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STUDIES OF STRAINED RING SYSTEMS: CYCLOPROPA[*l*]PHENANTHRENES

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I should like to thank Dr. B. Halton, who has been the complete supervisor these past three years.

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As well, I should like to thank Mr. B. Cockburn for interesting me in Chemistry to start with, and Messrs. I. Crighton, C. Snell and C. Taylor for their excellent technical assistance. Thanks also to the people who will make me remember my time in the Department with pleasure, especially Peter, Cliff, Ian, John, Peter, Richard and Stuart.

Finally, I wish to express my appreciation to Sue for carefully checking the manuscript and to my Mother for typing it so diligently.

CONTENTS

Abstract

The aim of the present study has been the synthesis of 1*H*-cyclopropa[*l*]phenanthrene (16a) and its derivatives, the sole remaining unknown structural type of the cycloproparenes. Established procedures for cycloproparene synthesis are not readily adaptable to this ring system, and routes based upon new bridgehead-substituted 1a,9b-dihydrocyclopropa[*l*]phenanthrenes are examined.

1,1-Dichloro-1a-phenylseleno-1a,9b-dihydrocyclopropa[*l*]phenanthrene (73) is prepared by the addition of dichlorocarbene to the corresponding phenanthrenyl selenide (72). *syn*-Selenoxide elimination of PhSeOH from the derived selenoxide (74) gives 1,1-dichloro-1*H*-cyclopropa[*l*]phenanthrene (76) which is intercepted by methanolysis. Labelling studies provide convincing evidence for the intermediacy of the 1*H*-cycloproparene.

The viability of an oxidative decarboxylation route to 1,1-dialkyl-1*H*-cyclopropa[*l*]phenanthrenes is investigated for the model compound 7,7-dimethylbicyclo[4.1.0]hept-3-ene-1-carboxylic acid (122). A product of formal cyclopropyl-allyl cation rearrangement is isolated.

1a-Methylseleno-1a,9b-dihydrocyclopropa[*l*]phenanthrene (174) is prepared by the unprecedented addition of methylselenide anion to 1a*H*-cyclopropa[*l*]phenanthrene (63) (generated by a new route involving the fluoride ion-promoted elimination of the elements of chlorotrimethylsilane from the isomeric 1-chloro-1a-trimethylsilyl-1a,9b-dihydrocyclopropa[*l*]phenanthrenes (170) and (171)). Treatment of the drived dimethylselenonium tetrafluoroborate (179) with base in the presence of furan gives the *endo*- and *exo*-furan cycloadducts (180) and (181) of 1*H*-cyclopropa[*l*]phenanthrene (16a).

The results presented herein provide the first conclusive evidence for the existence of the 1*H*-cyclopropa[*l*]phenanthrene ring system, both as the parent hydrocarbon (16a) and the 1,1-dichloro-derivative (76).

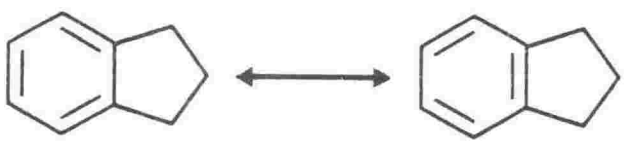
CHAPTER ONE

INTRODUCTION

Molecules which satisfy the criteria for aromaticity are unusually stable, whereas molecules incorporating strained rings are more reactive and less stable. How then might molecules containing **both** an 'aromatic' and a strained ring behave? This chapter investigates the juxtaposition of the concepts of aromaticity and strain within the family of the *ortho*-annelated aromatics - the cycloalkarenes.

The fascination[1] with the cycloalkarenes lies, in part, in trying to establish the limits to which such molecules may be stressed, yet still be stable enough to be observed. Such an outwardly sportive pursuit of 'the most strained cycloalkarene' (and of strained molecules in general) is underpinned, however, by contributions to the theories of structure, bonding and aromaticity. One of the main aims of contributors to this field is to obtain evidence concerning 'bond fixation', wherein an ostensibly 'aromatic' ring might become a π-localised cyclohexa-1,3,5-triene, as in the Kékule structure for benzene.

In 1930, Mills and Nixon[2] advanced the idea of bond fixation in cycloalkarenes by using simple geometric arguments to suggest that canonical form (1a) of indan would be lower in energy than the alternative form (1b). Thus, the resonance hybrid would



1a 1b

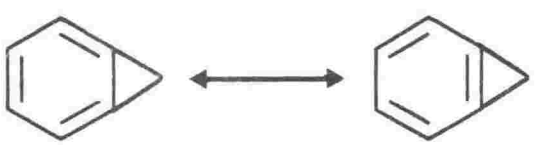
show properties consistent with largely single bond character at the bridge.

Early experimental work[3] on indan (and tetralin, the higher homologue with a six-membered ring fused to benzene) was incon-

clusive at best. Longuet-Higgins and Coulson[4], in a 1946 theoretical study, found that resonance form (1b) would contribute more to the resonance hybrid than would structure (1a), but a more recent semi-empirical investigation[5] revived the 'Mills-Nixon effect' by preferring the latter resonance form.

Plainly there is some doubt as to the reality and direction of bond fixation in indan, but the Mills-Nixon effect is attractive. The preference for one resonance form of a given cycloalkarene may become significant if (i) the size of the annelated ring were to be varied; (ii) the number and orientation of the annelated rings were to be changed; or (iii) the nature of the arene itself were to be altered.

If simple strain factors were responsible for any difference in energy between structures (1a) and (1b), then one might expect such a difference to increase when the fused ring is made smaller. Early CNDO/2 studies[5] of the smaller cycloalkarenes have borne this out. This difference in energy should be most noticeable for cyclopropabenzene (2), the lowest homologue of the series, and further discussion of the mono-annelated cycloalkarenes is accordingly confined mainly to this compound.

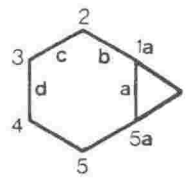


2a 2b

Mahanti[6] concluded, from his calculations of strain energy, bond length-bond order relationships and π-overlap populations, that resonance form (2a) contributes more to the resonance hybrid of cyclopropabenzene than does the alternative (2b). Dürr[7a] has employed the MINDO/3 and MNDO techniques to predict the bond lengths of cyclopropabenzene (2), whilst Apeloig[7b] has made STO-3G and 3-21G calculations. These results, together with experimental values for benzene, cyclopropane[8] and cyclopropene[9], are shown in Table 1. Provided bond length is indeed an accurate reflection of bond order, then Dürr's results

Table 1

Calculated Bond Lengths[a] of Cyclopropabenzene, and Experimental Bond Lengths of Benzene, Cyclopropane and Cyclopropene

Compound	Method	Ref.	a	b	c	d
 2	MINDO/3	7a	145.3	137.7	142.9	139.9
	MNDO	7a	142.8	136.1	144.1	139.8
	STO-3G	7b	137.4	135.7	141.4	136.2
	3-21G	7b	133.7	136.7	140.6	139.4
	Expt.		139.5			
	Expt.	8	151.0			
	Expt.	9	129.6			

a Bond lengths are in pm.

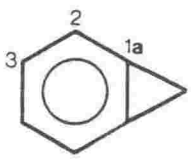
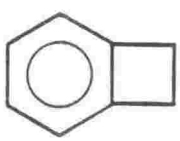
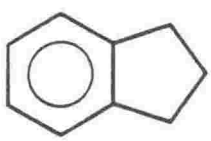
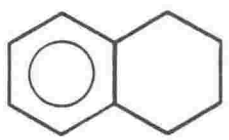
suggest that there is some bond fixation in the direction of structure (2a). In contrast, Apeloig's more sophisticated calculations show no significant preference for either canonical form. These theoretical studies have not been backed by an experimental determination of the structure of cyclopropabenzene itself, but molecular structures have been determined[10] by x-ray crystallography or microwave spectroscopy for four substituted cyclopropabenzenes. No pattern of alternating short and long bonds is observed, but it is likely that information about bond fixation has been obscured anyway by effects of the C-1 substituents (-fluoro,[10d] -chloro[10b] and

-carbomethoxy[10a,c] in the examples studied).

Nmr has been used extensively[11] for investigating the cycloalkarenes, and chemical shifts and coupling constants are summarised in Table 2. It can be seen that the effects of

Table 2

Selected Chemical Shifts and Coupling Constants of Cycloalkarenes[a]

				
δ/ppm				
C-1a	125.4	145.2	143.3	136.4
C-2	114.7	122.1	124.0	128.8
C-3	128.8	126.5	125.8	125.2
H-2	7.15	6.76	7.07	7.01
H-3	7.19	6.91	6.99	6.93
J/Hz				
(C-2)-H	168.5	162	155.5	155
(C-3)-H	159	157.5	157	159
(C-1a)-(C-2)	87.1	59.8	59.8	58.6
(H-2)-(H-3)	6.04	7.36	7.59	
(H-3)-(H-4)	7.63	7.79	7.20	

a Taken from Ref. 1e.

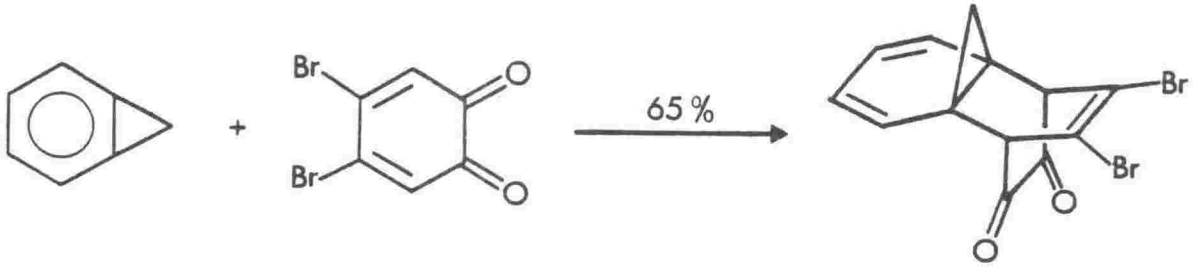
annelated ring size are most noticeable near the site of fusion. In addition, the diamagnetic ring current is not grossly perturbed by ring strain, since the protons of the six-membered ring in cyclopropabenzene, for example, resonate within the

usual aromatic region.

Some of the trends apparent from Table 2 have been rationalised[1e] in terms of the Streitweiser-Finnegan rehybridisation model[12], wherein the bridgehead carbons of the cycloalkarenes rehybridise to use orbitals of higher p-character in bonding to the small ring. This leaves an orbital of higher s-character to bond to C-2, which results in an inductive polarisation of the (C-2)-H bond. This is held to be in accordance with the high-field shift of C-2 and the increases in $J_{(C-2)-H}$ and $J_{(C-1a)-(C-2)}$ with increasing strain. It should be noted that the rehybridisation model does not require the operation of the Mills-Nixon effect.

The electronic spectra of the singly annelated benzenes have provided evidence neither for nor against bond fixation.[1] The infrared spectra are simple, reflecting the high symmetry of these molecules.[1]

Chemically, cyclopropabenzene has a much richer cycloaddition chemistry[13] than does benzene itself, although this enhanced reactivity may be due to lessened ring strain in the adducts, rather than bond fixation in the educt. The adduct (3) from cyclopropabenzene and 3,4-dibromo-*o*-benzoquinone is so far the only primary cycloaddition product whose geometry has been determined.[13b,c] This *exo*-geometry seems at first glance to

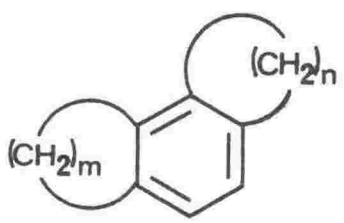


2 3

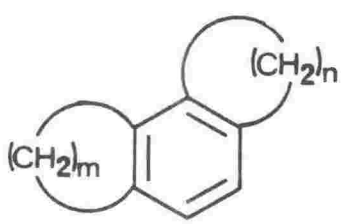
be consistent with a $[\pi 6_s + \pi 4_s]$ rather than a $[\pi 2_s + \pi 4_s]$ process, implying bond fixation in the direction of resonance

form (2a). It is certainly possible, however, that the observed geometry reflects minimisation of steric interference (which could lead to the *exo*-[$_{\pi}2_{s}$ + $_{\pi}4_{s}$] adduct), rather than minimisation of secondary orbital overlap in the transition state (leading to the identical *exo*-[$_{\pi}6_{s}$ + $_{\pi}4_{s}$] adduct[14]).

