu^t$; 122-133, aromatic carbon resonances; 136.0, Cl; 141.6, $ArCH=CHOBu^t$. m/e 254, 6%, 256, 6%, M^{+} ; 198, 100%, 200, 98%, $(M-C_4H_8)^{+}$.

(ii) The product mixture from 4,4,*endo*-8-tribromo-*cis-transoid-cis*-tricyclo[5,1,0,0^{3,5}]octane (115) in dimethyl sulfoxide gave two bands A and B with R_F values of 0.0 and 0.2 after a second elution with light petroleum.

Band A (R_F 0.0) was resubjected to preparative t.l.c. with a variety of eluents but no satisfactory resolution of the components was obtained.

Band B (R_F 0.2) yielded (*E*)- β -*t*-butoxystyrene (141) (45 mg, 3%) as a clear colourless oil identical in all respects to the sample previously obtained from the trichloro analogues (113).

(iii) The product mixture obtained from one reaction of 4,4,-*endo*-8-tribromo-*cis-transoid-cis*-tricyclo[5,1,0,0^{3,5}]octane in tetrahydrofuran resulted in two bands A and B with R_F values of 0.0 and 0.5 respectively.

Band A (R_F 0.0) was resubjected to preparative t.l.c. with a variety of eluents but no satisfactory separation of the components was achieved.

Band B (R_F 0.5) yielded a colourless oil proposed as (*Z*)- β -*t*-butoxystyrene (142) (30 mg, 2%). $\nu_{\max}$ 2955, 1635, 1483, 1441, 1410, 1365, 1265, 1172, 1080, 776 and 694 cm^{-1} . δ 1.35, s, $(\text{CH}_3)_3\text{C}$; 5.16, d, J 7.2 Hz $\text{ArCH}=\text{CHOBu}^t$; 6.41, d, J 7.2 Hz, $\text{ArCH}=\text{CHOBu}^t$; 7.15, complex m, H3-5; 7.50, complex m, H2 and H6. m/e 176, 17%, M^+ ; 120, 100%, $(\text{M}-\text{C}_4\text{H}_8)^+$.

(iv) Treatment of 3,3,8,8-tetrabromo-*cis-transoid-cis*-tricyclo[5,1,0,0^{2,4}]octane (118) as described above and under a variety of alternative conditions in either solvent afforded only uncharacterizable black tars.

(v) Treatment of the 1:2 epimeric mixture of 3,3,8-tribromo-*cis-transoid-cis*-tricyclo[5,1,0,0^{2,4}]octanes (119) under a variety of conditions in either solvent failed to yield any characterizable product.

Variations in the quantity of base employed in the above reactions had no effect on the yields of the styrene products.

Dehydrochlorination of 4,4,8,8-Tetrachloro-cis-transoid-cis-tricyclo[5,1,0,0^{3,5}]octane (112) with Sodium Methoxide

A solution of the tetrachlorotricyclo-octane (112) (2.0 g, 8.13 mmol) in dimethyl sulphoxide (50 cm³) was added dropwise over 0.5 h to a chilled (salt-ice) and stirred suspension of sodium methoxide (12.0 g, 27 mol. equiv.; eight fold excess) in the same solvent (100 cm³). The resultant black solution was stirred at ambient temperature for 16 h, diluted with water (200 cm³) and extracted with light petroleum (3×200 cm³). The combined organic extracts were washed with water (2×100 cm³), dried (Na₂SO₄) and concentrated in vacuum to a brown oil. The product mixture was subjected to preparative t.l.c. with light petroleum elution and gave two bands A and B with R_F values of 0.4 and 0.5, which were extracted with methylene chloride (25 cm³).

Band A (R_F 0.4) gave a clear colourless oil proposed as (E)- β -methoxy-4-chlorostyrene (147) (20 mg, 1.5%). $\nu_{\max}$ 2920, 1638, 1491, 1245, 1165, 1128, 1010, 939, 868 and 839 cm⁻¹. δ 3.63, s, 3H, -OCH₃; 5.70, d, J = 12.8 Hz, 1H, ArCH=CHOCH; 6.92, d, J = 12.8 Hz, 1H, ArCH=CHOCH; 7.05, broad s, 4H, aromatic protons. m/e 168, 6%, 170, 1.6%, M^{+} .

Band B (R_F 0.5) gave a clear colourless oil proposed as (Z)- β -methoxy-4-chlorostyrene (148) (c. 2 mg, c. 0.2%). m/e 168, 3%, 170, 1.5%, M^{+} .

Alkaline Permanganate Oxidation of the t-Butoxystyrenes (137), (138) and (141)

A 1:1 mixture of the t-butoxy-4-chlorostyrenes (137) and (138) (290 mg, 1.38 mmol) or β -t-butoxystyrene (141) (150 mg, 0.85 mmol) was heated under reflux, with occasional shaking, for 0.5 h with saturated aqueous potassium permanganate (12 cm³) and sodium hydroxide (2 M, 5 cm³). Excess permanganate was destroyed by reaction with sodium metabisulfite and the solution filtered. The inorganic residue was washed with ether (50 cm³) and the aqueous solution

extracted with ether (2×50 cm³). The combined organic extracts were washed with water (50 cm³), dried (Na₂SO₄) and concentrated in vacuum to a white solid identified as unchanged starting material (c. 5%). The aqueous phases from above were acidified (c. HCl) and the white solid removed by vacuum filtration.

(i) The product from the styrene (137) and (138) was recrystallised successively from acetic acid, aqueous ethanol and light petroleum to afford *p*-chlorobenzoic acid (116 mg, 55%), m.p. and mixture m.p. 234–236°.

(ii) The product from styrene (141) was recrystallized twice from water to afford benzoic acid (50 mg, 48%), m.p. and mixture m.p. 121–122°.

*Alkaline Permanganate Oxidation of the Bromo-*t*-butoxystyrenes*

(143) and (145)

The alkaline permanganate oxidation of the (*E*)- and (*Z*)-bromo-β-*t*-butoxystyrene mixtures (145) and (143) was carried out employing the method described above.

(i) The acidic product from the (*E*)-styrenes (145) had m.p. 205–215° (lit.⁹⁹ 4-bromobenzoic acid 254.5°). Esterification of the product with diazomethane gave methyl 4-bromobenzoate (14.5 mg, 23% overall) identified by comparison of its spectral data with those of an authentic sample. However, the product was contaminated with traces of a second isomer which has eluded spectroscopic characterization.

(ii) The acidic product from the (*Z*)-styrenes (143) (14 mg, 22% overall) behaved in the same manner as described above.

Methyl 2-, 3- and 4-bromobenzoate

An ethereal solution of diazomethane (prepared from N-nitrosomethylurea by the method of Vogel⁹⁸) was added in portions to a stirred suspension/solution of the appropriate bromobenzoic acid (0.5 g, 2.49 mmol) in dry distilled ether (8 cm³) until the yellow colour of diazomethane persisted. The resultant solution was stood with stirring overnight to remove excess diazomethane. The solution was acidified with dilute (2 M) hydrochloric acid (8 cm³), the organic phase separated, washed with saturated sodium bicarbonate (1×8 cm³), water (2×8 cm³), dried (Na₂SO₄), filtered and concentrated in vacuo to give the crude methyl benzoates.

(i) Recrystallization (ethanol/H₂O) of the product from 4-bromobenzoic acid, gave white needles of methyl 4-bromobenzoate (490 mg, 92%) m.p. 78.5–79° (lit.⁹⁹ 81°). δ ¹H; 3.84, s, 3H, $-\overset{\text{O}}{\parallel}\text{C}-\text{OCH}_3$; 7.63, AA'XX' system, 4H, aromatic protons. ¹³C; 52.21, $-\text{OCH}_3$; 128.02 (q), 129.10 (q), 131.12 and 131.71, aromatic carbons; 166.23, Ph- CO_2CH_3 . G.l.c. {5% C-20M glass column [6 mm (od.) by 1.5 m], 140°, N₂ at 40 cm³ min⁻¹} 525 s.

(ii) Recrystallization (ethanol/H₂O) of the product from 3-bromobenzoic acid, gave white plates of methyl 3-bromobenzoate (480 mg, 90%) m.p. 31–32° (lit.⁹⁹ 32°). δ ¹H; 3.85, s, 3H, $-\text{OCH}_3$; 7.15, t, $J_{\text{O}} = 7.3$ Hz, 1H, H5; 7.55, dt, $J_{\text{O}} = 7.3$ Hz, $J_{\text{m}} = 2.2$ Hz, 1H, H6; 7.82, dt, $J_{\text{O}} = 7.3$ Hz, $J_{\text{m}} = 2.2$ Hz, 1H, H4; 8.04, t, $J_{\text{m}} = 2.2$ Hz, 1H, H2. ¹³C; 52.33, $-\text{OCH}_3$; 122.47 (q), 128.13, 129.91, 132.10 (q), 132.59 and 135.82, aromatic carbons; 165.60, Ph- CO_2CH_3 . G.l.c. (conditions as above) 530 s.

(iii) Preparative t.l.c. (petroleum ether) gave a single band ($R_{\text{F}} = 0.60$) which on extraction with methylene chloride (50 ml) yielded methyl 2-bromobenzoate (500 mg, 93%) as a clear colourless oil. δ ¹H; 3.83, s, 3H, $-\text{OCH}_3$; 7.1–7.4, m, 2H, H4 and 5; 7.5–7.8, m, 2H, H3 and H6. ¹³C; 52.4, $-\text{OCH}_3$; 121.62 (q), 127.13, 131.28, 132.24 (q), 132.53 and 134.32, aromatic carbons; 166.55, Ph- $\overset{\text{O}}{\parallel}\text{C}-\text{OCH}_3$. G.l.c. (conditions as above) 532 s.

Butyl 2-, 3- and 4-bromobenzoate

The appropriate bromobenzoic acid (1.0 g, 4.97 mmol) was treated with freshly distilled thionyl chloride (10 cm³) and the mixture was heated under reflux under an oxygen free nitrogen atmosphere for 2.0 h. The resultant mixture was concentrated in vacuo, and the chilled (ice) residue was treated with a solution of freshly distilled butanol (0.5 cm³, 1.1 molar equiv.) in dry distilled pyridine (5 cm³). After stirring for 1.0 h at 0° the reaction mixture was allowed to warm to room temperature, and stirred for a further 48 h. The reaction mixture was poured onto crushed ice and extracted with ether (3×20 cm³). The combined organic phases were washed with cold dilute (2 M) hydrochloric acid (2×50 cm³), saturated sodium bicarbonate (2×50 cm³), saturated brine (1×50 cm³), water (1×50 cm³), and dried (Na₂SO₄, c. 5 g). Concentration in vacuo gave essentially pure *n*-butyl benzoates. The products thus obtained were subjected to preparative t.l.c. with ethyl acetate/petroleum ether (1:9) elution and the bands extracted with dichloromethane (50 cm³).

(i) The product mixture from esterification of 4-bromobenzoic acid resulted in a single band ($R_F = 0.8$) which yielded *butyl 4-bromobenzoate* (1.1 g, 86%) as a clear colourless oil (Found: C, 51.86, H, 5.09; Br, 31.23; C₁₁H₁₃BrO₂ requires C, 51.40; H, 5.10; Br, 31.08%). $\nu_{\max}$ 2890, 1696, 1564, 1472, 1250, 1090, 1078, 988, 732 cm⁻¹. δ 0.75-1.95, complex m, 7H, O-CH₂-(CH₂)₂CH₃; 4.24, t, $J = 6.5$ Hz, 2H, -O-CH₂-; 7.62, AA'XX' system, $J = 8.8$ Hz, 4H, aromatics. G.l.c. {5% C-20M glass column [6 mm (od.) by 1.5 m], 204°, N₂ at 40 cm min⁻¹} 478 s.

(ii) The product mixture from esterification of 3-bromobenzoic acid resulted in a single band ($R_F = 0.8$) which yielded *butyl 3-bromobenzoate* (1.0 g, 78%) as a clear colourless oil (Found: C, 51.66; H, 5.10; Br, 31.87; C₁₁H₁₃BrO₂ requires C, 51.40; H, 5.10; Br, 31.08%).

$\nu_{\max}$ 2890, 2860, 1700, 1402, 1270, 1240, 1100, 1046, 728, 696 cm^{-1} .
 δ 0.75-2.00 complex m, 7H, $\text{O-CH}_2\text{-(CH}_2\text{)}_2\text{CH}_3$; 4.23, t, $J = 6.2$ Hz, 2H,
 $\text{-O-CH}_2\text{-}$; 7.14, t, $J_{\text{O}} = 7.5$ Hz, 1H, H5; 7.52, dt, $J_{\text{O}} = 7.5$ Hz, $J_{\text{m}} = 2.2$ Hz,
 1H, H6; 7.81, dt, $J_{\text{O}} = 7.5$ Hz, $J_{\text{m}} = 2.2$ Hz, 1H, H4; 8.00, t, $J_{\text{m}} = 2.2$ Hz,
 1H, H3. G.l.c. (conditions as above) 485 s.

(iii) The product mixture from esterification of 2-bromobenzoic acid resulted in a single band ($R_{\text{F}} = 0.8$) which yielded *butyl 2-bromobenzoate* (1.1 g, 86%) as a clear colourless oil (Found: C, 51.80; H, 5.15; $\text{C}_{11}\text{H}_{13}\text{Br}_2\text{O}$ requires C, 51.40; H, 5.10%). $\nu_{\max}$ 1700, 1561, 1410, 1274, 1232, 1106, 1090, 1019, 1001, 721 cm^{-1} . δ 0.75-1.95, complex m, 7H, $\text{O-CH}_2\text{-(CH}_2\text{)}_2\text{CH}_3$; 4.32, t, $J = 6.5$ Hz, 2H, $\text{-O-CH}_2\text{-}$; 7.10-7.50, m, 2H, H4,5; 7.50-7.85, m, 2H, H3,6. G.l.c. (conditions as above) 491 s.

Attempts to separate authentic mixtures of the esters prepared above by g.l.c. methods on a variety of stationary phases and columns failed to give any satisfactory resolution of the three components.

2-Phenylethyl t-Butyl ether (146)

Mercuric cyanide (22.60 g, 90 mmol) was added in one portion to a solution of freshly distilled 2-phenylethanol (10.0 g, 82 mmol) and *t*-butylbromide (12.32 g, 90 mmol) in dry distilled nitromethane (100 cm^3). The resultant mixture was stirred at ambient temperature in a stoppered flask for 13.0 h. The reaction mixture was then poured into ether (150 cm^3) and the organics washed with water (1x150 cm^3), saturated sodium bicarbonate (1x150 cm^3) and water (1x150 cm^3). The organic phase was dried (Na_2SO_4), filtered, and concentrated in vacuo to give a red oil. Distillation of the oil gave a major fraction (11.4 g) b.p. = 126-128° at c. 15 mm as a slightly yellow oil. Analytical t.l.c. eluting with petroleum ether/ethyl acetate, 9:1, indicated small quantities of the starting alcohol as well as a

single more mobile product. Column chromatography on silica gel (400 g), eluting with the same solvent as above gave on concentration of the appropriate fractions in vacuo, 2-phenylethyl *t*-butyl ether (146) (10.5 g, 72%) as a clear colourless oil. (Found: C, 81.56; H, 10.30. $C_{12}H_{18}O$ requires requires C, 80.85; H, 10.18%). $\nu_{\max}$ (liquid film) 2900, 2790, 1473, 1432, 1370, 1343, 1212, 1181, 1060, 937, 678 cm^{-1} . δ 1.10, s, 9H, $(CH_3)_3CO$; 2.77, t, $J = 7.8$ Hz, 2H, α -protons; 3.48, t, $J = 7.8$ Hz, 2H, β -protons; 7.10, s, 5H, aromatic protons. T.l.c. (solvent system as above) indicates a single chromophoric spot at $R_F = 0.57$. G.l.c. {5% C-20M glass column [6 mm (od.) by 1.5 m], 132°, N_2 at 40 cm^3 min^{-1} } 162 s.