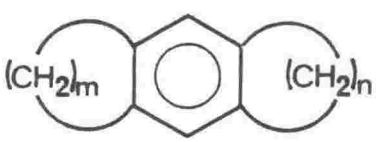
Having encountered quite small effects on the arene through variation of the size of the fused ring, the second factor to be considered is the effect of fusion of more than one ring to the benzene nucleus. Two small rings may be fused either *meta* (4) or *para* (5) to benzene. For the *para* case it is impossible



4a



4b



5

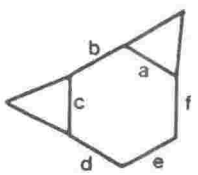
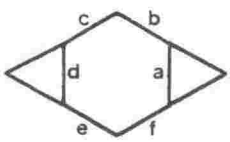
to write a resonance form where both sites of annelation have the same bond order; no significant bond localisation would be expected, provided m=n. The *meta*-fused bis-cycloalkarenes, however, could show a preference for one resonance form, since the double bonds could be localised either as in canonical form (4a), or as in structure (4b). Intuitively one would favour the former.

Neither of the bis-cyclopropabenzenes (4;m=n=1) or (5;m=n=1) is known, but most of the higher homologues have been prepared. It has been suggested[15] that the limit of stability for the cycloproparenes, at ambient temperature, might be reached with compound (5;m=n=1). Dürr[7a] predicted, at the MNDO level, the bond lengths shown in Table 3. Bond alternation is thus predicted to be more evident in compound (4;m=n=1) than in compound (5;m=n=1). Again assuming that bond length reflects bond order, this shows the angular isomer to prefer a degree of bond fixation in the direction of canonical form (4a). Re-

ports of the syntheses and physical data of the bis-cyclopropabenzenes are awaited with interest.

Table 3

Calculated Bond Lengths[a] of the bis-Cyclopropabenzenes[b]

	 4; m=n=1	 5; m=n=1
a	146.4	141.7
b	133.2	130.2
c		139.2
d	135.6	141.8
e	147.3	

a Bond lengths are in pm.

b Taken from Ref. 7a.

Both cyclobutacyclopropabenzenes, (4;m=1,n=2)[16] and (5;m=1,n=2),[16b,17] have been prepared. Nmr and electronic spectra have been obtained for these compounds[16,17] and for some higher homologues,[18] but no compelling evidence for or against bond fixation has been forthcoming.

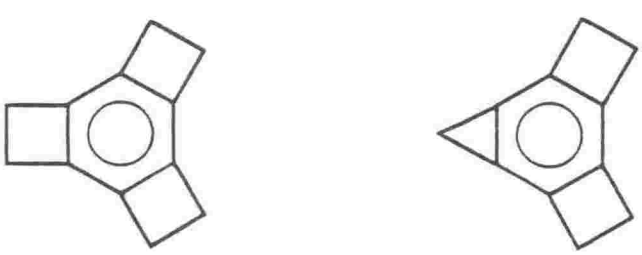
For the tris-annelated benzenes only *meta*-fusion is possible, and factors which might have altered the relative contributions of structures (4a) and (4b) to the resonance hybrids of the *meta*-fused bis-cycloalkabenzenes (4) should become even more important. The lowest homologue of the series, tris-cyclopropabenzene (6), is unknown, although Dewar[19] suggested recent-

ly that it might be a local minimum on the C_9H_6 hypersurface. His MNDO calculations showed a definite preference for the resonance form shown, but an *ab initio* study is clearly re-

6 7

quired to substantiate this apparent example of bond fixation. Dewar also predicted a barrier to cycloreversion, to give triyne (7), of only 33 kJ/mol. The formation of radical-derived products was not considered, but is a more likely option considering all that is known about the thermochemistry of other cycloproparenes.[1]

Among the homologues of compound (6), both tris-cyclobutabenzene[20] (8) and bis-cyclobutacyclopropabenzene[21] (9) have been prepared. Compound (8) melts without decomposition at



8 9

141° and compound (9) is stable at -20°. Since there are no protons on the central rings, any effect of tris-annelation on the diamagnetic ring current cannot be seen from the proton nmr spectra. The carbon-13 nmr and electronic spectra also give little information about possible bond fixation.

The third variation in the search for bond fixation is to change

the arene part of the cycloalkarene. Some cycloalka-pyridines and a -thiophene have been prepared.[22] The physical properties of these compounds have best been explained in terms of the Streitweiser-Finnegan rehybridisation model rather than by any bond localisation.[1e]

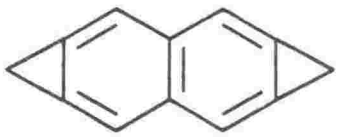
As well as the heteroaromatics, one might consider the higher aromatic hydrocarbons. Simple resonance theory predicts that canonical form (10a) contributes more to the resonance hybrid of naphthalene than does the alternative form (10b). Con-

10a 10b

11 12

sequently, annelation at position 'a' would give a compound (11), which might be less stable than compound (12) which results from annelation at position 'b'. Both cyclopropa-naphthalenes are known: the linear species (12) is stable above its melting point,[23] whilst the angular one (11) explodes on melting.[24] This difference in stability has not been associated with any π-localisation due to small-ring annelation, despite careful study[1c,e] of the spectra of these systems. In addition, the crystal structure[25] of compound (12) fails to indicate a consistent pattern of bond alternation, but rather shows that the compound is stabilised by other, less readily explained distortions in geometry.

Bis-cyclopropanaphthalene (13) has also been prepared.[15] It is shock-sensitive and explodes when heated to its melting



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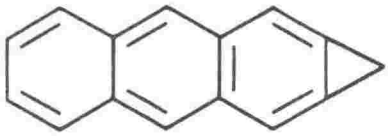

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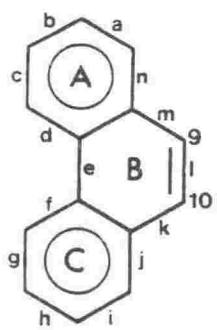
point. This compound begins to define the amount of strain which the less aromatic naphthalene nucleus can tolerate. Cyclopropa[*b*]anthracene (14) is known,[26] whilst cyclopropaphenanthrenes were unknown at the commencement of this study. The bond between the 9- and 10-positions of phenanthrene (15) has high π-character, and the fusion of a three-membered ring at this site should lead to a highly strained molecule, interesting not just as a synthetic exercise, but also because it should provide useful comparisons with cyclopropa[*a*]naphthalene (11), another molecule with a small ring fused across a 'partial double bond'. The work described herein concerns the syntheses of 1*H*-cyclopropa[*l*]phenanthrenes (16).



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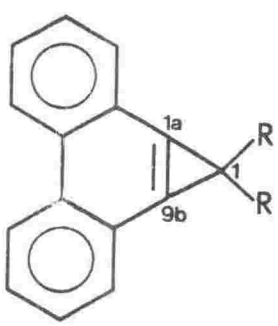
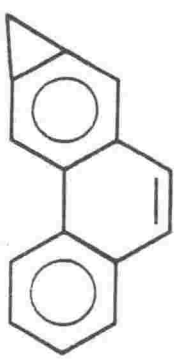


16 a;R=H

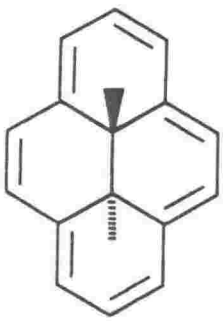


17

Three other cyclopropaphenanthrenes are possible (the 'b' isomer (17) has been made[27] recently), but they should not have properties markedly different from those of the cyclopropanaphthalenes, since the 'A' and 'C' rings of phenanthrene do not suffer significantly more π-localisation than does naphthalene.

Lastly, Mitchell *et al.*[28] have investigated the effect of small-ring fusion on the dihydropyrenes. They found that the

degree of bond localisation in dimethyldihydropyrene (18) may be calculated from the chemical shifts of the methyl protons.



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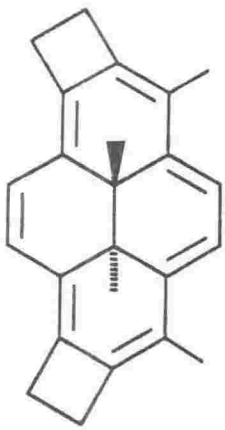

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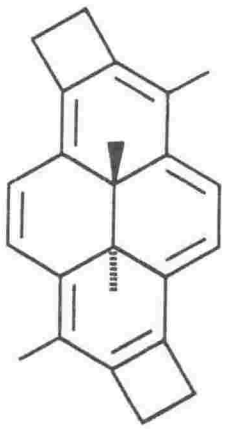

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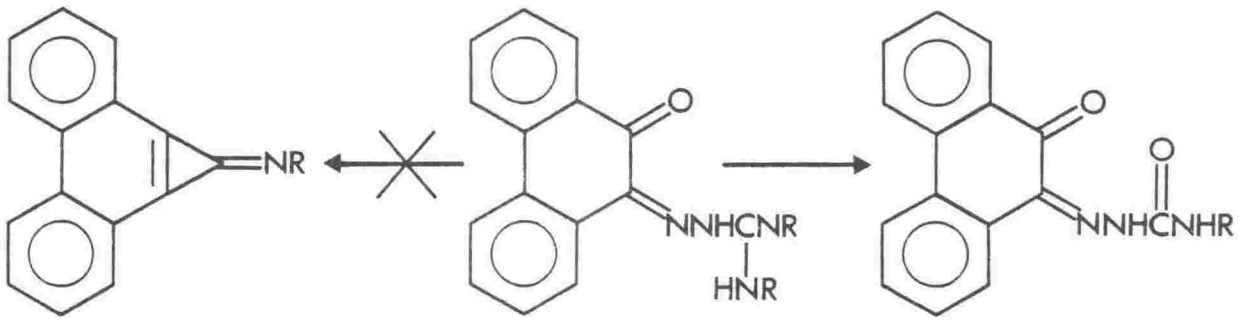
They reasoned that *meta*-fusion of two small rings, as in compound (19), would enhance the Mills-Nixon effect, whilst *para*-fusion of two small rings, as in compound (20), would eliminate it (compare with the earlier discussion of the *meta*- and *para*-bis-cycloalkabenzenes). Compounds (19) and (20) were synthesised and the authors claimed that the observed chemical shifts of the internal methyl protons showed there to be no significant Mills-Nixon effect for these molecules.

The remainder of this chapter is concerned with possible approaches to the synthesis of 1*H*-cyclopropa[*l*]phenanthrene (16a) and its derivatives.

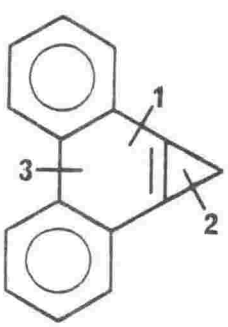
Historically it is interesting that the first claim for the synthesis of a cyclopropa[*l*]phenanthrene was made[29] in 1930, which pre-dated the isolation of the first cyclopropabenzene[30] by 34 years. De and Dutt[29] claimed that a series of iminosemicarbazones (21) decomposed to give the iminocyclopropa[*l*]phenanthrenes (22). A reinvestigation[31] established, however, that the only isolable products were the semicarbazones (23).