*Hydrogenation/Hydrogenolysis of the (Z)-bromo- β -*t*-butoxystyrenes*
(143)

A suspension of 5% palladium on charcoal¹⁰⁰ (500 mg) in ethyl acetate (7 ml) was hydrogenated at one atmosphere. A solution of the (Z)-bromo- β -*t*-butoxystyrenes (143) (76 mg, 0.3 mmol) in ethyl acetate (3 ml) was introduced, and after uptake of hydrogen ceased (c. 2 molar equiv.) the solution was filtered, washed with saturated sodium bicarbonate (1×15 ml), dried (Na_2SO_4), filtered and concentrated in vacuo to a yellow oil (35 mg). G.l.c. analysis of the product oil indicated the presence of several components. The major component (60%) (40% yield from styrene) was identified as 2-phenylethyl *t*-butyl ether (146) by comparison of retention times with that of an authentic sample on two columns. The 1H n.m.r. spectrum of the crude product confirmed the presence of the ether (146). Attempts to improve this yield by employing ethanolic sodium hydroxide to remove hydrogen bromide failed. Similar treatment of the (*E*)-bromo- β -*t*-butoxystyrenes (145) gave 2-phenylethyl *t*-butyl ether (146) in essentially the same yield.

1,2,5,6-Tetrabromocyclo-octane

A solution of *cis,cis*-cyclo-octa-1,5-diene (10 g, 0.09 mol) in a mixture of anhydrous chloroform/methylene chloride (1:1, 180 cm³) was cooled to c. -70° on a dry-ice/acetone bath. Bromine (30.6 g, 0.19 mol) in the same solvent mixture (45 cm³) was added in a dropwise fashion to the vigorously stirred solution, while maintaining an *internal* temperature below -55° (the bromine solution was added at such a rate that the bromination mixture never became orange in colour). When the addition was complete the reaction mixture was stirred for a further 0.75 h below -50°. The solvents were then removed in vacuum at room temperature to give a light brown crystalline solid. A small portion of chilled (0°) absolute methanol was added to the solid product and the resulting slurry was subjected to vacuum filtration and the solid was washed with a small quantity of methanol while suction was maintained. Drying in vacuum afforded 1,2,5,6-tetrabromocyclo-octane (mixture of isomers, c. 2:1) (31 g, 78%) as a white crystalline solid m.p. 103-121° (lit.¹⁰¹ 34%, 103-121°). T.l.c. (petroleum ether elution, iodine spray) indicated the presence of two components with R_F values of 0.3 and 0.5. $\nu_{\max}$ 1255, 1229, 1212, 1154, 1078, 1010, 996, 985, 930, 916, 891, 832, 812, 787, 729, 699, 681, 677 and 667 cm⁻¹. δ 1.80-3.00, complex m, 8H, methylene protons; 4.40-4.85, complex m, 4H, cyclopropyl protons.

Cyclo-octatetraene

Cyclo-octatetraene was prepared by dehydrobromination of 1,2,5,6-tetrabromocyclo-octane with potassium *t*-butoxide in DMSO according to the method of Gardner *et al.*¹⁰²

Yield: 30%, b.p. 29° at 10 mm (lit.⁹⁹ 29.1° at 10 mm). δ 5.69, s, vinylic protons.

Chloro- and Bromo-cyclooctatetraene

Chloro- and bromo-cyclooctatetraene were prepared, by controlled halogenation of cyclooctatetraene to give the corresponding cyclooctatetraene dihalide and subsequent in situ dehydrohalogenation with potassium *t*-butoxide, according to the method of Huisgen *et al.*⁵²

(i) Distillation of the crude oil resulting from sequential, chlorination and dehydrochlorination of cyclooctatetraene gave a yellow oil, b.p. 57-58°C at *c.* 7 mm Hg. T.l.c. eluting with petroleum ether indicated the presence of one major and one minor chromophoric product with R_F values of 0.66 and 0.51 respectively. Column chromatography on silica gel, eluting with petroleum ether, gave in order of elution

(a) Chlorocyclooctatetraene (155a) (58%) as a yellow oil, b.p. 57-58° at 6 mm (lit.⁵² 26-30° at 0.001 mm; lit.¹⁰³ 51-52° at 5.5 mm. Analytical t.l.c. eluting with petroleum ether indicated a homogeneous chromophoric spot with $R_F = 0.66$. $\nu_{\max}$ (liquid film) 2945, 1600, 980, 944, 920, 903, 825, 800, 747, 720, 670, 662, 646 cm^{-1} . δ 5.81, broad s, vinylic protons. m/e 138 (12%), 140 (3%), $M^{+\cdot}$; 137 (100%), $[M-H]^+$; 102 (76%), $[M-HCl]^+$.

(b) *trans*-7,8-Dichlorobicyclo[4,2,0]octa-2,4-diene (163a)¹⁰³ (14%) as a clear colourless oil. Analytical t.l.c. eluting with petroleum ether indicated a homogeneous chromophoric product spot with $R_F = 0.5$. $\nu_{\max}$ (liquid film) 3020, 2800, 1410, 1375, 1290, 1242, 1088, 850, 781, 740, 715 cm^{-1} . δ 2.60-3.70, m, 2H, 4.20-4.80, complex m, 2H, 5.30-6.10, complex m, 4H, vinylic protons.

(ii) Distillation of the crude oil resulting from sequential, bromination and dehydrobromination of cyclooctatetraene gave bromo-cyclooctatetraene (155b)⁵² (81%) as a clear yellow liquid, b.p. 33-34° at 0.2 mm Hg (lit.⁵² 52.5-53° at 1.8 mm Hg). (Found: C, 52.45, H, 3.72; Br, 42.75. Calculated for $\text{C}_8\text{H}_7\text{Br}$, C, 52.49; H, 3.85; Br, 43.66%).

Analytical t.l.c. eluting with petroleum ether indicated a homogeneous chromophoric spot with $R_F = 0.7$. $\nu_{\max}$ 2935, 1600, 930, 895, 834, 788, 753, 710, 640 cm^{-1} . δ broad singlet at 5.72 and shoulder at 6.02. m/e 182 (7%) M^{+} ; 103 (100%) $(M-Br)^{+}$.

Dehydrohalogenation of the Halogenocyclooctatetraenes (115a,b)

The halogenocyclooctatetraenes (115a,b) were subjected to dehydrohalogenation in dimethyl sulfoxide under the conditions described above for the tribromotricyclooctane (115a) and the trichlorotricyclooctanes (113a,b) respectively. However, to approximate the reaction medium present after double dehydrohalogenation of (115a) and (113a,b) 2-3 mol.equiv. of *t*-butanol and potassium halide were added to the base-solvent system. The yellow oils produced were subjected to preparative t.l.c. with light petroleum elution and the bands extracted with dichloromethane (50 cm^3).

(i) The oil from bromocyclooctatetraene (155b) gave two bands A and B with R_F values of 0-0.5 and 0.75.

Band A (R_F 0-0.5) was resubjected to preparative t.l.c. with the light petroleum/ethyl acetate (95:5) elution to give Band A' (R_F 0.90) which yielded *t*-butoxycyclooctatetraene (166)⁵³ (250 mg, 15%) as a clear yellow oil. $\nu_{\max}$ 2912, 2900, 2845, 1613, 1344, 1120, 676, 649, and 623 cm^{-1} . δ 1.30, s, $(\text{CH}_3)_3\text{C}$; 5.70, m, vinylic protons. m/e 176, 28%, M^{+} ; 120, 100% $(M-\text{C}_4\text{H}_8)^{+}$; 91, 23%, C_7H_7^{+} .

Band B (R_F 0.75) gave a yellow oily solid. Recrystallisation (ethanol) gave cycloocta-1,3,5-trieno[*b*]naphthalene (168) (20 mg, 2.1%) as a yellow crystalline material, m.p. 112.5-113.5° (lit.⁵³ 113-114°). m/e 204, 100%, M^{+} ; 178, 20%, $(M-\text{C}_2\text{H}_2)^{+}$.

(ii) The oil from chlorocyclooctatetraene (155a) afforded only one broad band (R_F 0-0.5) which when resubjected to preparative t.l.c. with light

petroleum/ethyl acetate (95:5) elution gave a single isolable band R_F 0.9. The product was identified as *t*-butoxycyclooctatetraene (267 mg, 16%) identical to that obtained above.

4-Chloro- and 4-Bromoacetophenone (185) and (186)

4-Chloro- and 4-bromoacetophenone were both prepared by Friedel-Crafts acylation of the appropriate halobenzene essentially according to the method of Noller and Adams.¹⁰⁴ A solution of the appropriate halobenzene (0.25 mol) in carbon disulphide (100 cm³) was treated with anhydrous aluminium chloride (67.32 g, 0.51 mol) in one portion. The resultant mixture was heated under reflux and treated in a dropwise fashion over a period of *ca.* 15 min. with acetic anhydride (23.60 cm³, 0.25 mol). The reaction mixture was heated under reflux for a further 1.0 h; cooled, and cautiously poured into ice/water. The lower organic layer was separated, and the aqueous phase extracted with ether (1×200 cm³). The combined organic phases were washed with water (2×200 cm³), dried (Na₂SO₄), filtered and concentrated in vacuo to give the crude acetophenones.

(i) Distillation of the oil resulting from acylation of chlorobenzene gave 4-chloro-acetophenone (185) (25.05 g, 65%) as a clear colourless liquid b.p. 107–108° at *c.* 15 mm (lit.¹⁰⁴ 99° at 7 mm). Analytical t.l.c. eluting with petroleum ether/ethyl acetate (9:1) indicated a single chromophoric spot with R_F = 0.49. $\nu_{\max}$ (liquid film) 1665, 1562, 1373, 1335, 1239, 1070, 988, 932, 809, 739 cm⁻¹. δ 2.52, s, 3H, -CH₃; 7.51 AA'XX' system, J = 9.5 Hz, 4H, aromatic protons. G.l.c. {5% C-20M glass column [6 mm (od.) by 1.5 m], 204°, N₂ at 40 cm min⁻¹} 96 s. m.p. of 2,4-dinitrophenylhydrazone 230.5–231° (lit.¹⁰⁵ 231°).

(ii) Distillation of the oil resulting from acylation of bromobenzene gave 4-bromoacetophenone (186) (35.0 g, 70%) as a clear colourless liquid

b.p. 116° at c. 7 mm (lit.¹⁰⁴ 117° at 7 mm) which crystallized on standing to give a white crystalline solid, m.p. 49-51°C (lit.¹⁰¹ 49-50.5°).

Analytical t.l.c. eluting with petroleum ether/ethyl acetate (9:1) indicated a single chromophoric spot with $R_F = 0.62$. $\nu_{\max}$ (solid film) 1648, 1558, 1400, 1372, 1332, 1253, 1080, 982, 800 cm^{-1} . δ 2.52, s, 3H, $-\text{CH}_3$; 7.60, AA'XX' system, $J = 9.2$ Hz, aromatic protons. G.l.c. (conditions as above) 170 s. m.p. of 2,4-dinitrophenylhydrazone derivative 233-234° (lit.¹⁰⁵ 230; 237 (cor.)).

4-Bromo- and 4-Chloro-phenylacetylene (179) and (180)

4-Bromo- and 4-chloro-phenylacetylene (180) and (179) were prepared by the methods of Jacobs⁵⁷ and Vaughn and Nieuland⁵⁷ respectively.

4-Bromophenylacetylene (180) (36%), b.p. 88-90°/16 mm (lit.⁵⁷ 88-90°/16 mm), m.p. 64-65° (lit.⁵⁷ 64-65°).

4-Chlorophenylacetylene (179) (35%), b.p. 68°/15 mm, m.p. 45-46° (lit.⁵⁷ 45.4-46.1°).

Reaction of the Phenylacetylenes (178), (179) and (180) with

Potassium t-Butoxide

The phenylacetylenes (178), (179) and (180) were subjected to the dehydrohalogenation conditions employed for the tricyclooctanes (112), (113), (114) and (115a) (see above). Potassium halide (3 mol.equiv.) and t-butanol (3 mol.equiv.) were added to the base-solvent system to simulate the reaction medium after tris-dehydrohalogenation. The oils thus generated were subjected to preparative t.l.c. with light petroleum elution.

(i) The oil resulting from reaction of phenylacetylene (178) in dimethyl sulfoxide afforded one band (R_F 0.62) which gave (dichloromethane extraction, 50 cm^3) a light yellow oil. Trituration and recrystallization

(methanol) yielded (*E*)-1,4-diphenylbut-2-ene (190) (250 mg, 26%) as off-white crystals, m.p. 95-96° (lit.⁵⁸ 95°), and with spectroscopic data fully consistent with those previously reported.⁵⁸

(ii) The oil resulting from reaction of 4-bromophenylacetylene (180) in tetrahydrofuran afforded starting material in a yield of 38% as the sole isolable product. No characterizable materials could be obtained from the reaction in dimethyl sulfoxide.

(iii) The oils resulting from reaction of 4-chlorophenylacetylene (179) in tetrahydrofuran and dimethyl sulfoxide gave starting material in yields of 69 and 3% respectively as the sole isolable product.

p-Dimethoxybenzene (196)

A three litre three-necked flask containing a mixture of Quinol (66 g, 0.60 mol) and boiling water (450 cm³) was heated on a steam bath. A solution of sodium hydroxide was prepared by dissolving sodium hydroxide (150 g, 3.75 mol) in 200-300 cm³ of water and diluting to 750 cm³. A portion (360 cm³) of this solution was heated to about 100°, and added in one lot to the hot mixture of quinol and water. The flask was then fitted with a reflux condenser, mechanical stirrer, and a dropping funnel.

Heating was continued on a steam bath, and dimethyl sulphate (189 g, 142 cm³, 1.50 mol) was added dropwise over 1.0 h. The reaction mixture was heated for 0.75 h, and an additional portion of dimethyl sulphate (39 g, 30 cm³, 0.31 mol) was added dropwise at the same rate as the first portion. After heating for a further 0.17 h the reaction mixture was rendered slightly alkaline by the addition of about 60 cm³ of the sodium hydroxide solution, and another 39 g (0.31 mol) of dimethyl sulphate was added. The alternate addition of sodium hydroxide solution and dimethyl sulphate (39 g portions) was repeated twice more so that a total of 345 g (2.7 mol) of dimethyl

sulphate was added. The reaction mixture was then made strongly alkaline by the addition of the sodium hydroxide solution (150 cm³) and was heated for twenty minutes after the last addition of dimethyl sulphate. The reaction mixture was cooled to room temperature and then extracted with diethyl ether (2×450 cm³). The combined organic phases are washed with water (1×500 cm³), dried (Na₂SO₄, 20 g), filtered and concentrated in vacuo gave a light brown solid. Recrystallization from methanol gave *p*-dimethoxybenzene (68.5 g, 83%) as white crystalline flakes, m.p. = 55-55.5° (lit.¹⁰⁶ 56°). δ 4.73, s, 6H, -OCH₃; 6.80, s, 4H, aromatic protons.

Birch Reduction of the Mono- and Di-methoxybenzenes (199), (200), (201) and (202)

The appropriate mono- or di-methoxybenzene (0.28 mol) in dry distilled ether (300 cm³) was added to stirred liquid ammonia (c. 400 cm³) maintained on a dry-ice/isopropyl alcohol bath. The resultant solution was treated cautiously with absolute alcohol (70 g, c. 5.5 mol.equiv.). Lithium wire (9.0 g, 1.3 g atom equiv.) was then added in portions (c. 500 mg) to the reaction mixture at such a rate that the blue colour was discharged between additions (total time c. 50 min). After the addition of the final portion of lithium stirring was continued for five minutes beyond the discharge of the blue colour. The ammonia was allowed to evaporate overnight, and the reaction vessel was then equipped with a reflux condenser. Ice-water (300 cm³) was added to the reaction mixture (maintained under an oxygen free nitrogen blanket) to dissolve the salts. Diethyl ether (150 cm³) was added and two layers which formed were separated. The aqueous phase was re-extracted with ether (1×300 cm³) and the combined organic phases were washed with saturated brine (1×200 cm³) and water (2×200 cm³). The organic phase was dried (Na₂SO₄) filtered and concentrated in vacuum, to a light yellow oil.