Cyclisation by the formation of one bond is conceptually the



22 21 23

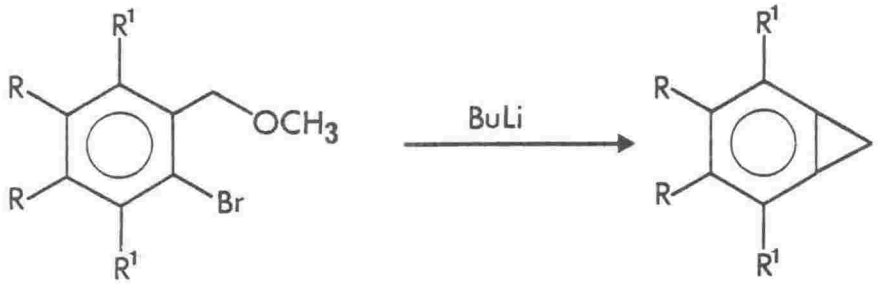
simplest route to the target molecule. Consequently one might consider, as a last step, cyclisation at any of the three positions shown:



16a

Disconnection at position (1) leads to a biphenyl-substituted cyclopropene. The difficulty expected in the synthesis of such a starting material has meant this route has not yet been investigated.

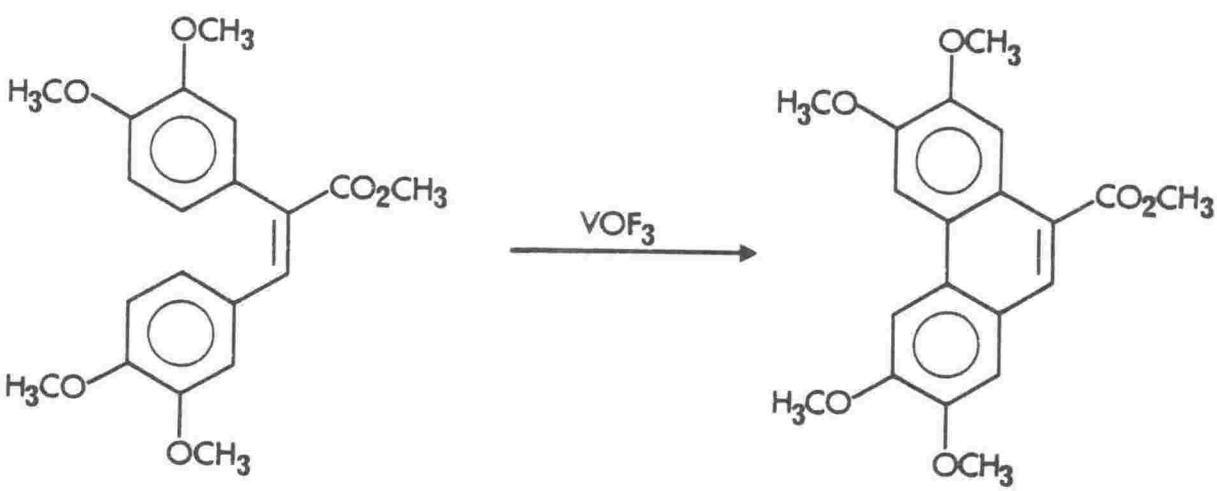
Disconnection at position (2) gives a substituted phenanthrene. An analogous precursor, compound (24a), was used in a claimed synthesis of cyclopropabenzene by Radlick and Crawford,[32] but investigations[33-35] into the validity of this report failed to give cyclopropabenzene, except in trace quantities. Extension of the reaction to the possible 1*H*-cyclopropa[*l*]phenanthrene precursor (24b) was also unsuccessful.[36]



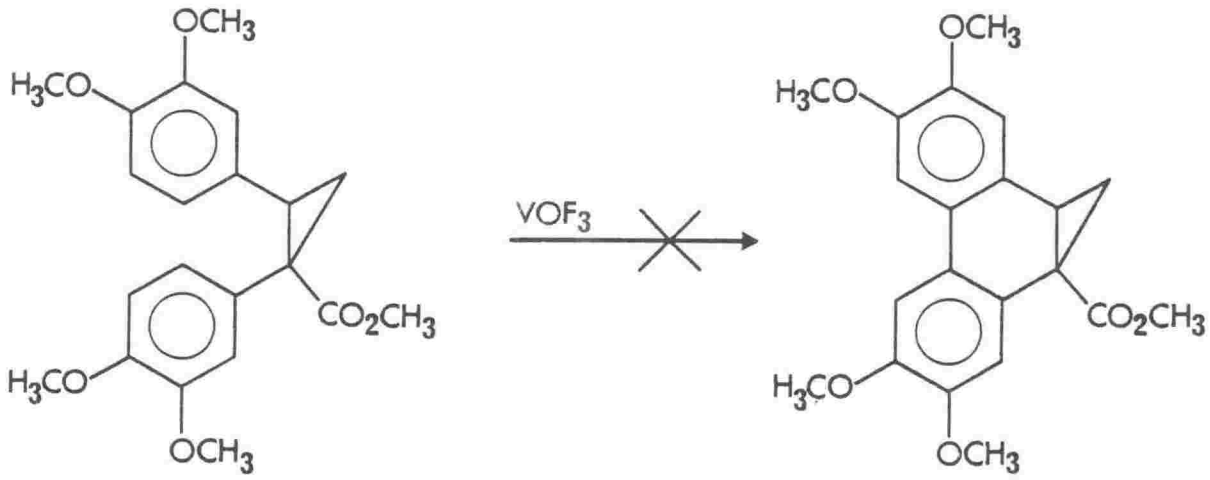
24 a; $R=R^1=H$
b; RR^1 = benzo-fusion

Disconnection at position (3) provides a 1,2-diarylcyclopropene. By analogy with the well-known oxidative photocyclisation of stilbenes,[37] photolysis of such a precursor might give 1*H*-cyclopropa[*l*]phenanthrene. The known examples of photolysis of 1,2-diarylcyclopropenes,[38] however, show that the dominant pathway is not the production of cycloproparenes, but either dimerisation or skeletal rearrangement.

Stilbenes may also be cyclised chemically, and the use of the oxidising agent vanadyl trifluoride has met with success in these laboratories[35,39] (for example, the conversion of stilbene (25) to phenanthrene (26)). Extension of this procedure to a diarylcyclopropane, for example compound (27), might give a dihydrocyclopropa[*l*]phenanthrene (28), whence a 1*H*-cyclopropa[*l*]phenanthrene might be obtained by elimination of the

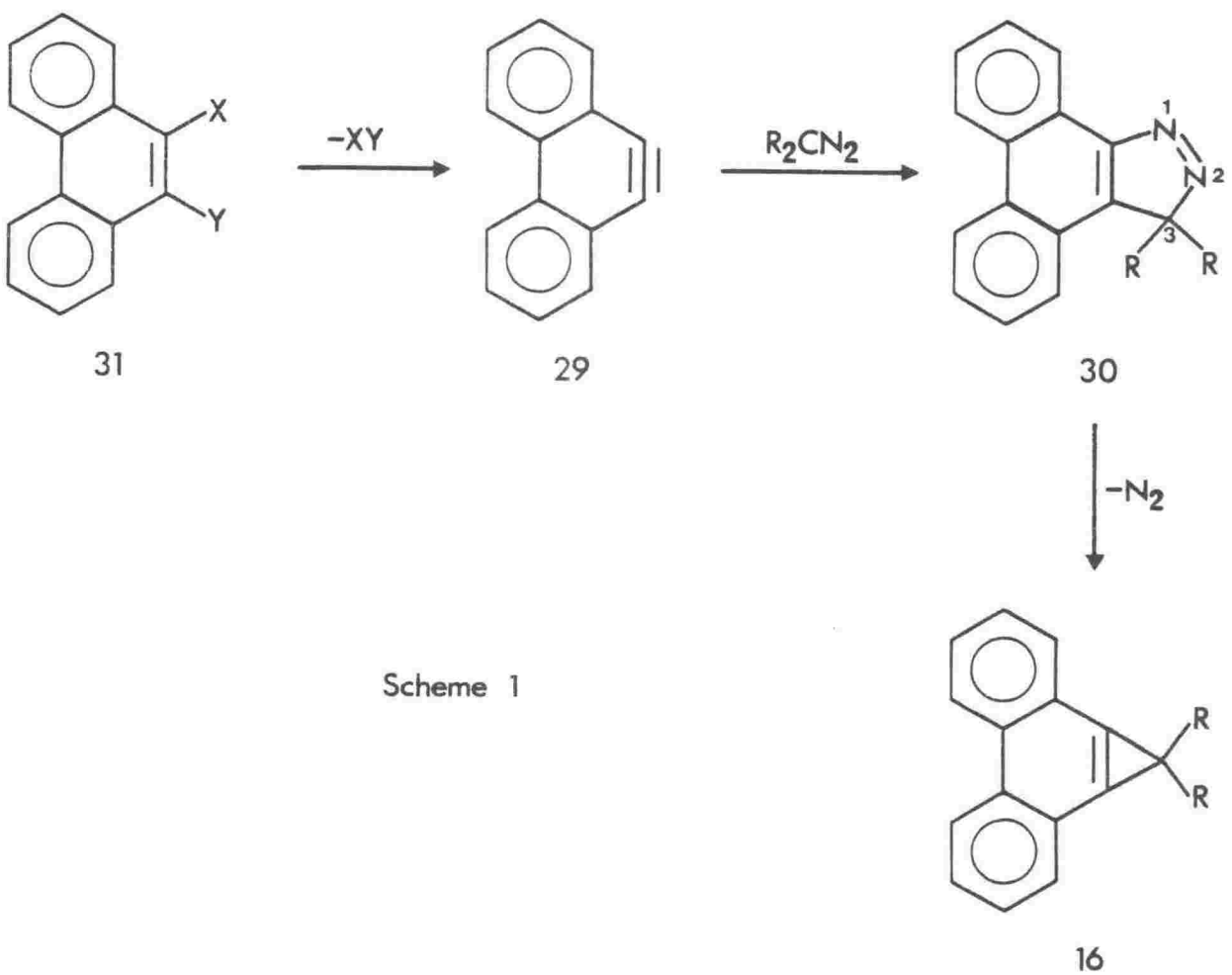


25 26



27 28

bridgehead substituents. The oxidative cyclisation of compound (27) was unsuccessful, however, with the small ring being cleaved instead.[35]

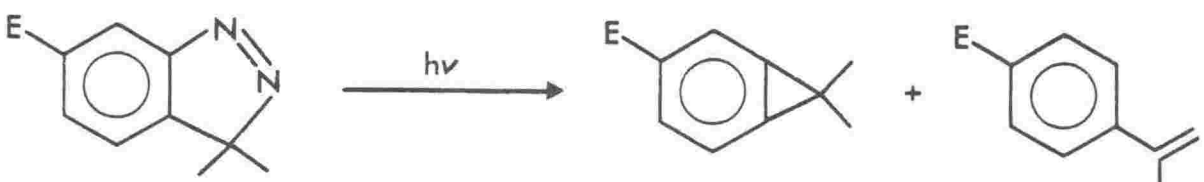


31 29 30 16

Scheme 1

In principle, 1*H*-cyclopropa[*l*]phenanthrenes might also be prepared by the addition of a carbene to 9,10-didehydrophenanthrene (29), although the generation of two short-lived intermediates and the necessary subsequent reaction of one with the other must be regarded as improbable. Scheme 1 shows an alternative based on the same concept: aryne (29) is intercepted by reaction with a diazoalkane, and expulsion of nitrogen from the resultant pyrazole (30) leads to a 1*H*-cyclopropa[*l*]-phenanthrene (16). Any diazoalkane used would ideally be stable to strong base, since the simplest ways of generating dehydrophenanthrene (29) involve the base-induced elimination of X and Y from substituted phenanthrenes (31).[40] In addition, the pyrazole (30) must not tautomerise, since nitrogen may be extruded only[41] from the 3*H*-tautomer shown. This constraint rules out the production of other than disubstituted 1*H*-cyclopropa[*l*]phenanthrenes, since all pyrazoles with a hydrogen substituent at C-3 exist solely as the 1*H*-tautomer.[42]

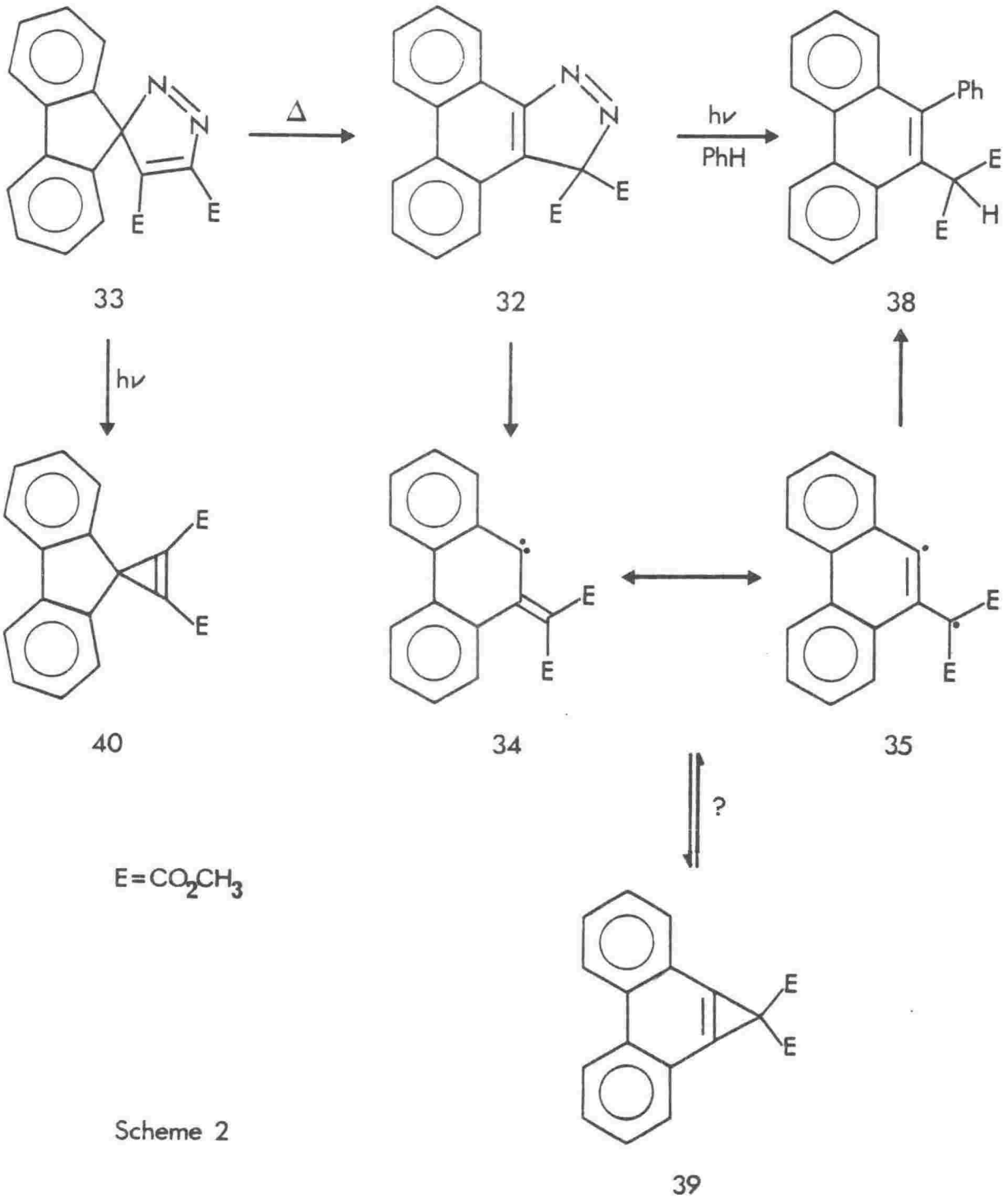
Although dehydrobenzene has been trapped with some heavily substituted diazo-compounds,[40a] dehydrophenanthrene (29) has not yet been intercepted in this way. In fact the literature contains but a single example[43] of the synthesis of a phenanthro[9,10-*c*]pyrazole, namely (32), which was produced in low yield from spiropyrazole (33) (Scheme 2). Photochemical extrusion of nitrogen from 3*H*-pyrazoles to give cyclopropenes is well-known[44] and is thought[41] to proceed *via* intermediates whose structures are hybrids of canonical forms analogous to (34) and (35) (Scheme 2). Indeed this reaction was the basis of the first synthesis of a cyclopropabenzene when, in 1964, Anet and Anet[30] found that the photolysis of indazole (36) provided carbomethoxycyclopropabenzene (37). This reaction has



36

E = CO_2CH_3

37

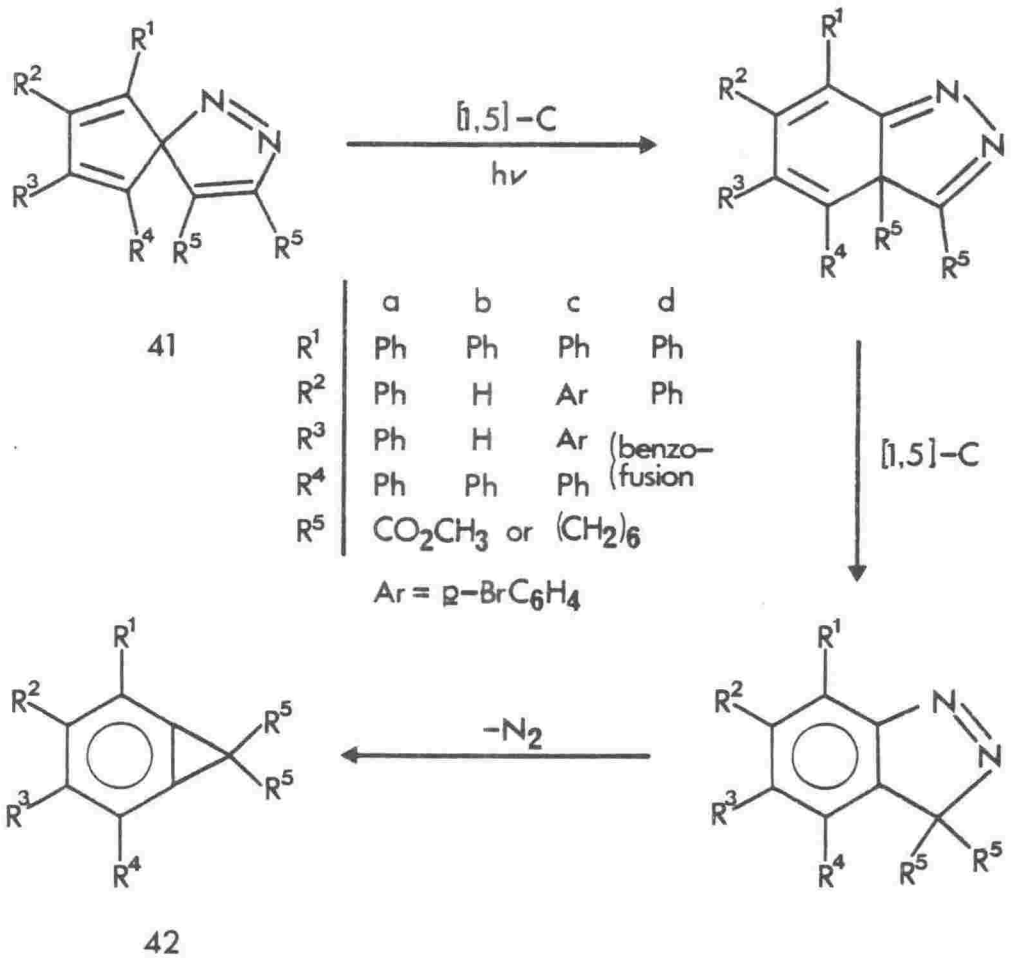


Scheme 2

been extended to the synthesis of other geminally disubstituted cyclopropabenzenes,[45] but when a benzene solution of phenanthropyrazole (32) was photolysed at room temperature, only substituted phenanthrene (38) was obtained,[43] in 18% yield (Scheme 2). It seems likely that this product resulted from the trapping by solvent of an intermediate represented by canonical

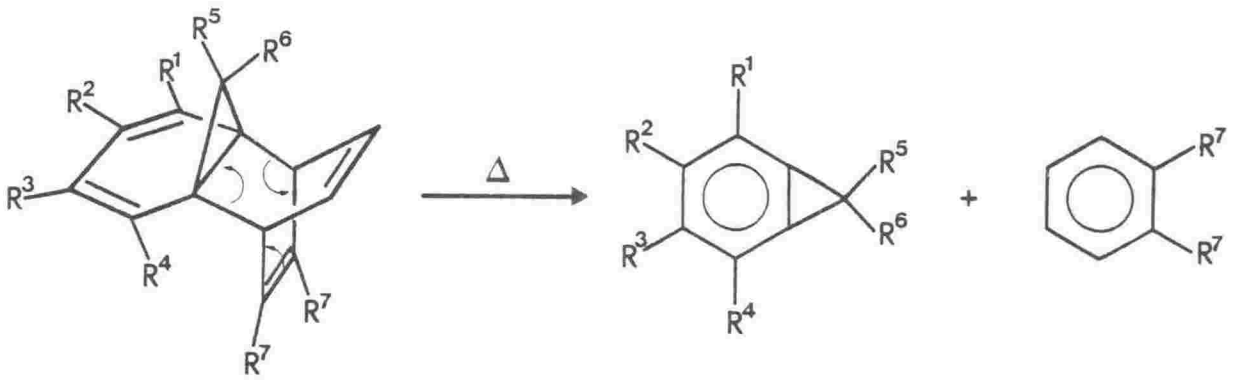
forms (34) and (35). Conceivably such a process could occur with cyclopropa[*l*]phenanthrene (39) as an intermediate, since other cycloproparenes are thought[1] to give biradicals, like (35), on thermolysis. It is possible that the photolysis of compound (32), under much milder conditions, could lead to 1*H*-cyclopropa[*l*]phenanthrene (39).

It is interesting also that the photolysis of spiropyrazole (33) leads[46] exclusively to cyclopropene (40) (Scheme 2), since other spiropyrazoles (41) are known[47] to deliver cycloproparenes (42), possibly by the pathway shown in Scheme 3. This pathway may fail to operate for spiropyrazole (33) because it is more rigid than the other spiropyrazoles (41), and so the initial [1,5]-C shift cannot occur so readily.