(i) The oil resulting from reduction of 1,4-dimethoxybenzene (196) solidified on standing. Recrystallization from methanol gave 1,4-dimethoxycyclohexa-1,4-diene (200) (32 g, 81%) as white crystalline flakes, m.p. 55-56° (lit.¹⁰⁷ 54°). $\nu_{\max}$ 2960, 2920, 2870, 2805, 1660, 1388, 1215, 1168, 1037, 943, 779 and 702 cm^{-1} . δ (acetone- d_6) 2.85, m, 4H, methylene protons; 3.65, s, 6H, $-\text{OCH}_3$; 4.70, broad s, 2H, vinylic protons.

(ii) Distillation of the oil resulting from reduction of 1,3-dimethoxybenzene (197) gave 1,5-dimethoxycyclohexa-1,4-diene (201) (34.8 g, 88%) as a clear colourless oil, b.p. 96-98° at 20 mm (lit.¹⁰⁸ 49° at 0.9 mm). $\nu_{\max}$ 2995, 2940, 2900, 2825, 1665, 1400, 1240, 1210, 1150, 778 and 710 cm^{-1} . δ 2.80, broad s, 4H, methylene protons; 3.55, s, 6H, $-\text{OCH}_3$; 4.65, broad s, 2H, vinylic protons.

(iii) Distillation of the oil resulting from reduction of 1,2-dimethoxybenzene (198) gave 1,2-dimethoxycyclohexa-1,4-diene (202) (32.4, 82%) as a clear colourless oil, b.p. 75-78° at 15 mm (lit.¹⁰⁷ 72-76° at 10 mm). $\nu_{\max}$ 2820, 1700, 1215, 1155, 1118, 1004, 950, 800 and 677 cm^{-1} . δ 2.83, broad s, 4H, methylene protons; 3.58, s, 6H, $-\text{OCH}_3$; 5.52, broad s, 2H, vinylic protons.

(iv) Distillation of the oil resulting from reduction of methoxybenzene (195) gave 1-methoxycyclohexa-1,4-diene (199) (25.7 g, 80%) as a clear colourless liquid b.p. 48-49° at 15 mm (lit.¹⁰⁹ 151° at 760 mm). $\nu_{\max}$ 2830, 1691, 1660, 1390, 1223, 1182, 1169, 1030, 961, 792, 757 and 680 cm^{-1} . δ 2.80, broad s, 4H, methylene protons; 3.58, s, 3H, $-\text{OCH}_3$; 4.67, broad s, 1H, H2; 5.75, broad s, 2H, H4 and 5.

The Synthesis of the 4,4,8,8-Tetrachloro-, mono- and di-methoxy-cis-transoid-cis-tricyclo[5,1,0,0^{3,5}]octanes (191), (192), (193) and (194)

Freshly prepared sodium methoxide (12.97 g, 0.24 mol) was suspended in a chilled (ice) solution of the appropriate mono- or di-methoxycyclohexa-1,4-diene (0.11 mol) in cyclohexane (80 cm³). A solution of ethyl trichloroacetate (106.9 g, 0.56 mol) in cyclohexane (80 cm³) was added in a dropwise fashion over c. 1 h to the mixture. The reaction mixture was stirred for a further 1 h on the ice bath and then stirred at ambient temperature for a further 20 h. The reaction mixture was quenched with water (200 cm³) and any precipitate was removed by vacuum filtration. The organic phase from the filtrate was separated and the aqueous phase was extracted with petroleum ether (250 cm³) and the combined organic phases were washed with water (2×300 cm³), dried (MgSO₄) filtered and concentrated in vacuum to give dark coloured solid oil mixtures. These crude products were combined with any materials removed by vacuum filtration, and then triturated with methanol. The precipitated materials were removed by vacuum filtration and washed under suction with chilled (0°) methanol (10 cm³).

(i) Recrystallization (ethanol) of the crude solid resulting from dichlorocarbene addition to 1-methoxycyclohexa-1,4-diene gave 4,4,8,8-tetrachloro-1-methoxy-cis-transoid-cis-tricyclo[5,1,0,0^{3,5}]octane (191) (17.2 g, 57%) as white crystalline plates, m.p. 99.5-100.5° (Found: C, 39.33; H, 3.65; Cl, 51.20; C₉H₁₀Cl₄O requires C, 39.17; H, 3.65; Cl, 51.38%). $\nu_{\max}$ 1370, 1192, 1129, 1076, 1062, 995, 980, 931, 781 and 762 cm⁻¹. δ ¹H: 1.70, m, 3H, cyclopropyl protons; 2.25, complex m, 4H, methylene protons; 3.42, s, 3H, -OCH₃. ¹³C: 14.6, C6; 17.2, C2; 23.16, C5; 24.9, C3; 30.6, C7; 54.5, OCH₃; 62.3, C1; 64.3, C4; 64.9, C8.

(ii) Recrystallization (ethanol) of the crude solid resulting from dichlorocarbene addition to 1,4-dimethoxycyclohexa-1,4-diene gave 4,4,8,8-tetrachloro-1,5-dimethoxy-*cis-transoid-cis*-tricyclo[5,1,0,0^{3,5}]octane (192) (28.16 g, 84%) as white crystalline masses, m.p. 158-158.5° (lit.⁵⁹ 155°) (Found: C, 39.23; H, 3.95, Cl, 46.08; Calc. for C₁₀H₁₂Cl₄O₂, C, 39.25; H, 3.95; Cl, 46.34%). $\nu_{\max}$ 3000, 1478, 1443, 1277, 1218, 1120, 1070, 919 and 848 cm⁻¹. δ ¹H: 1.69, dd, *J* = 7.8 and 2.0 Hz, 2H, H₃ and 7; 2.25, dd, *J* = 15.0 and 2.0 Hz, 2H, pseudo-axial methylene protons; 2.65, dd, *J* = 15.0 and 7.8 Hz, 2H, pseudo-equatorial methylene protons; 3.40, s, 3H, -OCH₃. ¹³C: 18.9, C₂ and 6; 31.8, C₃ and C₇; 54.8, OCH₃; 62.3, C₁ and 5; 65.3, C₄ and 8.

(iii) Recrystallization (methanol) of the crude solid resulting from dichlorocarbene addition to 1,5-dimethoxycyclohexa-1,4-diene gave 4,4,8,8-tetrachloro-1,3-dimethoxy-*cis-transoid-cis*-tricyclo[5,1,0,0^{3,5}]octane (193) (24.8 g, 74%) as thick white crystalline needles, m.p. = 111-112° (lit.⁵⁹ 114°) (Found: C, 39.52; H, 4.06; Cl, 45.69; Calc. for C₁₀H₁₂Cl₄O₂ requires C, 39.25; H, 3.95; Cl, 46.34%). $\nu_{\max}$ 2985, 1408, 1117, 1076, 1015, 960, 952, 871 and 838 cm⁻¹. δ ¹H: 1.64, dd, *J* = 6.0 and 4.0 Hz, 2H, cyclopropyl protons; 2.23, dd, *J* = 6.0 and 4.0 Hz, 2H, C₆ methylene protons; 2.62, s, 2H, C₂ methylene protons; 3.45, s, 3H, -OCH₃. ¹³C: 15.5, C₆; 22.5, C₂; 30.7, C₅ and C₇; 54.7, OCH₃; 63.6, C₁ and 3; 65.4, C₄ and 8.

(iv) Recrystallization (ethanol) of the crude solid resulting from dichlorocarbene addition to 1,2-dimethoxycyclohexa-1,4-diene gave 4,4,8,8-tetrachloro-1,7-dimethoxy-*cis-transoid-cis*-tricyclo[5,1,0,0^{3,5}]octane (194) (25.14 g, 75%) as fine white needles m.p. 125-126° (Found: C, 39.61, H, 3.97; Cl, 46.10; C₁₀H₁₂Cl₄O₂ requires C, 39.25; H, 3.95; Cl, 46.34%). $\nu_{\max}$ 2925, 2815, 1429, 1375, 1083, 940, 880, 806, 779 and 720 cm⁻¹.

δ 1.70, complex m, 2H, cyclopropyl protons; 2.43, complex m, 4H, methylene protons; 3.45, s, 6H, $-\text{OCH}_3$. m/e 269, 100%, 271, 97%, 273, 36%, $(M-\text{Cl})^+$.

4,4,8,8-Tetrabromo-1,5-dimethoxy-cis-transoid-cis-tricyclo[5,1,0,0^{3,5}]octane (109)

4,4,8,8-Tetrabromo-1,5-dimethoxy-cis-transoid-cis-tricyclo[5,1,0,0^{3,5}]octane (109) was prepared by essentially the same procedure as reported by Birch and co-workers.⁵⁹ Yield: 75%, m.p. 177-8° (lit.⁵⁹ 180°) (Found: C, 24.90; H, 2.69; Br, 65.85; $\text{C}_{10}\text{H}_{12}\text{Br}_4\text{O}_2$ requires C, 24.83; H, 2.50; Br, 66.06%). δ 1.82, dd, $J = 8.0$ and 1.5 Hz, 2H, H3 and 7; 2.25, dd, $J = 15.0$ and 1.5 Hz, 2H, pseudo-axial methylene protons; 2.70, dd, $J = 15.0$ and 8.0 Hz, 2H, pseudo-equatorial methylene protons; 3.49, s, 6H, $-\text{OCH}_3$.

Birch Reduction of Toluene, o-, m- and p-Xylene

The reduction of toluene, o-, m- and p-xylene was effected with sodium in liquid ammonia, using ethanol as the proton source, and diethyl ether as the co-solvent, and according to the method of Paquette and Barrett.⁹³

(i) Distillation of the crude product resulting from reduction of toluene afforded 1-methylcyclohexa-1,4-diene (218) (85%) as a clear colourless liquid, b.p. 117-118° at 760 mm (lit.¹¹⁰ 114-115° at 760 mm). ν_{max} 2955, 2895, 2805, 2780, 2740, 1430, 1413, 1365, 988, 940 and 650 cm^{-1} . δ 1.63, s, 3H, methyl protons; 2.55, broad s, 4H, methylene protons; 5.33, broad s, 1H, H2; 5.60, broad s, 2H, H4 and 5. G.l.c. {5% SE-30 glass column [6 mm (od.) by 1.5 m] at 63.5° with N_2 at 40 $\text{cm}^3 \text{min}^{-1}$ } 81 s.

(ii) Distillation of the crude product resulting from reduction of *p*-xylene afforded 1,4-dimethylcyclohexa-1,4-diene (219) (80%) as a clear colourless liquid, b.p. 140-142° at 760 mm (lit.¹¹¹ 140-142° at 760 mm). $\nu_{\max}$ 2940, 2900, 2850, 2795, 1442, 1371, 1176, 1050, 942, 790 and 759 cm^{-1} . δ 1.62, broad s, 6H, methyl protons; 2.49, broad s, 4H, methylene protons; 5.28, m, 2H, vinylic protons. G.l.c. {5% C-20M glass column [6 mm (od.) by 1.5 m] at 71° with N₂ at 24 $\text{cm}^3 \text{min}^{-1}$ } 168 s.

(iii) Distillation of the crude product resulting from reduction of *m*-xylene afforded 1,5-dimethylcyclohexa-1,4-diene (220) (81%) as a clear colourless liquid b.p. 141-142° at 760 mm (lit.¹¹¹ 142-144° at 760 mm). $\nu_{\max}$ 2900, 1640, 1435, 1380, 1120, 1044, 962, 925 and 760 cm^{-1} . δ 1.69, broad s, 6H, methyl protons; 2.60, broad s, 4H, methylene protons; 5.44, broad s, 2H, vinylic protons. G.l.c. {5% C-20M glass column [6 mm (od.) by 1.5 m] at 59° with N₂ at 40 $\text{cm}^3 \text{min}^{-1}$ } 360 s.

(iv) Distillation of the crude product resulting from reduction of *o*-xylene afforded 1,2-dimethylcyclo-1,4-diene (220a) (86%) as a clear colourless liquid 51-52° at 12 mm (lit.⁹³ 70-72 at 48 mm). δ 1.58, s, 6H, methyl protons; 2.18, s, 4H, methylene protons; 5.54, s, 2H, vinylic protons.

*The Synthesis of the 4,4,8,8-Tetrachloro- mono- and di-methyl
cis-transoid-cis-tricyclo[5,1,0,0^{3,5}]octanes (215), (216),
(217) and (217a)*

To a chilled (salt-ice) solution of benzyltriethylammonium bromide (800 mg) in chloroform (100 g) containing the appropriate diene (0.15 mol) was added aqueous sodium hydroxide (50% w/w, 160 cm³) over 10 min. The resultant reaction mixture was stirred vigorously at room temperature for 16 h. The reaction mixture was quenched with water (200 cm³) and any precipitated material was removed by vacuum filtration, and washed with chilled water (50 cm³) and absolute ethanol (50 cm³). The organic phase from the filtrate was separated and the aqueous phase was extracted with methylene chloride (2×80 cm³), and the combined organic phases were washed with water (2×200 cm³), dried (Na₂SO₄), filtered and concentrated in vacuum to give dark coloured solid oil mixtures. These crude products were combined with any materials removed by vacuum filtration, and then triturated with methanol. The precipitated materials were removed by vacuum filtration and washed under suction with chilled (0°) methanol (10 cm³).

(i) Recrystallization (twice from ethanol/activated charcoal) of the crude solid resulting from dichlorocarbene addition to 1-methylcyclohexa-1,4-diene gave 4,4,8,8-tetrachloro-1-methyl-cis-transoid-cis-tricyclo[5,1,0,0^{3,5}]octane (215) (75%) as white crystalline masses, m.p. 82-83°. (Found: C, 41.27; H, 3.98; Cl, 54.42. C₉H₁₀Cl₄ requires C, 41.58; H, 3.88; Cl, 54.54%). $\nu_{\max}$ 2985, 2915, 1442, 1200, 1104, 1018, 953, 935, 783 and 768 cm⁻¹. δ 1.05-1.80, complex m, 3H, cyclopropyl protons; 1.31, s, 3H, methyl protons; 1.80-2.45, complex m, 4H,

methylene protons. m/e (18 eV) 222, 63%, 224, 62%, 226, 20%, $(M-HCl)^+$.

(ii) Recrystallization (twice from chloroform/activated charcoal) of the crude solid resulting from dichlorocarbene addition to 1,4-dimethylcyclohexa-1,4-diene gave 4,4,8,8-tetrachloro-1,5-dimethyl-cis-transoid-cis-tricyclo[5,1,0,0^{3,5}]octane (216) (31.2 g, 76%) as white crystalline masses, m.p. 145–145.5° (Found: C, 44.00; H, 4.48; Cl, 51.55%. $C_{10}H_{12}Cl_4$ requires C, 43.83; H, 4.41; Cl, 51.76%).
 $\nu_{\max}$ 2905, 1443, 1427, 1293, 1190, 1028, 1010, 928 and 800 cm^{-1} .
 δ 1.25, dd, $J = 9$ and 1.5 Hz, 2H, cyclopropyl protons; 1.35, s, 6H, methyl protons; 1.86, dd, $J = 16.3$ and 1.5 Hz, 2H, pseudo-equatorial methylene protons; 2.27, dd, $J = 16.3$ and 9 Hz, 2H, pseudo-axial methylene protons.

(iii) Recrystallization (twice from absolute ethanol/activated charcoal) of the crude solid resulting from dichlorocarbene addition to 1,5-dimethylcyclohexa-1,4-diene gave 4,4,8,8-tetrachloro-1,3-dimethyl-cis-transoid-cis-tricyclo[5,1,0,0^{3,5}]octane (217) (29.18 g, 71%) as white crystalline masses, m.p. 90.5–91.5° (Found: C, 43.99; H, 4.48; Cl, 51.85; $C_{10}H_{12}Cl_4$ requires C, 43.83; H, 4.41; Cl, 51.76%).
 $\nu_{\max}$ 2985, 2960, 2930, 2895, 1448, 1385, 1230, 1179, 1115, 1078, 1060, 1028, 970 and 840 cm^{-1} . δ 1.22, dd (partially obscured), $J = 6.0$ and 4.0 Hz, 2H, cyclopropyl protons; 1.30, s, 6H, methyl protons; 1.91, s, 2H, C2 methylene protons; 2.16, dd, $J = 6.0$ and 4.0 Hz, C6 methylene protons.