Scheme 3

1*H*-Cyclopropa[*l*]phenanthrene might also be prepared from compound (43a) by thermal $[_{\pi}2_s + _{\sigma}2_s + _{\sigma}2_s]$ cycloreversion (Scheme 4). Vogel and co-workers have prepared the analogous precur-



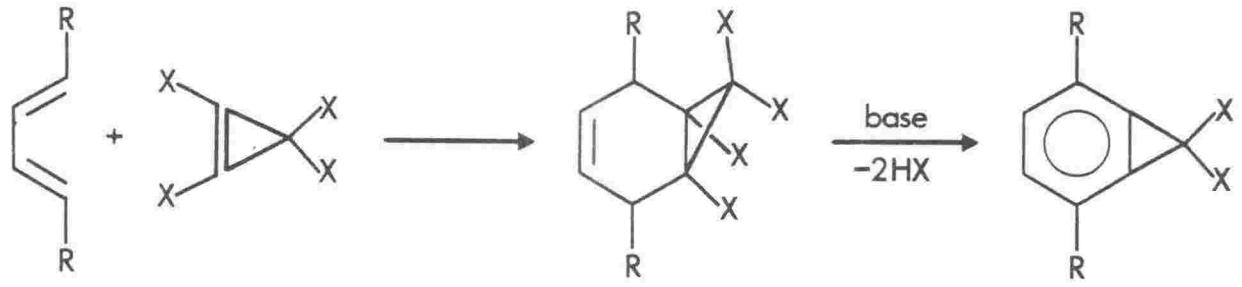
43

Scheme 4

	R^1	R^2	R^3	R^4	R^5	R^6	Ref.
a	benzo-fusion		benzo-fusion		H	H	
b	H	H	H	H	H	H	13a,48
c	H	H	H	H	F	H	33
d	H	H	H	H	F	F	49
e	benzo-fusion		H	H	H	H	24
	R^7=CN or CO_2CH_3						

sors (43b-e), and their notable successes with the Alder-Rickert cleavage have included the first synthesis[13a,48] of cyclopropabenzene (from compound (43b)) and the sole preparation[24] of cyclopropa[*a*]naphthalene (from compound (43e)). The recent synthesis[33] of compound (43a;R^7=CN) in Vogel's laboratories, and the results of its flash vacuum pyrolysis, are described in Chapter 4.

A cycloaddition-dehydrohalogenation route (Scheme 5) to cycloproparenes has also been developed,[49-53] whereby Diels-Alder addition of a variety of tetrahalocyclopropenes (44) to 1,3-dienes (45) gives a range of bicyclo[4.1.0]hept-3-enes (46). Subsequent bis-dehydrohalogenation is simple and leads to 1,1-dihalocycloproparenes (47) in good yields. This method has also been used in the syntheses of some cyclopropa[*b*]-naphthalenes[54,55] and -anthracenes.[56]

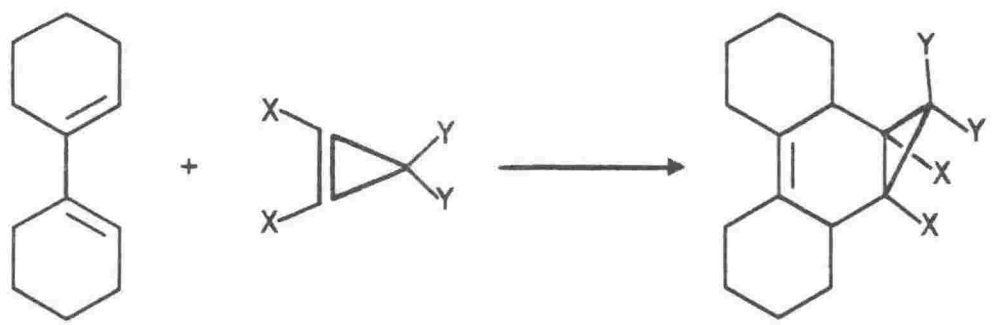


45 44 46 47

R=H or Ph
X= halogen

Scheme 5

Because of the method of ring construction, this latter route might provide access only to quite highly reduced 1*H*-cyclopropa[*l*]phenanthrenes. To this end, Halton and Officer[35,57] have construced the tetrahalotetracycles (48) by the addition of tetrahalocyclopropenes (49a-d) to 1,1'-bicyclohexenyl. They found, however, that the cycloadducts (48) were remarkably resistant to base-induced dehydrohalogenation, meaning that none of the octahydrocyclopropa[*l*]phenanthrenes (50) could be pre-



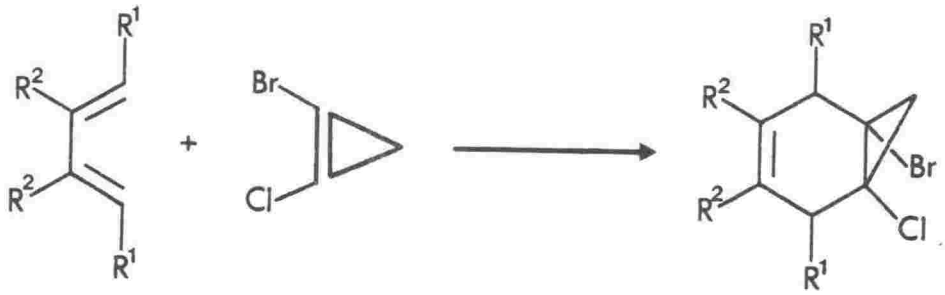
49 48

	X	Y
a	Cl	Cl
b	Cl	F
c	Br	Br
d	Br	F

50

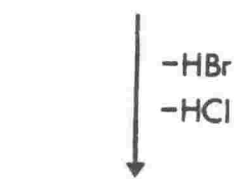
pared.

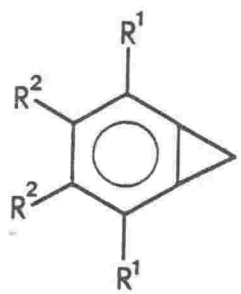
Billups *et al.*[21] were more successful when they used the recently synthesised[27] 1-bromo-1-chlorocyclopropene in cycloadditions with dienes (51a-c). Bis-dehydrohalogenation of the adducts (52) furnished cyclopropa*rene*s (53a-c) in acceptable yields. Billups' group has not yet reported attempts to oxidise octahydro-compound (53a) to 1*H*-cyclopropa[*l*]phenanthrene (16a) itself.



51 52

	R^1R^2
a	$(CH_2)_4$
b	$(CH_2)_3$
c	$(CH_2)_2$

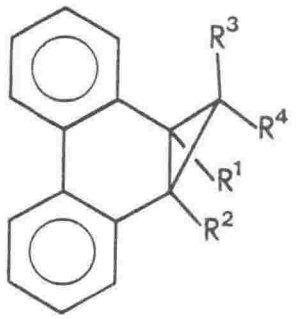




53

The final class of potential precursors of 1*H*-cyclopropa[*l*]-phenanthrenes to be discussed in this chapter is that of appropriately substituted dihydrocyclopropa[*l*]phenanthrenes (54), whence the desired cyclopropa*rene*s might be obtained by elimination reactions.

The parent compound (54a) has been prepared by addition of methylene to phenanthrene[58] and by reduction of dichloro-com-

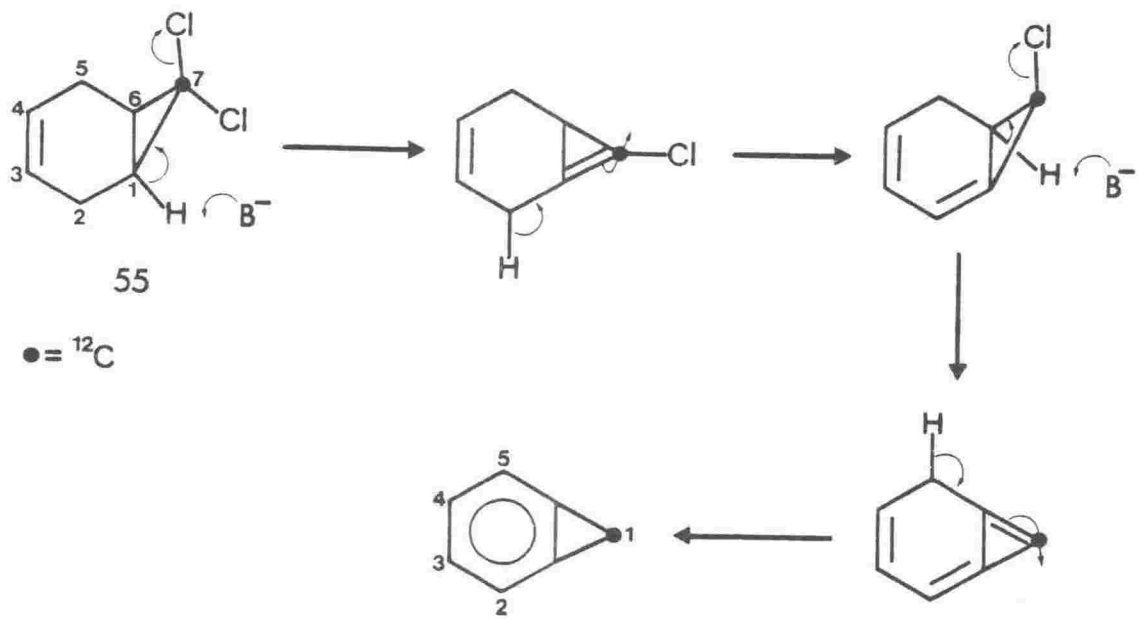


	R^1	R^2	R^3	R^4
a	H	H	H	H
b	H	H	Cl	Cl
c	H	H	Cl	H

54

pound (54b).[35] Direct aromatisation, by loss of the bridgehead hydrogen atoms, seems possible, but Officer[35] found that compound (54a) was resistant to treatment with either 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ)[59] or with butyllithium-tetramethylethylenediamine,[60] although both of these reagents have been used successfully to aromatise other dihydroaromatics.

Dihydro-compounds (54b) and (54c) were also recognised as possible precursors of 1*H*-cyclopropa[*l*]phenanthrenes, by analogy with a route to cycloproparenes developed by Billups *et al.*,[61] whereby cyclopropabenzene was prepared by bis-dehydrohalogenation of 7,7-dichlorobicyclo[4.1.0]hept-3-ene (55) (Scheme 6).



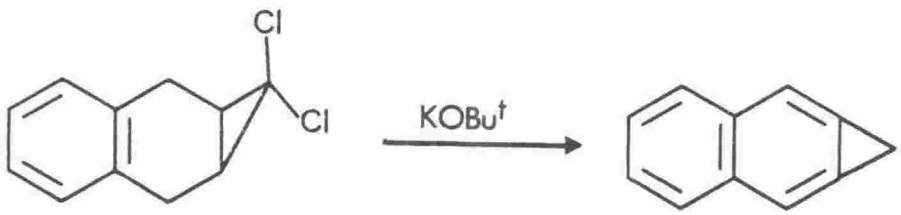
55

●= ^{12}C

Scheme 6

The proposed mechanism was supported by a labelling study,[62] which showed that C-7 of substrate (55) became C-1 of the product.

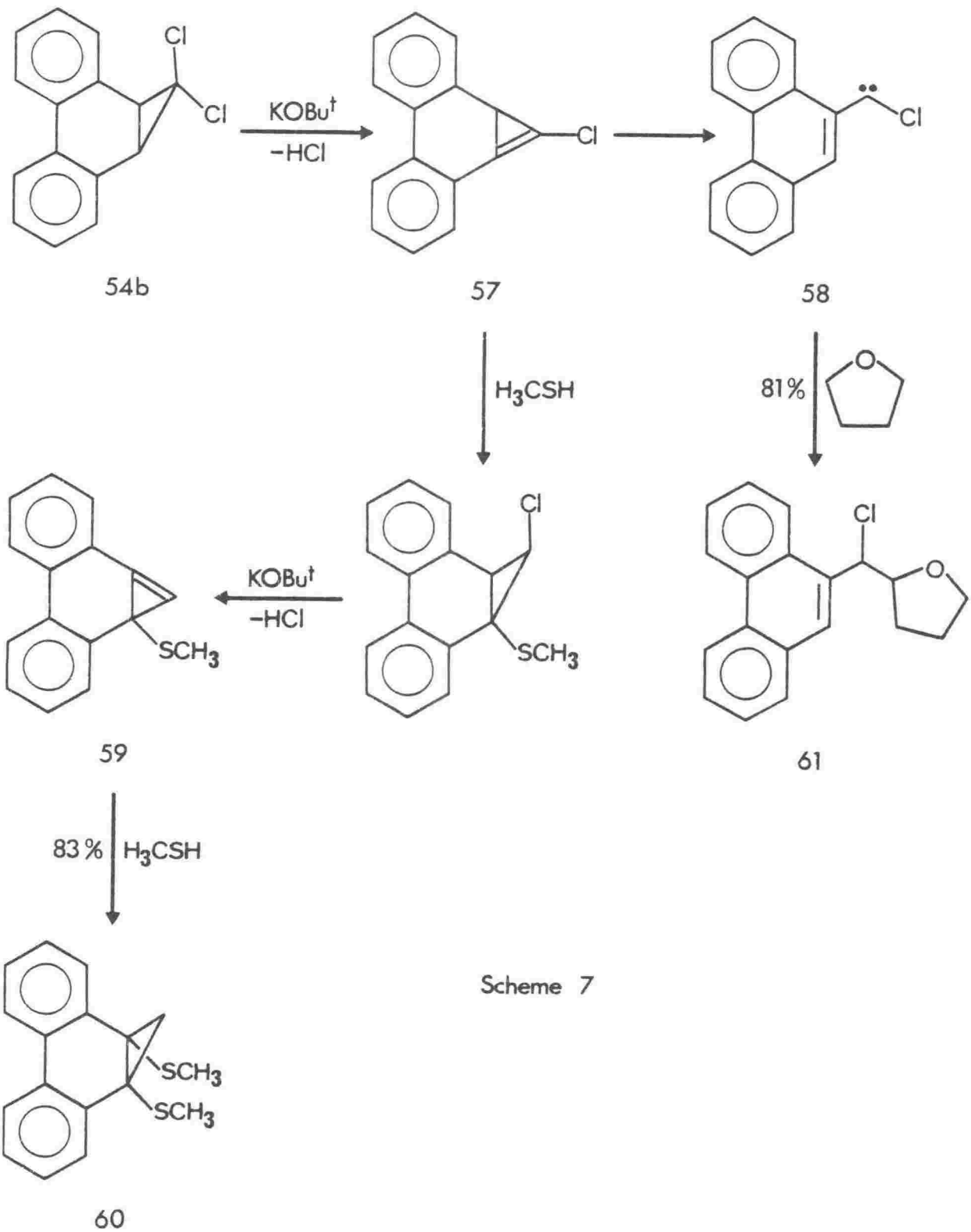
Many cyclopropa*rene*s have been prepared in this way,[15-17,23,63] including, for example, cyclopropa[*b*]naphthalene[23] (12) from precursor (56). The dehydrohalogenation of dichloro-compound



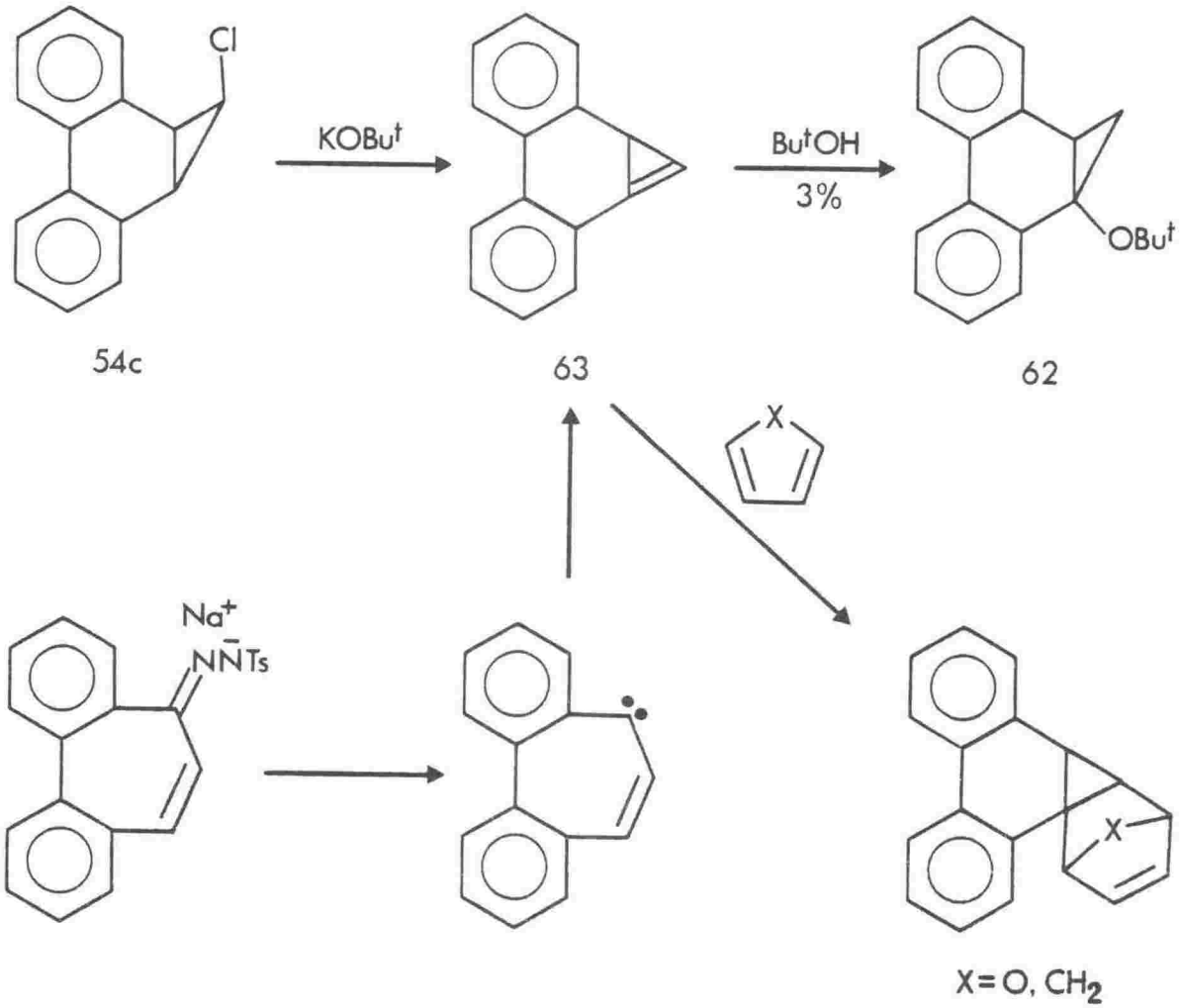
56 12

(54b) (prepared[64] by addition of dichlorocarbene to phenanthrene), however, leads[65] only to products derived from bicycloheptatriene (57) or aryl carbene (58) (Scheme 7). Thus, in the presence of methanethiol, compound (60) was isolated, resulting presumably from two dehydrochlorination-nucleophilic addition cycles, *via* bicycloheptatrienes (57) and (59). When the reaction was performed in the absence of added nucleophile, but in tetrahydrofuran as solvent, compound (61) was isolated in good yield. It seems likely that triene (57) was stabilised by opening to carbene (58), which was then intercepted by solvent to give compound (61). It is especially significant that bicycloheptatriene (57) was not observed to aromatise to a 1*H*-cyclopropa[*l*]phenanthrene in a manner analogous to the last step in Billups' synthesis[61] of cyclopropabenzene (Scheme 6).

Similar results were obtained when mono-chloro-compound (54c) (from the half-reduction[35,64-66] of compound (54b)) was treated with potassium t-butoxide. Billups' group claimed that compound (54c) was unreactive,[65] whilst Halton and Officer[66] obtained a low yield of t-butyl ether (62), resulting presumably from nucleophilic attack on bicycloheptatriene (63) by t-butoxide ion (Scheme 8). Again the presumed intermediate, bicyclo-


Cl
Cl
KOBu^t
–HCl
Cl
Cl
54b
57
58
H_3CSH
81%
O
Cl
O
KOBu^t
–HCl
SCH_3
SCH_3
59
61
83%
H_3CSH
SCH_3
SCH_3
60

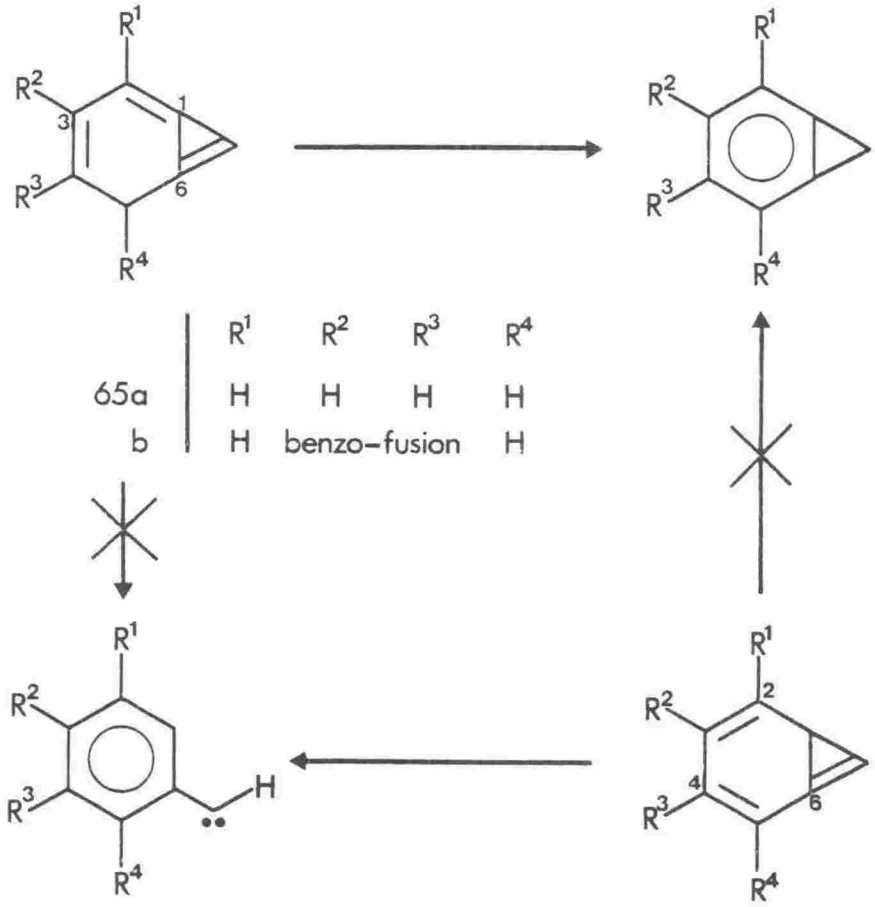
Scheme 7



Scheme 8

heptatriene (63), was not observed to aromatise. Coburn and Jones[67] generated the triene by a different route (Scheme 8) and established its formation by trapping it with furan and cyclopentadiene, but they too saw no sign of the isomerisation of compound (63) to 1*H*-cyclopropa[*l*]phenanthrene. Furthermore, the lower homologues of triene (63), namely compounds (64a) and (64b), have been produced[67,68] and none of these appeared to aromatise either. Thus, in the context of the Billups reaction (Scheme 6), it would appear that bicyclo-[4.1.0]hepta-1,3,6-trienes (65) aromatise, while the 2,4,6-isomers (63,64) do not, and lead instead to carbene-derived products (Scheme 9). No exceptions to this apparent dichotomy have yet been found.