(iv) Recrystallization (twice from methylene chloride/activated charcoal) of the crude solid resulting from dichlorocarbene addition to 1,2-dimethylcyclohexa-1,4-diene gave 4,4,8,8-tetrachloro-1,7-dimethyl-cis-transoid-cis-tricyclo[5,1,0,0^{3,5}]octane (217a) (30.01 g, 73%) as white crystalline plates, m.p. 126–126.5° (Found: C, 43.83; H, 4.65; Cl, 51.81).

$C_{10}H_{12}Cl_4$ requires C, 43.83; H, 4.41; Cl, 51.76%). $\nu_{\max}$ 2980, 2940, 2905, 2840, 1461, 1437, 1298, 1151, 1081, 1048, 978, 949, 938, 910, 849 and 788 cm^{-1} . δ 1.18, s, 6H, methyl protons; 1.68, complex m, 2H, cyclopropyl protons; 1.80-2.05, complex m, 4H, methylene protons.

Dehydrochlorination of the Tetrachloro-cis-transoid-cis-tricyclo[5,1,0,0^{3,5}]octanes (191)-(194) and (215)-(217a).

(Substrate to Base)

The dehydrochlorination of the mono- and di-substituted tetrachloro-tricyclo-octanes (191)-(194) and (215)-(217a) was effected by adding a solution of the substrate in THF to a chilled suspension of potassium t-butoxide in the same solvent. The procedure was exactly the same as that employed in the dehydrochlorination of the parent tetrachloro-tricyclo-octane (112), on p. 154

(i) The product mixture from 4,4,8,8-tetrachloro-1,5-dimethoxy-cis-transoid-cis-tricyclo[5,1,0,0^{3,5}]octane (192) on subjection to preparative t.l.c. (petroleum ether elution) afforded a single chromophoric band with an R_F value of 0.3. This band yielded a $C_{10}H_{11}Cl_3O_2$ species (3.7%) of undetermined structure as a clear colourless oil. (Found: C, 44.72; H, 4.07; Cl, 39.19. $C_{10}H_{11}Cl_3O_2$ requires C, 44.56; H, 4.11; Cl, 39.46%; M^+ 267.98298, 269.98071 and 271.97691. $C_{10}H_{11}Cl_3O_2$ requires M^+ 267.98245, 269.97950 and 271.97655). $\nu_{\max}$ 3100, 3050, 3010, 2925, 2835, 1645, 1610, 1388, 1339, 1237, 1203, 1068, 1010, 902, 875, 853, 782 and 683 cm^{-1} . $\lambda_{\max}$ (C_6H_{12}) 260 ($\log \epsilon$ 4.15). δ 1H : 2.20, d, $J = 8.5\text{ Hz}$, 1H; 2.80, overlapping dd, $J = 8.3$ and 6.3 Hz , 1H; 3.16, dd, $J = 6.3$ and 2.7 Hz , 1H; 3.55, s, 3H, $-OCH_3$; 3.71, s, 3H, $-OCH_3$; 5.63, d, $J = 2.7\text{ Hz}$, 1H; 6.02, d, $J = 1.0\text{ Hz}$, 1H; ^{13}C : 39.3, dd, CH_AH_B ; 50.4, d; 53.7, q, OCH_3 ; 56.3, q, OCH_3 ; 88.1, s; 89.7, s; 92.4, d;

108.7, d; 135.7, s, $\text{C}=\text{C}-\text{Cl}$; 164.9, s, $\text{C}=\text{C}-\text{OCH}_3$. m/e (15 eV) 268, 100%, 270, 97%, 272, 30%, $\text{M}^{+\cdot}$; 237, 31%, 239, 30%, 241, 11%, $(\text{M}-\text{OCH}_3)^+$; 233, 42%, 235, 41%, 237, 26%, $(\text{M}-\text{Cl})^+$; 201, 11%, 203, 6%, 205, 1%, $(\text{M}-\text{Cl}-\text{CH}_3\text{OH})^+$.

(ii) The severely discoloured product mixtures resulting from dehydrochlorination of the tetrachlorotricyclo-octanes (192)-(194) and (215)-(217a) as described above and under a variety of alternative conditions failed to yield any characterisable products.

*Procedure for the Preparation of a Solution of Potassium
t-Butoxide in THF*

A suspension of potassium *t*-butoxide (c. 20 g) in dry distilled THF (100 ml) was stirred in a stoppered flask at ambient temperature for 1.5 h. The suspension was then filtered rapidly under vacuum through a "Pyrex G2" sintered glass funnel. The resultant filtrate was used immediately.

Titration of a 1 ml aliquot of the filtrate prepared above, was performed by quenching the aliquot in distilled water and titrating with 1.053×10^{-2} M HCl using phenolphthalein as indicator. Titration gave 0.104 mmol of base per ml of solution, i.e. 10.425 mmol base in 100 ml of filtrate.

Dehydrohalogenation of the Tetrahalogeno-cis-transoid-cis-tricyclo[5,1,0,0^{3,5}]octanes (191)-(194), (112), (114), (109) and (215)-(217a). (Base to Substrate).

The solution of potassium t-butoxide in THF (100 cm³) (prepared as described above) was added in a dropwise fashion over a period of c. 0.5 h to a chilled (salt-ice) solution of the appropriate tricyclo-octane (8.1 mmol) in THF (40 cm³). The resultant solutions were stirred at ambient temperature for 12 h, and the reaction mixtures concentrated in vacuum. The residue was treated with petroleum ether (100 cm³) and water (100 cm³) in that order, and after vigorous shaking the organic phase separated. The aqueous phase was extracted with petroleum ether (2×100 cm³). The combined organic phases were washed with water (2×200 ml), dried (Na₂SO₄), filtered and concentrated in vacuum to red oils. The oils were subjected to preparative t.l.c. (petroleum ether elution) and the bands obtained extracted with dichloromethane (50 cm³).

(i) The product mixture from 4,4,8,8-tetrachloro-1,5-dimethoxy-*cis-transoid-cis*-tricyclo[5,1,0,0^{3,5}]octane (192) gave a single major chromophoric band with an R_F value of 0.3. This band yielded 4,8,8-trichloro-3,7-dimethoxybicyclo[5,1,0]octa-2,4-diene (203) [54% based on recovered (192)] as a clear colourless oil. (Found: (M-Cl)⁺ 233.01442 and 235.01132. C₁₀H₁₁Cl₂O₂ requires (M-Cl)⁺ 233.01360 and 235.01065). $\nu_{\max}$ 2915, 1630, 1577, 1379, 1234, 1164, 1106, 1044, 1011 and 833 cm⁻¹. $\lambda_{\max}$ (C₆H₁₂) 261 nm, 230 nm (sh). δ ¹H: 2.23, d, J = 6 Hz, 1H, cyclopropyl proton; 2.90, dd, J = 18 and 3 Hz, 1H, methylene proton; 3.29, dd, J = 18 and 3 Hz, 1H, methylene proton; 3.42, s, 3H, methoxyl protons at C7; 3.54, s, 3H, methoxyl protons at C3; 4.88, d, J = 6.0 Hz, 1H, H2; 6.47, t, J = 3.0 Hz, 1H, H5. ¹³C: 26.9, C6; 35.4, C1; 54.8, OCH₃; 55.0, OCH₃; 64.8, C7;

69.2, C8; 91.8, C2; 118.2, C5; 128.5, C4; 153.3, C3. m/e (12 eV) 268, 2.2%, 270, 2.2%, M^{+} ; 233, 100%, 235, 64%, 237, 38%, $(M-Cl)^{+}$ and $(M-CH_3O)^{+}$.

The remainder of the preparative t.l.c. plate was extracted (50 cm³ methylene chloride) and afforded 500 mg of starting material after recrystallization (20% recovery), as the only other characterisable material from this reaction mixture.

(ii) The product mixture from 4,4,8,8-tetrachloro-1-methoxy-*cis-transoid-cis*-tricyclo[5,1,0,0^{3,5}]octane (191) gave a single major chromophoric band with an R_F value of 0.7. This band yielded 4,4,8-trichloro-3-methoxybicyclo[5,1,0]octa-2,4-diene (205) (59%) as a white crystalline solid m.p. 61-62°. (Found: $(M-Cl)^{+}$ 203.00241 and 205.00021. $C_9H_9Cl_2O_2$ requires 203.00304 and 205.00009). ν_{max} 2940, 2910, 1638, 1585, 1441, 1425, 1233, 1145, 1090, 1009, 852, 805, 782 and 761 cm⁻¹. λ_{max} (C_6H_{12}) 260.5 nm, 235.5 nm, (sh). δ ¹H: 1.75-2.4, complex m, 2H, cyclopropyl protons; 2.7-2.95, m, 2H, methylene protons; 3.53, s, 3H, methoxyl protons at C3; 4.94, d, $J = 6$ Hz, 1H, H2; 6.44, t, $J = 3$ Hz, 1H, H5. ¹³C: 22.4, C6; 25.8, C7; 54.7, OCH₃; 66.6, C8; 91.9, C2; 117.8, C5; 128.0, C4; 153.2, C3. m/e (12 eV) 238, 22.5%, 240, 22.5%, M^{+} ; 203, 100%, 205, 66%, $(M-Cl)^{+}$.

No other characterisable materials could be obtained from this reaction mixture.

(iii) The product mixture from 4,4,8,8-tetrachloro-1,3-dimethoxy-*cis-transoid-cis*-tricyclo[5,1,0,0^{3,5}]octane (193) gave a single major chromophoric band with an R_F value of 0.53. This band yielded an inseparable c. 2:1 mixture of starting material (193) and 4,8,8-trichloro-1,3-dimethoxybicyclo[5,1,0]octa-2,4-diene (206) [18% based on recovered (193)]. (Found: $(M-Cl)^{+}$ 233.01117 and 235.01026. $C_{10}H_{11}Cl_2O_2$ requires $(M-Cl)^{+}$

233.01360 and 235.01065). $\nu_{\max}$ 3010, 1635, 1200, 1050, 1035, 755, 698 and 680 cm^{-1} . $\lambda_{\max}$ (C_6H_{12}) 257 nm, 234.5 nm (sh). $\delta^1\text{H}$: 1.94, broad t, $J = 6.0\text{ Hz}$, 1H, cyclopropyl proton; 2.89, overlapping dd, $J = 6.0$ and 3.0 Hz , 2H, methylene protons; 3.45, s, 3H, methoxyl protons at C1; 3.62, s, 3H, methoxyl protons at C3; 5.02, s, 1H, H2; 6.56, t, $J = 3.0\text{ Hz}$, 1H, H5. ^{13}C : 22.8, C6; 31.1, C7; 55.0, OCH_3 ; 55.4, OCH_3 ; 67.2, C1; 69.5, C8; 92.4, C2; 118.8, C5; 127.8, C4, 154.6, C3. m/e (12 eV) 268, 2.5%, 270, 2.4%, M^{+} ; 233, 100%, 235, 66%, 237, 39%, $(\text{M}-\text{Cl})^{+}$ and $(\text{M}-\text{CH}_3\text{O})^{+}$.

(iv) The product mixture from 4,4,8,8-tetrachloro-1,7-dimethoxy-*cis-transoid-cis*-tricyclo[5,1,0,0^{3,5}]octane (194) gave starting material (194) (81% recovery) as the only characterisable component of the mixture.

(v) The product mixture from 4,4,8,8-tetrabromo-1,5-dimethoxy-*cis-transoid-cis*-tricyclo[5,1,0,0^{3,5}]octane (109) gave a single major chromophoric band with an R_F value of 0.5. This band yielded a clear colourless and unstable oil proposed as 4,8,8-tribromo-3,7-dimethoxybicyclo[5,1,0]octa-2,4-diene (211) (43%). $\delta^1\text{H}$: 2.34, d, $J = 7.0\text{ Hz}$, 1H, cyclopropyl proton; 3.06, dd, $J = 7.0$ and 2.8 Hz , 1H, methylene proton; 3.53, dd, $J = 7.0$ and 2.8 Hz , 1H, methylene proton; 3.49, s, 3H, methoxyl protons at C7; 3.59, s, 3H, methoxyl protons at C3; 4.97, d, $J = 7.0\text{ Hz}$, 1H, H2; 6.68, t, $J = 2.8\text{ Hz}$, 1H, H5. m/e (12 eV) 321, 55%, 323, 100%, 325, 52%, $(\text{M}-\text{Br})^{+}$.

(vi) The product mixtures from both 4,4,8,8-tetrabromo- and 4,4,8,8-tetrachloro-*cis-transoid-cis*-tricyclo[5,1,0,0^{3,5}]octane (114) and (112) gave starting materials (86%) and (95%) respectively as the only characterized materials. However there was limited evidence (analytical t.l.c.) for the presence of the appropriate (*E*)- and (*Z*)- β -t-butoxystyrenes (143), (145), (137) and (138).

(vii) The product mixtures from the 4,4,8,8-tetrachloro-, mono- and dimethyl-*cis-transoid-cis*-tricyclo[5,1,0,0^{3,5}]octanes (215), (216), (217) and (217a) gave starting materials (95%), (96%), (94%) and (97%) respectively as the only characterizable materials.

Reaction of 4,8,8-Trichloro-3,7-dimethoxybicyclo[5,1,0]octa-2,4-diene (203) with Various Dienophiles

(i) With Tetracyanoethylene (TCNE): Treatment of the diene (203) in THF with TCNE (1 mol.equiv.) at room temperature for 30 h gave rise to a large number (16) of products by t.l.c. The ¹H n.m.r. spectrum of the crude reaction mixture revealed aromatic as well as vinylic resonances, but no resonances corresponding to the anticipated 1:1 adduct.

(ii) With 4-Phenyl-4H-1,2,4-triazoline-3,5-diene (PTAD) in Ethyl Acetate: Treatment of the diene (203) in ethyl acetate with PTAD (1 mol. equiv.) at room temperature resulted in the discharge of the characteristic crimson colour of the dienophile in c. 6 h. After this time work up afforded an amorphous brown solid. The ¹H n.m.r. spectrum of this product mixture reveals a large number of aromatic resonances, and was not consistent with the presence of significant amounts of a 1:1 adduct. T.l.c. revealed no discrete products.

(iii) With PTAD in Chloroform: Reaction of the diene (203) in chloroform with PTAD as described above resulted in the discharge of the crimson colour of the dienophile in c. 2 h. The same amorphous brown solid was obtained.

Variations in the reaction temperature failed to deliver any characterizable products.

Treatment of the unknown C₁₀H₁₁Cl₃O₂ species in chloroform with PTAD as for (iii) above resulted in the discharge of the crimson colour of the dienophile after c. 16 h. No characterizable adducts could be obtained.

*Treatment of the 4,8,8-Trichloro- mono- and di-methoxybicyclo-
[5,1,0]octa-2,4-dienes (203), (205) and (206) with Potassium
t-Butoxide*

The bicyclo-octa-2,4-dienes (203), (205) and (206) were resubjected to treatment with potassium t-butoxide in THF (either mode of addition) as detailed on p.154 and 181. The crude oils produced were subjected to preparative t.l.c. with light petroleum elution and the bands extracted with dichloromethane (50 cm³).

(i) The oil resulting from addition of a filtered solution of base in THF to 4,8,8-trichloro-3,7-dimethoxybicyclo[5,1,0]octa-2,4-diene (203) in THF afforded starting material (62% recovery) as the only characterizable material.

(ii) The oil resulting from addition of a filtered solution of base in THF to 4,8,8-trichloro-3-methoxybicyclo[5,1,0]octa-2,4-diene (205) in THF afforded starting material (65% recovery) as the only characterizable material.

(iii) The oil resulting from addition of a filtered solution of base in THF to the 2:1 mixture of 4,4,8,8-tetrachloro-1,3-dimethoxy-*cis-transoid-cis*-tricyclo[5,1,0,0^{3,5}]octane (193) and 4,8,8-trichloro-1,3-dimethoxybicyclo[5,1,0]octa-2,4-diene (206) in THF afforded the same mixture (60% recovery) as the only characterizable materials.

(iv) The oil resulting from addition of a solution of 4,8,8-trichloro-3,7-dimethoxybicyclo[5,1,0]octa-2,4-diene (203) in THF to base in the same solvent afforded starting material (23% recovery) as the only characterizable material.

7,7-Dibromobicyclo[4,1,0]heptane

7,7-Dibromobicyclo[4,1,0]heptane was prepared by the method of Doering and Hoffmann.¹¹²

Yield: 73%, b.p. 117-120° at *c.* 20 mm (lit.¹¹² 75%, b.p. 100° at 8 mm Hg). $\nu_{\max}$ 3020, 2970, 2860, 1465, 1448, 1338, 1170, 1022 and 735 cm^{-1} . δ 1.20-1.80, complex m, 4H; 1.70-2.60, complex m, 6H.

Cyclohepta-1,3,5-triene

Cyclohepta-1,3,5-triene was prepared by thermolysis of 7,7-dibromobicyclo[4,1,0]heptane in hot quinoline according to the published procedure.⁶⁵

Yield: 67%, b.p. 110-114° at 760 mm (lit.⁶⁵ 68%, b.p. 110-114° at 760 mm). $\nu_{\max}$ 3040, 3000, 2940, 2860, 2810, 1430, 1390, 741, 710 and 661 cm^{-1} . δ 2.20, t, $J = 7.0$ Hz, 2H, H7; 5.28, m, 2H, H1; 6.12, m, 2H, H2; 6.55, m, 2H, H3.

8,8-Dichlorobicyclo[5,1,0]octa-2,4-diene (223)

To a stirred suspension of sodium methoxide (16.2 g, 0.30 mol) in light petroleum (112 cm^3) was added cycloheptatriene (10.0 g, 0.11 mol) and the resultant mixture cooled in an ice-salt bath. Ethyl trichloroacetate (41.5 g, 0.22 mol) was added dropwise over a period of 1 h, the salt-ice bath removed and the stirring continued for a further 20 h. The mixture was poured into water (150 cm^3) the organic phase separated and the aqueous phase re-extracted with light petroleum (80 cm^3). The combined organic phases were washed with water (2×150 cm^3), dried (Na_2SO_4), filtered and concentrated in vacuum to a red oil. Vacuum distillation afforded 8,8-dichlorobicyclo[5,1,0]octa-2,4-diene (223) (4.09 g, 21%) as a clear colourless oil, b.p. 77-82° at 3.5 mm (lit.⁶³ 20%, 102.5° at 20 mm) (Found: C, 54.84;

H, 4.48; Cl, 40.26; Calc. for $C_8H_8Cl_2$ C, 54.89; H, 4.61; Cl, 40.50%).
 $\nu_{\max}$ 3020, 1620, 1445, 1240, 1210, 1085, 860, 820, 803, 701 and 675 cm^{-1} .
 δ 2.05-2.75, complex m, 4H, methylene and cyclopropyl protons; 5.55-6.40, complex m, 4H, vinylic protons. m/e 174, 37%, 176, 24%, 178, 4.6%, M^{+} ; 139, 100%, 141, 33%, $(M-Cl)^{+}$.

8,8-Dibromobicyclo[5,1,0]octa-2,4-diene (224)

8,8-Dibromobicyclo[5,1,0]octa-2,4-diene was prepared by a modification of the method of Mienwald and co-workers.⁶⁴ A freshly prepared solution of potassium t-butoxide in t-butanol (0.75 M, 62.5 ml, 0.05 mol) was added in a dropwise fashion to a solution of freshly distilled bromoform (21.17 g, 0.08 mol) in distilled cycloheptatriene (25 g, 0.27 mol). The solution of base was added at such a rate that the internal temperature of the reaction mixture was maintained between $-5 - 0^{\circ}$. After the addition was complete (c. 2 h) the ice bath was removed and stirring continued for an additional 2.0 h, allowing the reaction mixture to warm up to room temperature. The mixture was then poured into water (250 cm^3) and the dark-brown organic layer (lower phase) was separated and washed with water (2 $\times$ 250 cm^3). The aqueous layer was extracted with methylene chloride (2 $\times$ 70 ml) and these extracts and the organic layer were combined and dried overnight (Na_2SO_4). The solvent and excess cycloheptatriene were removed under reduced pressure and the residue (c. 6 g) was subjected to column chromatography on silica gel (200 g) with light petroleum elution. Concentration of the appropriate fractions in vacuum afforded 8,8-dibromobicyclo[5,1,0]octa-2,4-diene (224) (4.5 g, 34% based on t-BuOK) as a clear colourless oil. (Found: C, 36.60; H, 3.21, Br, 60.48; Calc. for $C_8H_8Br_2$ C, 36.40, H, 3.05; Br, 60.55%).
 $\nu_{\max}$ 3020, 1620, 1440, 1240, 1205, 1075, 1055, 810, 750, 700 and 665 cm^{-1} .

δ 2.0-2.9, complex m, 4H, methylene and cyclopropyl protons; 5.35-6.30, complex m, 4H, vinylic protons. m/e 262, 12.6%, 264, 18.4%, 266, 10.3%, M^{+} ; 104, 100%, $(M-Br)^{+}$; 91, 17%, $C_7H_7^{+}$.

Dehydrohalogenation of the gem-Dihalogenobicyclo[5,1,0]octa-2,4-dienes (223) and (224), and trans-7,8-Dichlorobicyclo[4,2,0]octa-2,4-diene (163a).

The bicyclo-octa-2,4-dienes (223), (224) and (163a) were subjected to dehydrohalogenation in THF and/or DMSO under the conditions described above (see p.154) for the trihalogenotricyclo-octanes (113) and (115a). However, to approximate the reaction medium present after double dehydrohalogenation of (113) and (115a) 2-3 mol. equiv. of *t*-butanol and potassium halide were added to the base solvent system. The oils produced were subjected to preparative t.l.c. with light petroleum elution and the bands extracted with methylene chloride (50 cm³).

(i) The oil from dehydrochlorination 8,8-dichlorobicyclo[5,1,0]octa-2,4-diene (223) in DMSO gave two major bands A and B with R_F values of 0.1 and 0.5 respectively.

Band A (R_F 0.1) yielded (*E*)- β -*t*-butoxystyrene (141) (5.4%) as a clear colourless oil identical in all respects to the samples obtained above.

Band B (R_F 0.5) yielded (*Z*)- β -*t*-butoxystyrene (142) (2%) as a colourless oil. (Found: C, 81.73; H, 8.50; $C_{12}H_{16}O$ requires C, 81.77; H, 9.15%). ν_{max} 2955, 1635, 1483, 1441, 1410, 1365, 1265, 1172, 1080, 776 and 694 cm⁻¹. δ 1.35, s, 9H, (CH₃)₃C; 5.16, d, 1H, J = 7.2 Hz, $ArCH=CHOBu^{+}$; 6.41, d, J = 7.2 Hz, 1H, $ArCH=CHOBu^{+}$; 7.15, complex m, 3H, H3-5; 7.50, complex m, 2H, H2 and H6. m/e 176, 17%, M^{+} ; 120, 100%, $(M-C_4H_8)^{+}$.

No other characterizable materials could be obtained from this reaction.

(ii) The oil from dehydrobromination of 8,8-dibromobicyclo[5,1,0]octa-2,4-diene (224) in DMSO gave two major bands A and B with R_F values of 0.1 and 0.5 respectively.

Band A (R_F 0.1) yielded (*E*)- β -t-butoxystyrene (141) (4%) as a clear colourless oil identical in all respects to the samples obtained above.

Band B (R_F 0.5) yielded (*Z*)- β -t-butoxystyrene (142) (3%) as a clear colourless oil identical in all respects to the sample obtained above.

No other characterizable materials could be obtained from this reaction.

(iii) The oil from dehydrobromination of 8,8-dibromobicyclo[5,1,0]octa-2,4-diene (224) in THF gave a single major band with an R_F value of 0.1. This band yielded (*E*)- β -t-butoxystyrene (141) (5%) as a clear colourless oil identical in all respects with an authentic sample.

(iv) The oil from reaction of 8,8-dichlorobicyclo[5,1,0]octa-2,4-diene (223) with potassium t-butoxide in THF gave starting material (53% recovery) as the only characterizable component from this reaction.

(v) The oil from dehydrochlorination of *trans*-7,8-dichlorobicyclo[4,2,0]octa-2,4-diene (163a) in DMSO gave two major bands A and B with R_F values of 0.1 and 0.5 respectively.

Band A (R_F 0.1) yielded (*E*)- β -t-butoxystyrene (141) (0.5%) as a clear colourless oil identical in all respects with an authentic sample.

Band B (R_F 0.5) yielded (*Z*)- β -t-butoxystyrene (142) (1.0%) as a clear colourless oil identical in all respects with an authentic sample.

No other characterizable materials were obtained from this reaction mixture.

trans-1,2-Dihydrophthalic Acid

trans-1,2-Dihydrophthalic acid was prepared by sodium amalgam reduction of phthalic acid in sodium acetate buffered 50% acetic acid according to the method of McDonald and Reineke.¹¹³

Yield: 60%, m.p. 209-210° (lit.¹¹³ 210°). (Found: C, 57.23; H, 4.86; Calc. for C₈H₈O₄ C, 57.14; H, 4.80%). δ (acetone-d₆) 3.70, s, 2H, methine protons; 5.89, s, 4H, vinylic protons.

Dimethyl trans-1,2-Dihydrophthalate (240)

Dimethyl *trans-1,2-dihydrophthalate* was prepared by treatment of the acid with an excess of ethereal diazomethane (see p.161)

Yield: 96%, b.p. 101-102° at 1.5 mm (lit.⁷⁰ 83-85° at 0.3 mm). $\nu_{\max}$ 2925, 1735, 1432, 1361, 1300, 1260, 1195, 1150, 1019 and 682 cm⁻¹. δ 3.75, s, 6H, methyl protons; 3.80, broad s (partially obscured), 2H, methine protons; 5.90, complex m, 4H, vinylic protons.

Attempted Dichlorocarbene Addition to Dimethyl trans-1,2-dihydrophthalate (240)

(i) Under Phase Transfer Conditions: Aqueous sodium hydroxide (7 cm³, 50% w/w) was added in one portion to a solution of the title diester (1.87 g, 9.54 mmol) in chloroform (8 cm³) containing triethylbenzylammonium bromide (60 mg). The severely discoloured mixture was stirred vigorously for 22 h at room temperature. Conventional work-up (chloroform extraction) afforded a viscous black oil (no acid precipitated products were obtained from the aqueous phase). Vacuum

distillation afforded dimethyl phthalate (242) (556 mg, 30%) as a clear colourless oil with b.p. 115-118° at 1.5 mm Hg (lit.¹¹⁵ 283.8° at 760 mm), and with spectroscopic data fully consistent with those of an authentic sample. No other characterizable products were obtained from this reaction mixture. There was no evidence (¹H n.m.r.) for the presence of the desired dichlorocarbene adduct in either the crude or residual product materials.

(ii) With Sodium Methoxide/Ethyl Trichloroacetate: Treatment of the 1,2-dihydrophthalate (240) with sodium methoxide and ethyl trichloroacetate in pentane as detailed for the addition of dichlorocarbene to cyclohexa-1,3-diene (130) (p. 145) gave a yellow-orange product oil. Vacuum distillation afforded a light yellow oil b.p. 118-120° at 1.0 mm as the major volatile fraction. This material is proposed as a *c.* 3:2 mixture of dimethylphthalate and the *trans*-esterified ethyl methyl phthalate (243) on the basis of its spectroscopic data. No other characterizable materials were obtained from this reaction mixture.

(iii) Neutral Phase Transfer Conditions: Sodium trichloroacetate was added to a refluxing solution of the diene (240) in chloroform containing triethylbenzylammonium bromide as detailed by Dehmlow *et al*¹¹⁵ for the generation of dichlorocarbene under neutral conditions. However work-up afforded only intractable black tars.

4,4-Dichloro-8-oxa-cis-transoid-cis-tricyclo[5,1,0,*0*^{3,5}]octane (244)
m-Chloroperbenzoic acid (6.48 g, 84% technical grade, 31.5 mmol) in dry distilled chloroform (81 cm³) was added in a dropwise fashion over a period of 2 h to vigorously stirred 7,7-dichlorobicyclo[4,1,0]hept-3-ene (30) (5.0 g, 30.7 mmol). The mixture was then heated under reflux on a steam bath for 3 h and then left standing at room temperature overnight. The reaction mixture was cooled on an ice bath and the precipitated *m*-chloro-

benzoic acid was removed by vacuum filtration. The filtrate was washed with sodium metabisulphite (20% w/w, $1 \times 10 \text{ cm}^3$), sodium bicarbonate (10% w/w, $3 \times 20 \text{ cm}^3$), saturated sodium chloride ($1 \times 20 \text{ cm}^3$) and dried (MgSO_4). The dried reaction mixture was filtered and concentrated in vacuum to a light yellow oil. Vacuum distillation gave 4,4-dichloro-8-oxa-cis-transoid-cis-tricyclo[5,1,0, $0^{3,5}$]octane (244) (4.0 g, 73%) as a clear colourless oil, b.p. $95-97^\circ$ at 5.5 mm. (Found: C, 47.00; H, 4.52; Cl, 39.30; $\text{C}_7\text{H}_8\text{Cl}_2\text{O}$ requires C, 46.96; H, 4.50; Cl, 39.60). ν_{max} 2950, 2920, 1470, 1431, 1235, 1090, 1025, 950, 891, 800 and 760 cm^{-1} . δ 1.95, complex m, 6H, cyclopropyl and methylene protons; 2.82, broad s, 2H, H1 and 7. G.l.c. {25% E-30 glass column [0.95 cm (od.) by 2.1 m], 144, N_2 at $100 \text{ cm}^3 \text{ min}^{-1}$ } 538 s.

Reaction of 4,4-Dichloro-8-oxa-cis-transoid-cis-tricyclo[5,1,0, $0^{3,5}$]-octane (244) with Lithium Diethylamide

Treatment of the title epoxide (244) with lithium diethylamide (2.5 molar equiv.) in refluxing diethyl ether for 5 h, as detailed by Rickborn and Thummel,⁷² afforded a dark red oil on work-up. The ^1H n.m.r. and infra-red spectra revealed the presence of hydroxyl and olefinic moieties, but a sodium fusion test on a small portion of crude product gave no silver nitrate precipitated materials. G.l.c. and t.l.c. analysis of the product oil revealed at least eight major components. No attempt was made to characterize these products.

Attempted Photo-oxygenation of 7,7-Dichlorobicyclo[4,1,0]hept-3-ene (30)

A gentle stream of oxygen was bubbled through a solution of the Δ^3 -norcarene (30) (100 mg) and rose bengal (40 mg) in methylene chloride-methanol (9:1,

150 ml). The reaction mixture was irradiated at ambient temperatures with a Hanovia photoreactor until the colour of the sensitizer had faded (c. 48 h). Sodium borohydride (100 mg) was added and the mixture was stirred at room temperature for 30 min. This solution was washed with water (3×25 ml), dried (Na_2SO_4), filtered and concentrated in vacuo to give a light yellow oil (95 mg), identified as the starting olefin (30) (95% recovery).

Variations in the solvents, sensitizer and light source also returned only unreacted starting material.

Reaction of 4,4-Dichloro-8-oxa-cis-transoid-cis-tricyclo[5,1,0,0^{3,5}]-octane (244) with Bromine in the Presence of White Light

A solution of bromine (1.09 g, 6.8 mmol) and the title epoxide (1.22 g, 6.8 mmol) in dry distilled carbon tetrachloride (19 cm³) was maintained under reflux, in an oxygen free nitrogen atmosphere, by irradiation of the reaction vessel (50 cm³ pyrex flask) with a 250 watt I.R. Philips heat lamp. After the discharge of the colour of bromine (c. 5 min) the cooled reaction mixture was washed with sodium bicarbonate (10% w/w, 1×50 cm³) and dried (MgSO_4). Filtration and concentration in vacuo gave a light yellow oil (2.02 g). Preparative t.l.c. (petroleum ether/ethyl acetate, 4:1) afforded a major mobile band (R_F 0.65) together with numerous more minor components and baseline material. Extraction of the major band (chloroform, 50 cm³) afforded (1 α , 4 β , 7 α)-4-bromo-7,7-dichlorobicyclo[4,1,0]hept-3-one (248) (103 mg, 6%) as a white crystalline solid, m.p. 60.5–61.5°, m.m.p. 60.5–62°. The spectroscopic data for this compound was in full agreement with that of the authentic material prepared below.