From the foregoing discussion, it is evident that an approach

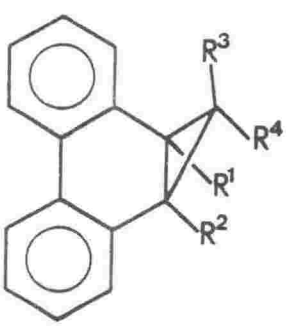


	R^1	R^2	R^3	R^4
65a	H	H	H	H
b	H	benzo-fusion		H

	R^1	R^2	R^3	R^4
63	benzo-fusion		benzo-fusion	
64a	H	H	H	H
64b	benzo-fusion		H	H

Scheme 9

to 1*H*-cyclopropa[*l*]phenanthrene which relies on the aromatisation of 2,4,6-triene (63) has little chance of success. Consequently, the functions to be eliminated from a dihydrocyclopropa[*l*]phenanthrene (54) should lie not at the apex of the small ring, but at the bridgehead. In this way, elimination



54

of R^1R^2 from compound (54) would lead directly to the desired cyclopropaarene. The work to be described herein is concerned with the syntheses and subsequent transformations of some bridgehead-substituted dihydrocyclopropa[*l*]phenanthrenes (54).

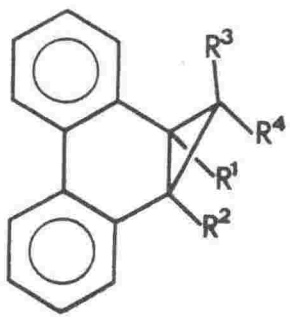
CHAPTER TWO

1,1-DIHALO-1*H*-CYCLOPROPA[*l*]PHENANTHRENES

A simple way of constructing bridgehead-substituted dihydrocyclopropa[*l*]phenanthrenes would involve the addition of carbenes to 9,10-substituted phenanthrenes. Indeed, dihydrocompounds (54a,b,d-h) have previously been prepared in this way[58,64,65,69] (Table 4). The applicability of this method is

Table 4

Dihydrocyclopropa[*l*]phenanthrenes Prepared by the Addition of Carbenes to 9,10-Substituted Phenanthrenes

Compound		R^1	R^2	R^3, R^4	Yield	Ref.
	54a	H	H	H	5%	58
	b	H	H	Cl	65	64
	d	H	H	H,COOEt[a]	-	69a
	e	H	H	Br	-	69b
	f	H	H	H,Ph[b]	0.2	69c
	g	OCH_3	H	Cl	52	69d
	h	CH_3	H	Cl	62	65

54

a Both stereoisomers were obtained.

b The stereochemistry was not specified.

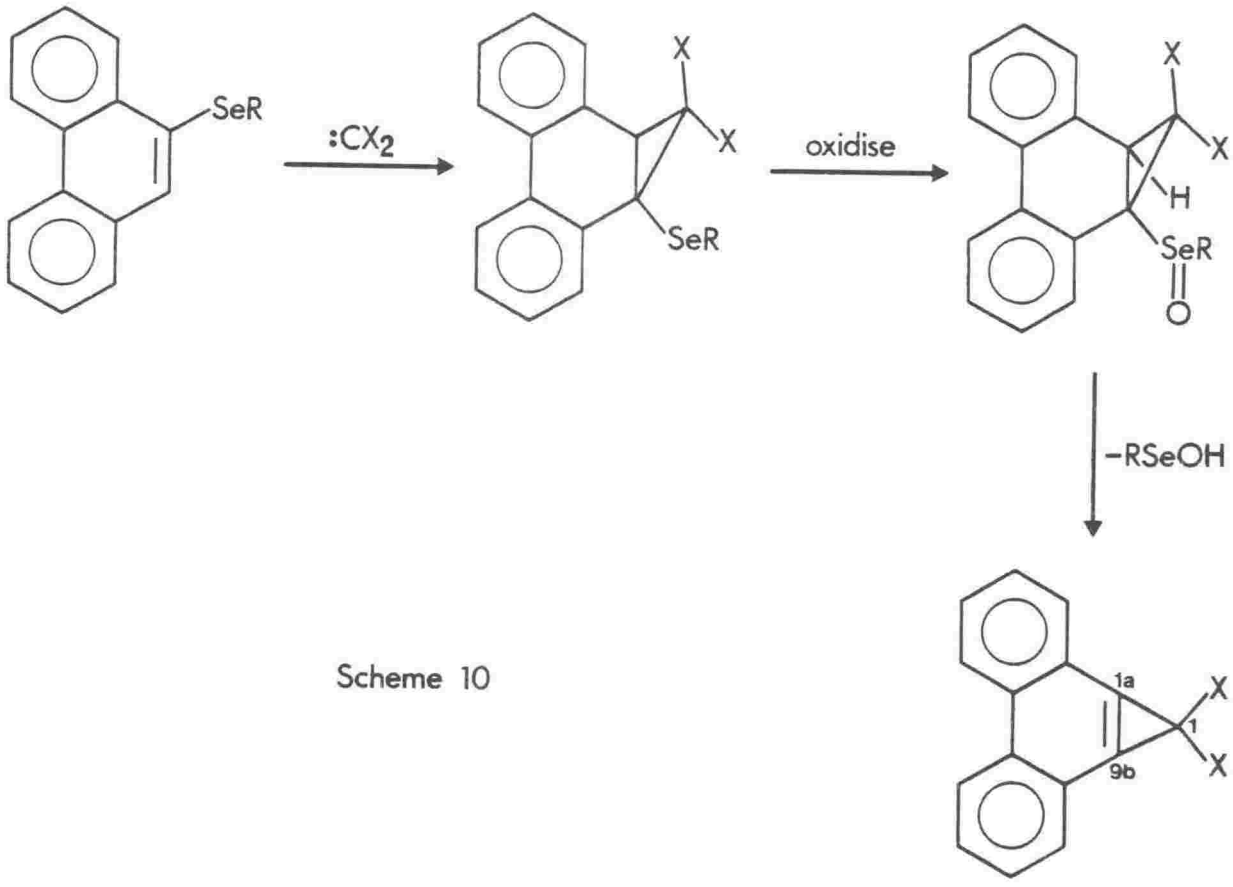
limited by the availability of 9,10-substituted phenanthrenes and by the ease of addition of carbenes thereto. A number of mono-substituted phenanthrenes is readily available, but the range of 9,10-disubstituted phenanthrenes is very restricted: even 9,10-dibromophenanthrene, which might be used directly or transformed into other useful starting materials, is difficult

to make.[70] Many of the more accessible carbenes are electrophilic, so they add most readily to electron-rich double bonds. The 9-10 positions of phenanthrenes are not inherently rich in electrons regardless of substituents, and it is likely that the provision of one or two electron-withdrawing groups would make the addition of electrophilic carbenes almost impossible. An inspection of the bridgehead substituents of the known adducts (54) reveals the absence of what is regarded to be electron-withdrawing functionality. In addition, the most facile and high-yielding reactions have involved the use of dichlorocarbene.

There is a dilemma involved in the construction of viable 1*H*-cyclopropa[*l*]phenanthrene precursors of type (54), then, in that R^1 and R^2 should be electron-donating to facilitate the addition of carbenes, yet one of them should be nucleofugic to enable the subsequent elimination of R^1R^2. Another problem is that R^1R^3, for example, might be eliminated instead, leading to an unwanted 1a*H*-cyclopropa[*l*]phenanthrene. Furthermore, the mode of ring construction requires the substituents at the bridgehead of compound (54) to be *syn*-disposed, and any elimination strategy must take this into account.

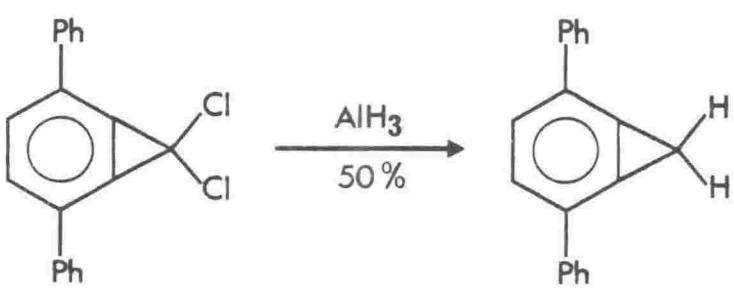
With these limitations in mind, it was decided to investigate the addition of dihalocarbenes to some 9-phenanthrenyl selenides. In this way, mesomeric donation from selenium might provide sufficient electron density at the 9-10 bond to permit the addition of a dihalocarbene (Scheme 10). Oxidation at the heteroatomic site and *syn*-selenoxide elimination[71] might then lead directly to a 1,1-dihalo-1*H*-cyclopropa[*l*]phenanthrene. Selenoxide fragmentations are known to occur, possibly in a concerted fashion, at or below room temperature and would thus appear to be a method of choice for the synthesis of thermally labile molecules such as cycloproparenes.

The presence of two halogen substituents at C-1 of the carbene adduct depicted in Scheme 10 means that the elimination of RSeOH might proceed in one direction only, thus avoiding formation of the alternative 1a*H*-cyclopropa[*l*]phenanthrene. The desired 1,1-dihalo-1*H*-cyclopropa[*l*]phenanthrene could even be converted



Scheme 10

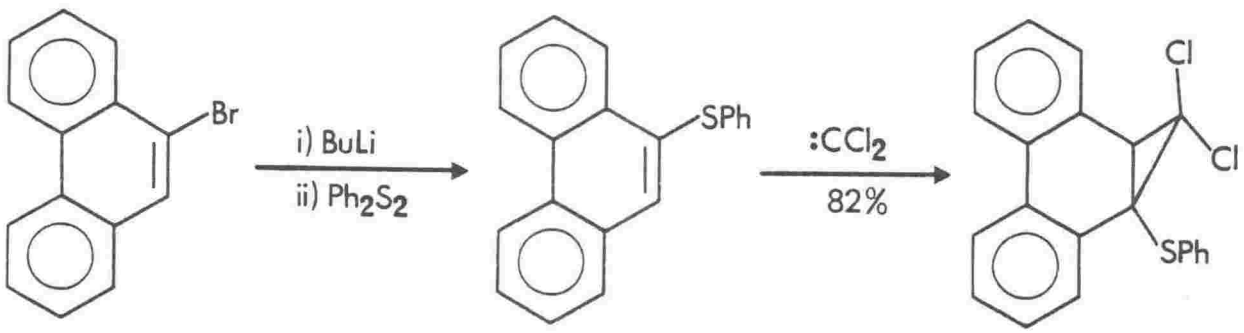
to the parent hydrocarbon, by analogy with the known[50] transformation of, for example, compound (66) into compound (67).



66 67

Because selenium compounds are highly toxic and since the specific transformations depicted in Scheme 10 were unprecedented, the viability of carbene addition to phenanthrenyl chalcogenides was tested by the reaction of dichlorocarbene with a readily accessible sulfur compound. Although 9-phenylthiophenanthrene (68) has been synthesised previously[72] by oxida-

tive photocyclisation of the appropriate stilbene, it was prepared by us according to Scheme 11. Halogen-lithium exchange on 9-bromophenanthrene, followed by quenching with diphenyl disulfide, was sufficient to provide compound (68) in 85% yield.