Extraction of the baseline material and resubjection to preparative t.l.c. under a variety of conditions failed to yield any characterizable materials.

(1α,3α,4β,7α)-4-Bromo-7,7-dichlorobicyclo[4,1,0]heptan-3-ol (250)

Freshly recrystallized *N*-bromosuccinimide (17.8 g, 0.1 mol) was added in one portion to a solution of 7,7-dichlorobicyclo[4,1,0]hept-3-ene (8.15 g, 0.05 mol) in DMSO (250 cm³) containing distilled water (2.25 cm³, 0.12 mol) and maintained on a cold water bath under an oxygen free nitrogen atmosphere. The resultant bright yellow reaction mixture was stirred at cold water temperatures for 0.5 h, then quenched with saturated sodium bicarbonate (1000 cm³) and extracted with diethyl ether (2×500 cm³). The combined organic phases were washed with water (2×1000 cm³), dried (Na₂SO₄), filtered and concentrated in vacuum to give a light yellow oil which crystallized on standing. Recrystallization (twice from petroleum ether) gave *(1α,3α,4β,7α)-4-bromo-7,7-dichlorobicyclo[4,1,0]heptan-3-ol (250)* (10.5 g, 81%) as white microcrystalline masses, m.p. 210 (Found: C, 32.37; H, 3.50; Br, 30.64; Cl, 27.20; C₇H₉BrCl₂O requires C, 32.34; H, 3.49; Br, 30.74; Cl, 27.28%). $\nu_{\max}$ 3360, 2897, 1308, 1187, 1118, 1068, 1057, 1000, 872, 839, 829, 789, 777 and 639 cm⁻¹. δ 1.30-3.0, complex m, 7H, H1, 2, 5 and 6 and -O-H; 3.30-4.21, complex m, 2H, H3 and 4.

(1α,4β,7α)-4-Bromo-7,7-dichlorobicyclo[4,1,0]hept-3-one (248)

Jones reagent⁷⁹ (19.5 cm³) was added in a dropwise fashion over a period of 0.5 h to a chilled (0°) solution of *(1α,3α,4β,7α)-4-bromo-7,7-dichlorobicyclo[4,1,0]heptan-3-ol (250)* (13.0 g, 50 mmol) in dry distilled acetone (325 cm³). The resultant deep red reaction mixture was stirred at room temperature for 22 h after which time no starting material (t.l.c.) remained. Methanol (26 cm³) was added to the reaction mixture to destroy any excess oxidant and the solvent was removed in vacuum. The residue was dissolved in ether (300 cm³) and the resultant solution was washed with saturated sodium chloride (2×200 ml), water (2×300 ml), dried (Na₂SO₄), filtered and

concentrated in vacuum to a light yellow oil, which crystallized on standing. Recrystallization (petroleum ether) afforded (1 α ,4 β ,7 α)-4-bromo-7,7-dichlorobicyclo[4,1,0]hept-3-one (248) (12.85 g, 99.5%) as white crystalline masses, m.p. 60.5-61.5° (Found: C, 32.43; H, 2.83; Br, 30.82; Cl, 27.36; C₇H₇BrCl₂O requires C, 32.59; H, 2.74; Br, 30.98; Cl, 27.49%). ν_{max} 2885, 1720, 1431, 1260, 1183, 1070, 801, 731 and 702 cm⁻¹. δ 1.55-3.50, complex m, 6H, H1, 2, 5 and 6; 4.04, t, J = 3.0 Hz, 1H, H4.

This product discolours on prolonged standing at room temperature, but can be stored successfully for extended periods at -5°C.

Attempted Dehydrobromination of (1 α ,4 β ,7 α)-4-Bromo-7,7-dichlorobicyclo[4,1,0]hept-3-one (248)

(i) Reaction of (248) with Pyridine: A solution of the bromoketone (248) (570 mg) in dry distilled pyridine (10 ml) was stirred at room temperature for 23 h, after which time the reaction mixture had become yellow in colour. Conventional work-up afforded starting material (342 mg, 60% recovery; m.p. and m.m.p. 60.5-61.5°) as the only characterizable product.

(ii) Reaction of (248) with sodium iodide/triethyl amine in Acetone: A solution of the bromoketone (280 mg, 1.11 mmol) and sodium iodide (340 mg, 2.27 mmol) in dry acetone (1.08 g) was shaken at room temperature for 15 min. Triethyl amine (480 mg, 4.74 mmol) was added and the reaction mixture was shaken at room temperature for a further 1 h. Conventional work-up (methylene chloride extraction) gave intractable red gums. T.l.c. revealed no discrete components.

(iii) Reaction of (248) with 1,5-Diazabicyclo[4,3,0]non-5-ene (DBN) in Benzene: DBN (200 μ l) was added in one portion to a refluxing solution of the bromoketone (100 mg) in benzene (2.15 cm³) maintained under an oxygen free nitrogen atmosphere. A deep red colour developed immediately on

addition of the base, and a black tar was deposited on the walls of the reaction vessel. Subsequent work-up afforded no characterizable materials.

Bicyclo[4,1,0]hept-3-ene (252)

Bicyclo[4,1,0]hept-3-ene was prepared by controlled Simmons-Smith cyclopropanation of cyclohexa-1,4-diene following the method of Friedrich.⁸¹ A zinc-copper couple (60 g, 0.92 mol) was prepared from zinc granules by the procedure of LeGoff.¹¹⁶ The couple was covered with anhydrous diethyl ether (200 cm³) and over a period of 1 h while stirring and heating under reflux, was treated in a dropwise fashion with a mixture of di-iodomethane (170 g, 0.63 mol) and cyclohexa-1,4-diene (25 g, 0.31 mol). After addition was complete the reaction mixture was stirred and refluxed for a further 22 h. The mixture was worked up in the usual manner by *cautious* addition of saturated aqueous ammonium chloride solution (400 cm³), separation of the organic phase, followed by washing with saturated ammonium chloride (1×400 cm³), saturated sodium carbonate (2×300 cm³), water (2×300 cm³) and dried (MgSO₄). Distillation through a Vigreux column (25 cm) gave bicyclo[4,1,0]hept-3-ene (252) (85% pure, 28% yield) as a clear colourless liquid, b.p. 112–116° at 760 mm (lit.⁸¹ 114–114.5° at 760 mm). $\nu_{\max}$ 3040, 2990, 2870, 2815, 1475, 1438, 1019, 929, 879, 828 and 732 cm⁻¹. δ 0.6, complex m, 4H, cyclopropyl protons; 2.25, complex m, 4H, methylene protons; 5.40, broad s, 2H, vinylic protons. G.l.c. {25% E-30 glass column [0.95 cm (od.) by 2.1 m], 71, N₂ at 100 cm³ min⁻¹} 160 s.

4-oxa-cis-transoid-cis- and 4-oxa-cis-cisoid-cis-
 tricyclo[5,1,0,0^{3,5}]octane (253)

m-Chloroperbenzoic acid (10.62 g, 85% technical grade, 0.053 mol) in dry distilled chloroform (133 ml) was added in a dropwise fashion over a period of 2 h to a vigorously stirred slurry of anhydrous sodium bicarbonate (5.63 g) and bicyclo[4,1,0]hept-3-ene (4.73 g, 85% pure, 0.040 mol). The mixture was then stirred at ambient temperature for 24 h, diluted with water (200 cm³) and the organic phase separated. The organic phase was washed with saturated sodium metabisulphite (2×200 cm³), saturated sodium bicarbonate (2×200 cm³) and saturated sodium chloride (1×200 cm³) prior drying (MgSO₄). The mixture was filtered and concentrated in vacuo to give a light yellow oil. Vacuum distillation gave a c. 2:1 mixture of 4-oxa-cis-transoid-cis- and 4-oxa-cis-cisoid-cis-tricyclo[5,1,0,0^{3,5}]octane⁷⁴ (253a,b) (5.0 g, 90%) as a clear colourless oil, b.p. 34-35° at 1.75 mm. (Found: C, 76.08; H, 8.83; Calc. for C₇H₁₀O; C, 76.32; H, 9.15) $\nu_{\max}$ 2990, 2910, 2840, 1440, 1025, 924, 859, 810, 764 and 738 cm⁻¹. δ *cis-transoid-cis*-isomer (253a): -0.40, complex m, 1H, *endo*-H₈; -0.1-1.00, complex m, 3H, remaining cyclopropyl protons; 1.50-2.61, complex m, 4H, methylene protons; 2.95, broad s, 2H, H₃ and 5; *cis-cisoid-cis*-isomer (253b): -0.1-1.00, complex m, 4H, cyclopropyl protons; 1.50-2.61, complex m, 4H, methylene protons; 2.95, broad s, 2H, H₃ and 5. G.l.c. {5% E-30 glass column [6 mm (od.) by 1.5 m], 62°, N₂ at 35 cm³ min⁻¹} *cis-transoid-cis*-isomer (253a) 288 s; *cis-cisoid-cis*-isomer (253b) 264 s (*cis-transoid-cis/cis-cisoid-cis* 2:1). T.l.c. (ethyl acetate/petroleum ether, 1:4) reveals two components with *R_F* values of 0.65 and 0.75.

(1 α ,4 α ,6 α)- and (1 α ,4 β ,6 α)-Bicyclo[4,1,0]hept-2-en-4-ol (254a,b)

n-Butyllithium (110.5 cm³, 15% solution in hexane) was added to a stirred solution of freshly distilled dipropylamine (25.08 g, 0.25 mol) in anhydrous diethyl ether (135 cm³) maintained on a cold water bath and under an oxygen free nitrogen atmosphere. A 2:1 mixture of 4-oxa-*cis-transoid-cis*- and 4-oxa-*cis-cisoid-cis*-tricyclo[5,1,0,0^{3,5}]octane (253) (10.9 g, 99 mmol) was added in one portion and the reaction mixture was heated under reflux. The course of the reaction was followed by withdrawing aliquots (1 cm³), quenching in saturated aqueous sodium chloride (1 cm³) and g.l.c. analysis on a 5% C-20M glass column [6 mm (od.) by 1.5 m] with a nitrogen (carrier gas) flow rate of 30 cm³ min⁻¹ and an oven temperature of 121°C. After 7.5 h when essentially all the starting materials were consumed, the reaction mixture was cooled and poured cautiously into saturated aqueous sodium chloride (250 cm³). The organic phase was separated, and the aqueous phase extracted with diethyl ether (1×250 cm³). The combined organic phases were washed with water (1×300 cm³), dried (MgSO₄), filtered and concentrated in vacuum to a light red oil. Vacuum distillation gave a 1:2 mixture of (1 α ,4 α ,6 α)- and (1 α ,4 β ,6 α)-bicyclo[4,1,0]hept-2-en-4-ol⁷⁴ (254b,a) (6.65 g, 61%) as a clear colourless oil, b.p. 75-76° at 2.0 mm. (Found: C, 76.17; H, 9.12; Calc. for C₇H₁₀O C, 76.33; H, 9.15%).

$\nu_{\max}$ 3320, 3040, 3005, 2895, 2830, 1058, 1024, 1012, 793, 722 and 698 cm⁻¹. δ 0.20-2.10, complex m, 5H, H5, 6 and 7; 2.40, complex m, 1H, H1; 3.10, broad s, 1H, -O-H; 4.10, complex m, 1H, H4; 5.48, complex m, 1H, H2; 6.10, complex m, 1H, H2. m/e (14 eV) 110, 47% M⁺; 109, 18% (M-H)⁺; 95, 100% (M-CH₃)⁺; 92, 82% (M-H₂O)⁺; 91, 34% (C₇H₇)⁺. G.l.c. {5% C-20M glass column [6 mm (od.) by 1.5 m], 121°, N₂ at 30 cm³ min⁻¹} (1 α ,4 α ,6 α)-isomer (254b) 392 s; (1 α ,4 β ,6 α)-isomer (254a) 528 s.

(1 α ,4 α ,6 α)- and (1 α ,4 β ,6 α)-4-Acetoxy-bicyclo[4,1,0]hept-2-ene
(255a,b)

A solution of a 1:2 mixture of (1 α ,4 α ,6 α)- and (1 α ,4 α ,6 α)-bicyclo[4,1,0]-hept-2-en-4-ol (254a,b) (2.50 g, 23 mmol) in dry distilled pyridine (40 cm³) was cooled with stirring on an ice bath. The solution was treated in one portion with cold (0°) acetic anhydride (4.37 cm³, 46.3 mmol) and the stoppered reaction flask was stirred on the ice bath for 1.5 h. The ice bath was then removed and the reaction mixture stirred at ambient temperatures for 24 h. The reaction mixture was poured into ice-water (200 cm³) and extracted with pentane (3×150 cm³). The combined organic phases were washed with cold hydrochloric acid (2 M, 2×150 cm³), saturated sodium bicarbonate (1×200 cm³), saturated sodium chloride (1×200 cm³), dried (MgSO₄), filtered and concentrated in vacuum to a light yellow sweet smelling oil (3.48 g). Column chromatography on silica gel (ethyl acetate/petroleum ether, 1:9) afforded on concentration of the appropriate fractions an undetermined mixture of (1 α ,4 α ,6 α)- and (1 α ,4 β ,6 α)-4-acetoxy-bicyclo[4,1,0]hept-2-ene (255) (2.42 g, 70%) as a clear colourless oil.

(Found: C, 70.98; H, 7.54; C₉H₁₂O₂ requires C, 71.03; H, 7.95%).

$\nu_{\max}$ 3040, 3010, 2980, 2905, 1725, 1369, 1245, 1050, 1022, 952, 905, 795 and 708 cm⁻¹. δ 0.25-1.80, complex m, 5H, H5, 6 and 7; 2.01, s, 3H, acetoxy methyl protons; 2.40, complex m, 1H, H1; 4.80-5.20, complex m, 2H, H2 and 4; 6.08, d of m, 1H, H3. m/e (17 eV) 152, 3.5%, M⁺; 93, 100% (M-CH₃CO₂)⁺; 91, 14%, (C₇H₇)⁺. G.l.c. {5% C-20M glass column [6 mm (od.) by 1.5 m], 121, N₂ at 30 cm³ min⁻¹} 380 s. T.l.c. (ethyl acetate/petroleum ether, 1:9) reveals a single spot with an R_F value of 0.6.

Hydrolysis of (1 α ,4 α ,6 α)- and (1 α ,4 β ,6 α)-4-Acetoxy-bicyclo[4,1,0]-hept-2-ene (255a,b)

A freshly prepared solution of sodium methoxide in methanol (0.2 M, 20 cm³) was added in one portion to a stirred solution of (1 α ,4 α ,6 α)- and (1 α ,4 β ,6 α)-4-acetoxy-bicyclo[4,1,0]hept-2-ene (255a,b) (200 mg, 1.31 mmol) in dry distilled methanol (6.6 cm³) maintained at room temperature. Samples of the reaction mixture (1 cm³) were withdrawn at various times and shaken with water (2 cm³) and methylene chloride (0.5 cm³). The composition of the methylene chloride phase was analysed by g.l.c. on a 5% C-20M analytical column [6 mm (od.) by 1.5 m] using a nitrogen flow rate of 40 cm³ min⁻¹ and an oven temperature of 139°. Percentage compositions were obtained by cutting and accurately weighing the g.l.c. recorder trace. The analysis data are provided on p.117.

(1 α ,2 β ,4 β ,5 α ,7 α)- and (1 α ,2 β ,4 β ,5 β ,7 α)-5-Acetoxy-3,3-dichloro-cis-transoid-cis-tricyclo[5,1,0,0^{2,4}]octane (256a,b)

A solution of a mixture of (1 α ,4 α ,6 α)- and (1 α ,4 β ,6 α)-4-acetoxy-bicyclo[4,1,0]hept-2-ene (255a,b) (2.71 g, 17.8 mmol) in dry distilled chloroform (9.62 cm³, filtered through basic alumina immediately prior to use) and containing triethylbenzylammonium bromide (60 mg) was treated in one portion with freshly prepared aqueous sodium hydroxide (50% w/w, 8.5 cm³). The resultant mixture was stirred vigorously at room temperature for 40 h after which time essentially all the starting materials had been consumed (g.l.c.). The reaction mixture was then quenched with water (50 cm³) and the lower organic phase separated. The aqueous phase was extracted with chloroform (4 $\times$ 35 cm³) and the combined organic phases were washed with water (2 $\times$ 100 cm³), dried (Na₂SO₄), filtered and concentrated in vacuum to a red oil (3.75 g).

Column chromatography on silica gel (ethyl acetate/petroleum ether (1:9) elution) afforded on concentration of the appropriate fractions an undetermined mixture of (1 α ,2 β ,4 β ,5 α ,7 α)- and (1 α ,2 β ,4 β ,5 β ,7 α)-5-acetoxy-3,3-dichloro-cis-transoid-cis-tricyclo[5,1,0,^{2,4}]octane (256a,b) (3.35 g, 80%) as a clear colourless sweet smelling oil. (Found: C, 50.90; H, 4.98; Cl, 30.87; C₁₀H₁₂Cl₂O₂ requires C, 51.09; H, 5.14; Cl, 30.16%). ν_{max} 3060, 2995, 2920, 2865, 1730, 1370, 1240, 1024, 980, 843 and 805 cm⁻¹. δ -0.1-0.3, complex m, 1H, H_{8_{exo}}; 0.4-0.85, complex m, 1H, H_{8_{endo}}; 0.9-2.46, complex m, 6H, H₁, 2, 3, 6 and 7; 2.10, s, 3H, acetoxy methyl protons; 5.20, m, 1H, H₅. m/e (18 eV) 234, 2.5%, 236, 1.5%, 238, 0.2%, M⁺; 175, 59%, 177, 37%, 179, 6%, (M-CH₃CO₂)⁺; 139, 100%, 141, 33%, (M-CH₃CO₂-HCl)⁺. G.l.c. {5% C-20M glass column [0.6 mm (od.) by 1.5 m], 254°, N₂ at 35 cm³ min⁻¹} 94 s. T.l.c. (ethyl acetate/petroleum ether, 1:9) revealed a single spot with an R_F value of 0.5.

On elution of the tricyclic acetates (256), the column was stripped with methanol and the eluent concentrated in vacuum to give a light yellow oil identified (see below) as a c. 3.5:1 mixture of the tricyclo-octanols (258a,b) (variable yield, ‡2%).

In subsequent runs the crude tricyclic acetate mixture (256) was converted directly to the corresponding alcohols which were then, more readily, isolated by column chromatography.

(1 α ,2 β ,4 β ,5 α ,7 α)- and (1 α ,2 β ,4 β ,5 β ,7 α)-5-Acetoxy-3,3-dibromocis-transoid-cis-tricyclo[5,1,0,^{2,4}]octane (257a,b)

A solution of a mixture of (1 α ,4 α ,6 α)- and (1 α ,4 β ,6 α)-4-acetoxy-bicyclo[4,1,0]hept-2-ene (256a,b) (3.0 g, 19.7 mmol) in dry distilled benzene (50 cm³) containing bromoform (126 g, 43.6 cm³) and triethylbenzylammonium bromide (50 mg) was treated in one portion with freshly prepared aqueous sodium

hydroxide (50% w/w, 27 cm³). The resultant mixture was stirred vigorously at room temperature for 42 h after which time the reaction mixture was quenched with water (50 cm³), and the resultant mixture was extracted with chloroform (4×40 cm³). The combined organic phases were washed with water (2×100 cm³), dried (Na₂SO₄), filtered and concentrated in vacuum to a red oil. Column chromatography on silica gel (ethyl acetate/petroleum ether (1:9) elution) afforded on concentration of the appropriate fractions a c. 1:3.5 mixture of (1 α ,2 β ,4 β ,5 α ,7 α)- and (1 α ,2 β ,4 β ,5 β ,7 α)-5-acetoxy-3,3-dibromo-cis-transoid-cis-tricyclo[5,1,0,^{2,4}]octane (257a,b) (3.89 g, 61%) as a clear colourless sweet smelling oil. (Found: C, 36.89; H, 3.73; Br, 48.89; C₁₀H₁₂Br₂O₂ requires C, 37.07; H, 3.73; Br, 49.32%). $\nu_{\max}$ 3050, 2985, 2905, 2855, 1730, 1449, 1369, 1240, 1020, 979, 903, 842, 779 and 753 cm⁻¹. δ 5 β -acetoxy-isomer: -0.1-0.3, complex m, 1H, H_{8^{exo}}; 0.35-2.55 complex m, 7H, H₁, 2, 3, 6, 7 and 8_{endo}; 2.08, s, 3H, acetoxy methyl protons; 5.15, m, 1H, H5 α . 5 α -acetoxy-isomer: -0.1-0.3, complex m, 1H, H_{8^{endo}}; 0.35-2.55, complex m, 7H, H₁, 2, 3, 4, 6, 7 and 8_{endo}; 1.99, s, 3H, acetoxy methyl protons; 5.15, m, 1H, H5 α . T.l.c. (ethyl acetate/petroleum ether, 1:9) revealed a single spot with an R_F value of 0.45.

On elution of the tricyclic acetates (257a,b), the column was stripped with methanol and the eluent concentrated in vacuum to give a light yellow oil identified (see below) as a c. 3.5:1 mixture of the tricyclo-octanols (259a,b) (variable yield >2.5%).

In subsequent runs the crude tricyclic acetate mixture (257) was converted directly to the corresponding alcohols which were more readily isolated by column chromatography.

(1 α ,2 β ,4 β ,5 α ,7 α)- and (1 α ,2 β ,4 β ,5 β ,7 α)-3,3-Dichloro-cis-transoid-cis-tricyclo[5,1,0, $0^{2,4}$]octan-5-ol (258a,b) and

(1 α ,2 β ,4 β ,5 α ,7 α)- and (1 α ,2 β ,4 β ,5 β ,7 α)-3,3-Dibromo-cis-transoid-cis-tricyclo[5,1,0, $0^{2,4}$]octan-5-ol (259a,b)

A chilled (0°) solution of freshly prepared sodium methoxide in methanol (0.2 M, 40 cm³) was added in one portion to a solution of the appropriate acetate (2.6 mmol) in dry methanol (14 ml) maintained on an ice-bath. The resultant reaction mixture was stirred on the ice bath for 2 h, and then at room temperature for a further 48 h. The reaction mixture was quenched with cold water (150 cm³) and extracted with methylene chloride (4×30 cm³). The combined organic phases were washed with water (3×50 cm³), dried (Na₂SO₄), filtered and concentrated in vacuum to a solid-oil mixture.

(i), Recrystallization (pentane) of the solid-oil mixture resulting from hydrolysis of the *gem*-dichloro-acetates (256a,b) afforded (1 α ,2 β ,4 β ,5 β ,7 α)-3,3-dichloro-cis-transoid-cis-tricyclo[5,1,0, $0^{2,4}$]octan-5-ol (258a) (54%) as fine white crystalline needles, m.p. 72-72.5° (Found: C, 49.74; H, 5.18; Cl, 36.17; C₈H₁₀Cl₂O requires C, 49.77; H, 5.22; Cl, 36.72%). $\nu_{\max}$ 3250, 3040, 2980, 2915, 2845, 1447, 1349, 1060, 1030, 991, 845 and 800 cm⁻¹. δ 0.08, m, 1H, H₈_{exo}; 0.6, m, 1H, H₈_{endo}; 1.25, complex m, 2H, H₁ and 7; 1.60-2.40, complex m, 4H, H₂, 4 and 6; 3.10, broad s, 1H, -O-H; 4.06, ddd, J = 10.0, 8.5 and 5.5 Hz, 1H, H₅ α . m/e 148, 21%, 150, 13%, 152, 4.6% (M-C₂H₄O)⁺; 113, 60%, 115, 27%, (M-C₂H₄O-Cl)⁺. T.l.c. (ethyl acetate/petroleum ether, 1:9) revealed a single spot with an R_F value of 0.2.

Concentration of the mother liquors left an oily residue shown by ¹H n.m.r. to be a c. 1:1 mixture of (1 α ,2 β ,4 β ,5 β ,7 α)- and (1 α ,2 β ,4 β ,5 α ,7 α)-3,3-dichloro-cis-transoid-cis-tricyclo[5,1,0, $0^{2,4}$]-octan-5-ol (258a,b) (44%) by comparison with the spectra of the authentic separated epimers (258a, above) and (258b, see p.208).

(ii) Recrystallization (pentane) of the solid-oil mixture resulting from hydrolysis of the *gem*-dibromo-acetates (257a,b) afforded (1 α ,2 β ,4 β ,5 β ,7 α)-3,3-dibromo-*cis-transoid-cis-tricyclo*[5,1,0,0^{2,4}]octan-5-ol (259a) (54%) as fine white crystalline needles, m.p. 77.5-78.5° (Found: C, 34.23; H, 3.46; Br, 57.06; C₈H₁₀Br₂O requires C, 34.08; H, 3.57; Br, 56.68%). $\nu_{\max}$ 3250, 3060, 2995, 2935, 2860, 1451, 1350, 1072, 1061, 1033, 991, 842, 783, 757 and 750 cm⁻¹. δ -0.1-0.3, m, 1H, H8_{exo}; 0.37-0.85, m, 1H, H8_{endo}; 0.95-1.50, complex m, 2H, H1 and 7; 1.78-2.50, complex m, 4H, H2, 4 and 6; 3.10, broad s, 1H, -O-H; 4.15, ddd, J = 11.0, 9.0 and 5.8 Hz, 1H, H5 α . m/e (18 eV) 236, 7.6%, 238, 13.8%, 240, 6.7%, (M-C₂H₄O)⁺; 201, 4.6%, 203, 4.4%, (M-C₂H₄O-Br)⁺. T.l.c. (ethyl acetate/petroleum ether, 1:9) revealed a single spot with an R_F value of 0.2.

Concentration of the mother liquors left an oily residue shown by ¹H n.m.r. to be a c.1:1 mixture of (1 α ,2 β ,4 β ,5 β ,7 α)- and (1 α ,2 β ,4 β ,5 α ,7 α)-3,3-dibromo-*cis-transoid-cis-tricyclo*[5,1,0,0^{2,4}]-octan-5-ol (259a,b) (44%) by comparison with the spectra of the authentic separated epimers (259a, above) and (259b, see p. 211).

*Reaction of (1 α ,2 β ,4 β ,5 β ,7 α)-3,3-Dichloro-*cis-transoid-cis-tricyclo*[5,1,0,0^{2,4}]octan-5-ol (258a) with Toluenesulphonic Acid in Benzene*

A solution of *p*-toluenesulphonic acid monohydrate (120 mg) in dry distilled benzene (77 cm³) in a flask fitted with a Dean-Stark apparatus was heated under reflux until all traces of water had been removed (c. 90 min). The tricyclo-octan-5 β -ol (258a) (100 mg) was added in one portion to the solution prepared above and reaction mixture was heated under reflux for 2.0 h. T.l.c. revealed all starting material had

been consumed after this time. The cooled reaction mixture was poured into saturated sodium bicarbonate (100 cm³), the organic phase separated, washed with saturated sodium chloride (1×70 cm³), water (2×100 cm³) and dried (Na₂SO₄). Filtration and concentration in vacuum of the processed organic phase afforded a yellow-brown oil (110 mg). T.l.c. (ethyl acetate/petroleum ether, 1:4) revealed at least seven mobile components. The ¹H n.m.r. spectrum of the crude product revealed aromatic and benzylic resonances, but none consistent with the presence of the desired *anti*-bishomobenzene (121).

No attempt was made to characterize any of the products from the above reaction.

Reaction of (1 α ,2 β ,4 β ,5 β ,7 α)-3,3-Dichloro-cis-transoid-cis-tricyclo[5,1,0,0^{2,4}]octan-5-ol (258a) with Phosphorous Oxytrichloride and Thionyl Chloride in Pyridine

A chilled (0°) solution of (1 α ,2 β ,4 β ,5 β ,7 α)-3,3-Dichloro-cis-transoid-cis-tricyclo[5,1,0,0^{2,4}]octan-5-ol (258a) (0.50 mmol) in pyridine was treated with the appropriate dehydrating agent (POCl₃ or SOCl₂) as detailed elsewhere.^{117,118} Work-up after the prescribed time afforded light yellow oils. Preparative t.l.c. (light petroleum elution) afforded a single major band (R_F = 0.75) which on extraction (methylene chloride, 50 cm³) gave a c. 1:1 mixture of compounds and proposed as (1 α ,2 β ,4 β ,5 α ,7 α)- and (1 α ,2 β ,4 β ,5 β ,7 α)-3,3,5-trichloro-cis-transoid-cis-tricyclo[5,1,0,0^{2,4}]octane (270) (c. 30%) as a clear colourless oil. (Found: C, 45.64; H, 4.21. C₈H₉Cl₃ requires C, 45.43; H, 4.29%). δ -0.1-2.8, complex m, 8H, H1, 2, 4, 6, 7 and 8; 3.90, m, 1H, H5. m/e (12 eV) 210, 18%, 212, 17%, 214, 6%, M⁺; 174, 100%, 176, 64%, 178, 10%, (M-HCl)⁺. G.l.c. {5% C-20M glass column [6 mm (od.) by 1.5 m], 154°, N₂ at 35 cm³ min⁻¹} 324 and 660 s.

General Procedure for Mesylation of the Tricyclo-octanols

(258) and (259)

Freshly distilled methanesulphonyl chloride (150 mg, 1.31 mmol) was added in a dropwise fashion over a period of 15 min to a chilled (ice-salt bath) solution of the appropriate alcohol (1.16 mmol) in methylene chloride (6 cm³) containing freshly distilled triethyl amine (180 mg, 1.78 mmol). The reaction mixture was stirred at c. 0° for 1 h and then at room temperature for a further 1 h. The reaction mixture was transferred to a separating funnel with the aid of more methylene chloride (25 cm³) and was extracted with ice-water (1×30 cm³), cold hydrochloric acid (2 M, 1×30 cm³), saturated sodium bicarbonate (2×30 cm³) and saturated sodium chloride (1×30 cm³). Drying (Na₂SO₄) of the methylene chloride solution followed by solvent removal gave the crude oily mesylates (89-91%) which were generally used immediately and without purification.

(i) Mesylation of (1 α ,2 β ,4 β ,5 β ,7 α)-3,3-dichloro-*cis-transoid-cis*-tricyclo[5,1,0,0^{2,4}]octan-5-ol (258a) gave on crystallization (pentane/methylene chloride) the corresponding 5 β -mesylate (260a) (93%) as thick white crystalline needles, m.p. 101.5-102.5° (Found: C, 39.97, H, 4.48; Cl, 26.46; S, 11.78; C₉H₁₂Cl₂O₃S requires C, 39.87; H, 4.46; Cl, 26.15; S, 11.70%). $\nu_{\max}$ 3050, 300, 2920, 2862, 1451, 1352, 1171, 949, 920, 830 and 802 cm⁻¹. δ -0.1-0.25, m, 1H, H_{8^{exo}}; 0.46-0.91, m, 1H, H_{8^{endo}}; 1.0-1.45, complex m, 2H, H1 and 7; 1.80-2.55, complex m, 4H, H1, 3 and 6; 3.05, s, 3H, mesylate methyl protons; 5.13, m, 1H, H5 α . m/e (16 eV) 174, 28.6%, 176, 18.8%, 178, 2.9%, (M-CH₃SO₃H)⁺; 139, 100%, 141, 31%, (M-CH₃SO₃H-Cl)⁺. T.l.c. (ethyl acetate/petroleum ether, 1:9) revealed a single spot with an R_F value of 0.1.

(ii) Mesylation of the crude mixture of *gem*-dichloro-5-ols (258a,b) obtained directly from the acetates (258) afforded a foul smelling clear colourless oil (89%), the ^1H n.m.r. spectrum of which in addition to displaying all the resonances corresponding to the pure 5β -mesylate revealed a sharp singlet resonance at 2.95 p.p.m. and further more coupled signals at higher field consistent with the presence of the 5α -mesylate (Ratio $5\beta/5\alpha = 3.5:1$). m/e (16 eV) 174, 30%, 176, 19.2%, 178, 3.0%, $(\text{M}-\text{CH}_3\text{SO}_3\text{H})^+$; 139, 100%, 141, 31%, $(\text{M}-\text{CH}_3\text{SO}_3\text{H}-\text{Cl})^+$.

(iii) Mesylation of $(1\alpha,2\beta,4\beta,5\beta,7\alpha)$ -3,3-dibromo-*cis-transoid-cis*-tricyclo[5,1,0, $0^{2,4}$]octan-5-ol (259a) gave on crystallization (pentane/methylene chloride) the corresponding 5α -mesylate (261a) (91%) as fine white crystalline needles, m.p. 94-95°. (Found: C, 30.20; H, 3.35; Br, 43.90; S, 8.70; $\text{C}_9\text{H}_{12}\text{Br}_2\text{O}$ requires C, 30.02; H, 3.36; Br, 44.38; S, 8.90%). ν_{max} 3060, 3000, 2920, 1450, 1345, 1170, 1029, 910, 819 and 745 cm^{-1} . δ -0.1-0.3, m, 1H, $\text{H}8_{\text{exo}}$; 0.45-0.90, m, 1H, $\text{H}8_{\text{endo}}$; 1.00-1.45, complex m, 2H, H1 and 7; 1.90-2.80, complex m, 4H, H2, 4 and 6; 3.10, s, 3H, mesylate methyl protons; 5.15, m, 1H, $\text{H}5\alpha$.

(iv) Mesylation of the crude mixture of *gem*-dibromo-5-ols (259a,b) obtained directly from the acetates (259a,b) afforded a foul smelling colourless oil (92%) the ^1H n.m.r. spectrum of which in addition to displaying all the resonances corresponding to the pure 5β -mesylate revealed a sharp singlet resonance at 2.95 p.p.m. and further more coupled envelopes consistent with the presence of the 5α -mesylate (261b).

Reaction of (1 α ,2 β ,4 β ,5 β ,7 α)-3,3-Dichloro-5-mesyloxy-cis-transoid-cis-tricyclo[5,1,0,0^{2,4}]octane (260a) with 1,8-Diazabicyclo[5,4,0]-undec-7-ene (DBU) in DMSO

A solution of (1 α ,2 β ,4 β ,5 β ,7 α)-3,3-dichloro-5-mesyloxy-cis-transoid-cis-tricyclo[5,1,0,0^{2,4}]octane (200 mg, 0.74 mmol) in dry DMSO (3.7 cm³) was treated in one portion with dry DBU (290 mg, 2.57 mol equiv.). The resultant red solution was stirred on an oil bath at 70-72° and under an oxygen free nitrogen atmosphere for 96 h. T.l.c. revealed that essentially all the starting material had reacted after this time. The cooled reaction mixture was quenched with water (20 cm³) and extracted with chloroform (3×10 cm³). The combined organic phases were washed with cold hydrochloric acid (2 M, 2×15 cm³), saturated sodium bicarbonate (1×20 cm³), saturated sodium chloride (20 cm³), water (3×50 cm³) and dried (Na₂SO₄). The filtered organic solution was concentrated in vacuum to give a red oil (170 mg) which was immediately subjected to preparative t.l.c. (light petroleum elution), and afforded two bands A and B with R_F values of 0.0-0.75 and 0.8 respectively.

Band A was resubjected to preparative t.l.c. (ethyl acetate/petroleum ether, 1:9) and afforded a single major band with an R_F value of 0.2. Extraction of this band afforded (1 α ,2 β ,4 β ,5 α ,7 α)-3,3-dichloro-cis-transoid-cis-tricyclo[5,1,0,0^{2,4}]octan-5-ol (258b) (14%) as a clear colourless oil.

ν_{max} 3280, 3040, 2960, 1445, 1337, 1045, 995, 920, 830 and 800 cm⁻¹.
 δ 0.3, m, 1H, H8_{exo}; 0.60-2.63, complex m, 7H, H1, 2, 4, 6, 7 and 8_{endo}; 2.92, broad s, 1H, -O-H; 3.75, m, 1H, H5 β . m/e 148, 20%, 150, 13%, 152, 4.5%, (M-C₂H₄O)⁺; 113, 70%, 115, 26%, (M-C₂H₄O-Cl)⁺. This product was further characterized by conversion to its 3,5-dinitrobenzoate derivative. Thus a solution of the alcohol (80 mg, 0.41 mmol) in dry distilled pyridine (2.5 ml) was treated in one portion with 3,5-dinitrobenzoylchloride (150 mg, 0.65 mmol) and the resultant light yellow solution stirred at ambient

temperatures for 20 h. Conventional work-up (chloroform extraction) afforded an oily-solid (158 mg, 99.5%). Recrystallization (pentane/chloroform) gave the 3,5-dinitrobenzoate of the 5 α -ol (258b) as off-white crystalline masses, m.p. 159.5-161° (Found: C, 46.69; H, 3.29; Cl, 18.55; N, 7.57. C₁₅H₁₂Cl₂N₂O₆ requires C, 46.54; H, 3.12, Cl, 18.31; N, 7.24%). $\nu_{\max}$ 3100, 1725, 1545, 1295, 1280, 1172, 800, 730 and 723 cm⁻¹. δ 0.35, m, 1H, H_{8^{exo}}; 0.65-2.80, complex m, 7H, H1, 2, 4, 6, 7 and H_{8^{endo}}; 5.12, m, 1H, H5; 9.19, broad s, 3H, aromatic protons. T.l.c. (ethyl acetate/petroleum ether, 1:9) revealed a single chromophoric spot with an R_F value of 0.37.

Band B (R_F 0.8) the petroleum ether mobile component from the reaction of the mesylate (260a) with DBU in DMSO on extraction (methylene chloride, 50 cm³) afforded 3,3-dichloro-cis-transoid-cis-tricyclo[5,1,0,0^{2,4}]octan-5-ene (121) [59% based on recovered alcohol (258b)] as a clear colourless oil. (Found: M^{+} 173.9999 C₈H₈Cl₂ requires 174.0003, Δ = 2.3 p.p.m.). $\nu_{\max}$ 3060, 3000, 2920, 1650, 1025, 1015, 898, 850, 825 and 732 cm⁻¹. δ 0.56, complex m, 1H, H_{8^{exo}}; 1.25, d, J = 2.8 Hz, 1H, H7; 0.90-1.60, complex m, 2H, H1 and 8_{endo}; 1.75, dd, J = 10.2 and 4.8 Hz, 1H, H4; 2.21, d, J = 10.2 Hz, 1H, H2; 5.49, dd, J = 10.0 and 4.8 Hz, 1H, H6; 5.96, d of m, J = 10.0 Hz, 1H, H5. m/e 174, 3.9%, 176, 2.5%, 178, 0.4%, M^{+} ; 159, 3.2%, 161, 2.4%, (M-CH₃)⁺; 139, 12%, 141, 4%, (M-Cl)⁺; 83, 100%, 85, 65%, 87, 10%, (CHCl₂)⁺. G.l.c. {5% C-20M glass column [6 mm (od.) by 1.5 m], 132.5°, N₂ at 30 cm³ min⁻¹} 450 s. T.l.c. (petroleum ether) reveals a single spot with an R_F value of 0.80.

Repeating the dehydromesylation of the ester (260a) under strictly anhydrous conditions on the same scale as above afforded the *anti*-bishomobenzene (121) in 59% yield. There was no evidence (t.l.c. and i.r.) for the 5 α -alcohol (258b).

Mesylation of the pure 5 α -alcohol (258b) and subjection to DBU in DMSO afforded a single major product with an identical retention time on a variety of columns to the isolated *anti*-bishomobenzene (121). T.l.c. also revealed a major component with the same R_F value as authentic (121).

Reaction of (1 α ,2 β ,4 β ,5 β ,7 α)-3,3-Dibromo-5-mesyloxy-cis-transoid-cis-tricyclo[5,1,0, $0^{2,4}$]octane (261a) with DBU in DMSO

A solution of (1 α ,2 β ,4 β ,5 β ,7 α)-3,3-dichloro-5-mesyloxy-cis-transoid-cis-tricyclo[5,1,0, $0^{2,4}$]octane (267 mg, 0.74 mmol) in dry DMSO (3.7 cm³) was treated in one portion with dry DBU (290 mg, 2.57 mol. equiv.). The resultant red solution was stirred on an oil bath at 70-72° and under an oxygen free nitrogen atmosphere for 96 h. T.l.c. revealed that essentially all the starting material had reacted after this time. The cooled reaction mixture was quenched with water (20 cm³) and extracted with chloroform (3 $\times$ 10 cm³). The combined organic phases were washed with cold hydrochloric acid (2 M, 2 $\times$ 15 cm³), saturated sodium bicarbonate (1 $\times$ 20 cm³), saturated sodium chloride (20 cm³), water (3 $\times$ 50 cm³) and dried (Na₂SO₄). The filtered organic solution was concentrated in vacuum to give a red oil which was immediately subjected to preparative t.l.c. (light petroleum elution), and afforded two bands A and B, with R_F values of 0.0-0.75 and 0.8 respectively.

Band B (R_F = 0.8) afforded 3,3-dibromo-cis-transoid-cis-tricyclo[5,1,0, $0^{2,4}$]oct-5-ene (122) [59% based on recovered alcohol (259b)] as a clear colourless oil. (Found: M^+ 263.8979. C₈H₈Br₂ requires 263.8974, Δ = 1.9 p.p.m.). $\nu_{\max}$ 3050, 3000, 2920, 1650, 1450, 842, 781 and 751 cm⁻¹. δ 0.56, complex m, 1H, H8_{exo}; 1.05, d, J = 2.5 Hz, 1H, H7; 0.70-1.55 complex m, 2H, H1 and 8_{endo}; 1.78, dd, J = 10.2 and 4.8 Hz, 1H, H4; 2.25 d, J = 10.2 Hz, 1H, H2; 5.45, dd, J = 10.0 and 4.8 Hz, 1H, H6; 5.96, d of m,

$J = 10.0$ Hz, 1H, H5. m/e 262, 1%, 264, 2%, 268, 1%, M^{+} ; 171, 50%, 173, 100%, 175, 49% (CHBr_2)⁺. G.l.c. {5% C-20M glass column [6 mm (od.) by 1.5 m], 132.5°, N_2 at $30 \text{ cm}^3 \text{ min}^{-1}$] 1368 s. T.l.c. (petroleum ether) reveals a single spot with an R_F value of 0.80.

Band A ($R_F = 0.0$ – 0.75) was resubjected to preparative t.l.c. (ethyl acetate/petroleum ether, 1:9) and afforded a single major band with an R_F value of 0.2. Extraction of this band afforded (1 α ,2 β ,4 β ,5 α ,7 α)-3,3-dibromo-*cis-transoid-cis*-tricyclo[5,1,0,0^{2,4}]octan-5-ol (259b) (14%) as a clear colourless oil. ν_{max} 3280, 3050, 2960, 1450, 820 and 745 cm^{-1} . δ 0.35, m, 1H, H8_{exo}; 0.60–2.70, complex m, 7H, H1, 2, 4, 6, 7 and 8_{endo}; 2.85, broad s, 1H, -O-H; 3.90, m, 1H, H5 β .

Repeating the dehydromesylation of the ester (261a) under strictly anhydrous conditions on the same scale as above afforded the *anti*-bishomobenzene (122) in 59% yield. There was no evidence (t.l.c. and i.r.) for the 5 α -alcohol (259b).

Mesylation of the pure 5 α -alcohol (259b) and subjection to DBU in DMSO afforded a single major product with an identical retention time on a variety of columns to the isolated *anti*-bishomobenzene (122). T.l.c. also revealed a major component with the same R_F value as authentic (122).

Reductive Debromination of 3,3-Dibromo-cis-transoid-cis-tricyclo-[5,1,0,0^{2,4}]oct-5-ene (122)

To a stirred mixture of 3,3-dibromo-*cis-transoid-cis*-tricyclo[5,1,0,0^{2,4}]oct-5-ene (122) (100 mg, 0.38 mmol), dry *t*-butyl alcohol (3.24 mmol) and dry, freshly distilled, tetrahydrofuran (3 cm^3) under an atmosphere of dry oxygen free nitrogen was added lithium wire (100 mg, 0.014 g-atom) cut into small pieces in the neck of the flask. The reaction mixture was stirred at ambient temperature for 24 h. The resultant cloudy mixture was poured into ice-water (15 cm^3) through a glass-wool plug and the organic solids thus retained

washed with pentane (15 cm³). The filtrate was extracted with pentane (2×20 cm³) and the combined organic phases were washed with water (2×25 cm³), dried (Na₂SO₄), filtered and concentrated in vacuum on an ice-bath to a very light yellow oil identified as *cis-transoid-cis-tricyclo*[5,1,0,0^{2,4}]oct-5-ene (238) (31 mg, 77%). δ 0.48, d, J = 4.2 Hz, 2H, *exo*-cyclopropyl protons; 0.80, d, J = 6.0 Hz, 4H, *endo*-cyclopropyl protons and H1 and 2; 1.40, m, 2H, H4 and 7; 5.47, broad s, 2H, vinylic protons. G.l.c. {5% C-20M glass column [6 mm (od.) by 1.5 m] 58°, N₂ at 30 cm³ min⁻¹} 264 s. The ¹H n.m.r. spectrum of the reduction product is identical to that of the authentic material.

Reductive Dechlorination of 3,3-Dichloro-cis-transoid-cis-tricyclo[5,1,0,0^{2,4}]oct-5-ene (121)

To sodium sand [prepared by shaking molten sodium (380 mg, 0.019 g-atom) in hot dry, freshly distilled o-xylene and washing the cooled sand with ether (3×5 cm³) and freshly distilled tetrahydrofuran (2×20 cm³)] was added a solution of the *gem*-dichloro-*anti*-bishomobenzene (70 mg, 0.40 mmol) and dry *t*-butyl alcohol (90 mg, 1.22 mmol) in dry THF (2 cm³). The ensuing mixture was heated under reflux under an atmosphere of nitrogen for 2 h and filtered through a pad of glass wool into water (10 cm³). The inorganic salts were washed with pentane (5 cm³) and the aqueous phase extracted with pentane (3×5 cm³). The combined organic extracts were dried (Na₂SO₄) and concentrated in vacuum on an ice-bath to a very pale yellow oil identified as *cis-transoid-cis-tricyclo*[5,1,0,0^{2,4}]oct-5-ene (238) (28 mg, 66%). The ¹H n.m.r. spectrum of this product was identical to that obtained from the *gem*-dibromo-*anti*-bishomobenzene, and in addition had the same retention time as the sample obtained from the dibromo compound (122) on a 5% C-20M column. A mixture of the two reduction products showed a single peak on both 5% SE-30 and 3% OV-1 columns.

Dehydrochlorination of 3,3-Dichloro-cis-transoid-cis-

tricyclo[5,1,0,0^{2,4}]octane (121) with Potassium t-Butoxide in DMSO

A solution of 3,3-dichloro-*cis-transoid-cis*-tricyclo[5,1,0,0^{2,4}]oct-5-ene (121) (80 mg, 0.46 mmol) in dry distilled DMSO (7 cm³) was added in a dropwise fashion over a period of 0.5 h to a chilled (salt-ice) suspension of *t*-BuOK (2.5 g, 40 mol. equiv.) in DMSO (13 cm³). The resultant pitch black reaction mixture was stirred at room temperature for 16 h, diluted with water (20 cm³) and extracted with methylene chloride (3×10 cm³). The combined organic phases were washed with water (2×50 cm³), dried (Na₂SO₄), filtered and concentrated in vacuum to a waxy yellow solid. The ¹H n.m.r. spectrum of the crude reaction product displayed only traces of olefinic and aromatic materials. T.l.c. reveals only very minor quantities of discrete reaction products. No attempt was made to characterize these materials because of the small quantities involved.

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