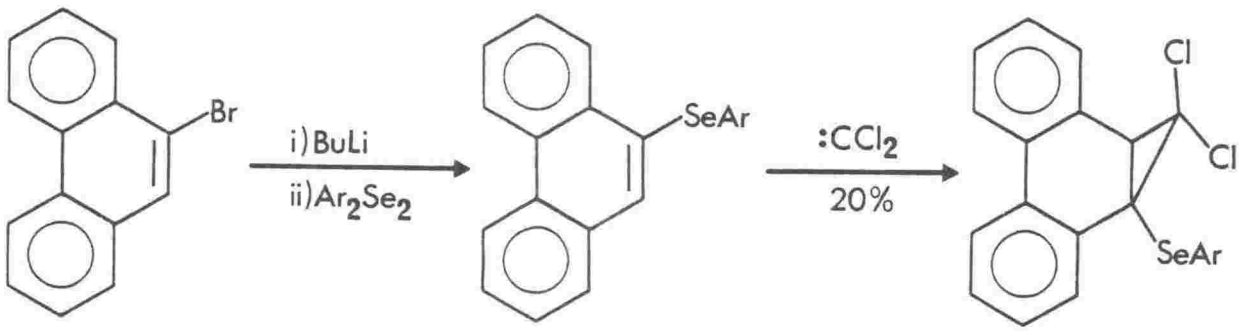


68 85% 69

Scheme 11

The expected low reactivity of the 9-10 bond in compound (68) led to the need for a method which would provide cheaply a large excess of dichlorocarbene. The phase-transfer method was the obvious choice and, indeed, the reaction of sulfide (68) with chloroform-sodium hydroxide, in the presence of benzyltriethylammonium chloride gave, in 82% yield, a crystalline compound identified as 1,1-dichloro-1a-phenylthio-1a,9b-dihydrocyclopropa[*l*]phenanthrene (69). Nmr and mass spectra, together with elemental analysis, established the structure unambiguously.

The ready synthesis of the model sulfur compound encouraged us to attempt to prepare some organoselenium analogues. Since it is known[71] that selenoxide eliminations proceed most readily when the selenoxide carries an electron-withdrawing substituent, and because it would be desirable to prepare the dihalocyclopropa[*l*]phenanthrene under the mildest conditions possible, the synthesis of selenide (70) was attempted (Scheme 12). 9-Phenanthrenyllithium was reacted with the electrophilic selenium reagent 4,4'-dichlorodiphenyl diselenide to provide the hitherto unknown 9-(4'-chlorophenylseleno)phenanthrene (71). In contrast to the ease of this first step, the addition of dichloro-



71 59%

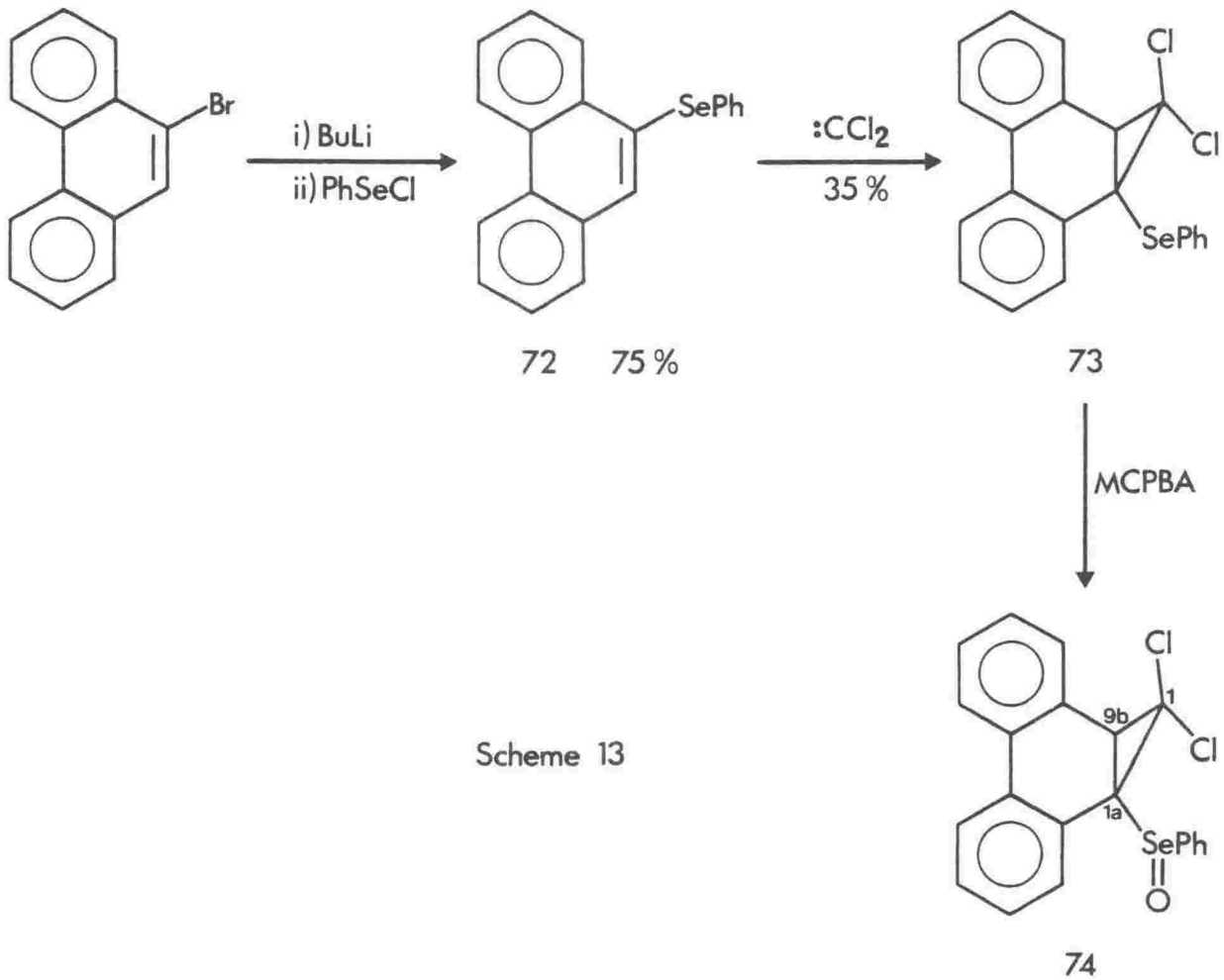
70

Ar = p-ClC_6H_4

Scheme 12

carbene (generated under phase-transfer conditions) was very slow, possibly because electron withdrawal by the arylseleno group rendered the 9-10 bond of compound (71) less reactive than was hoped for. After several days of reaction, however, the desired adduct (70) was isolated, albeit in 20% yield.

Because of the length of time required for the carbene addition, the difficulty of isolation of the product, and the low yield, compound (70) was not considered to be a viable precursor of 1,1-dichloro-1*H*-cyclopropa[*l*]phenanthrene. Accordingly, attention was given to the synthesis of an analogue of compound (70) which contained the less electron-withdrawing phenylseleno group (Scheme 13). The requisite precursor, 9-phenylseleno-phenanthrene (72), is already known[73], having been obtained through a photostimulated reaction of phenylselenide anion with 9-bromophenanthrene. For ease of preparation, however, 9-phenanthrenyllithium was reacted with phenylselenenyl chloride to provide compound (72) in 75% yield. The reaction of selenide (72) in chloroform-sodium hydroxide under phase-transfer catalysis was again slow, but a regime of reaction conditions and work-up procedure was ultimately found which enabled the dichlorocarbene adduct (73) to be isolated in gram quantities (Experimental). Selenide (73) is a moderately stable crystalline compound which yellows slightly upon prolonged storage at ambient temperature. The mass spectra of selenides (70) and (73) display envelopes of molecular ions which are consistent with the presence of one selenium atom and three or two chlorine atoms respectively. Their elemental analyses gave the approp-



Scheme 13

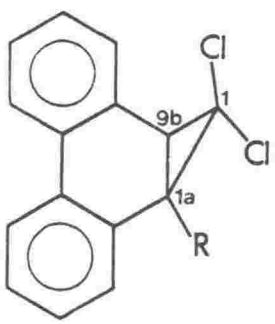
riate results. Important nmr data for selenides (70) and (73), and for sulfide (69), are collected in Table 5. The observed chemical shifts are typical for protons[74] and carbon atoms[75] in benzylic and cyclopropyl environments.

There have been very few instances of successful carbene additions to any vinyl selenides[76] and, to our knowledge, the syntheses of dihydro-compound (70) from substituted phenanthrene (71) and of compound (73) from compound (72) are the first examples of carbene additions to phenanthrenyl selenides.

Selenide (73) was oxidised by use of *m*-chloroperbenzoic acid (MCPBA) to selenoxide (74), an unstable compound characterised only by its proton nmr spectrum, in which the singlet due to H-9b was at δ 4.21, 0.72 ppm downfield from its counterpart in compound (73). The selenoxide was allowed to decompose in dichloromethane-pyridine, since other studies[71] have shown that

Table 5

Selected Nmr Chemical Shifts[a] for Dihydrocyclopropa[*l*]-phenanthrenes (69), (70) and (73)

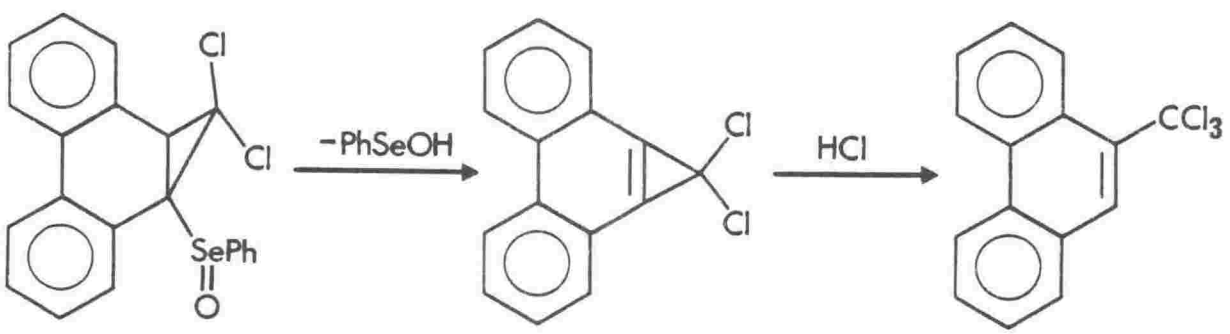
Compound	R	H-9b	C-1	C-1a	C-9b
					
69	SPh	3.45	64.6	43.6	46.0
70	SeAr[b]	3.50	64.3	40.6	46.4
73	SePh	3.49	64.6	40.4	46.2

a Chemical shifts are in ppm downfield from tetramethylsilane.
b Ar=*p*-ClC_6H_4.

amine bases can prevent the re-additon of the initially formed 'PhSeOH' to reactive double bonds. During the reaction, which took about two days at 20°, much decomposition was evident by thin-layer chromatography (tlc). At least five discrete products were observed, but the material balance on work-up was poor (Experimental). One of the two most chromatographically mobile products was diphenyl diselenide, produced by the disproportionation[71] of 'PhSeOH'. The other, which in our hands could not be separated from diphenyl diselenide, was observed to decompose on tlc and to contain only aromatic protons (from the nmr spectrum). In order to isolate this latter compound pure, it was decided to prevent the formation of diphenyl diselenide by performing the selenoxide elimination in the presence of an excess of oxidant. In this way, the 'PhSeOH' formed is known[71] to be rapidly and quantitatively converted to phenylseleninic acid, $PhSeO_2H$. Accordingly, from reaction mixtures which contained an excess of t-butyl hydroperoxide,[71]

the most mobile product was isolated by chromatography on neutral alumina. As far as can be seen from the proton nmr spectrum, this compound is identical to that previously obtained in admixture with diphenyl diselenide. Among the aromatic multiplets is a singlet, δ 8.57, which would be expected for H-10 of a 9-substituted phenanthrene. The high-resolution mass spectrum shows molecular ions at m/z 294, 296 and 298, in a ratio consistent with the presence of three chlorine atoms. This information enabled the compound to be identified as 9-trichloromethylphenanthrene (75) (2-15% by nmr).

Compound (75) could have been formed by the reaction of the desired 1,1-dichloro-1*H*-cyclopropa[*l*]phenanthrene (76) with hydrogen chloride[1a] (Scheme 14). The elements of hydrogen

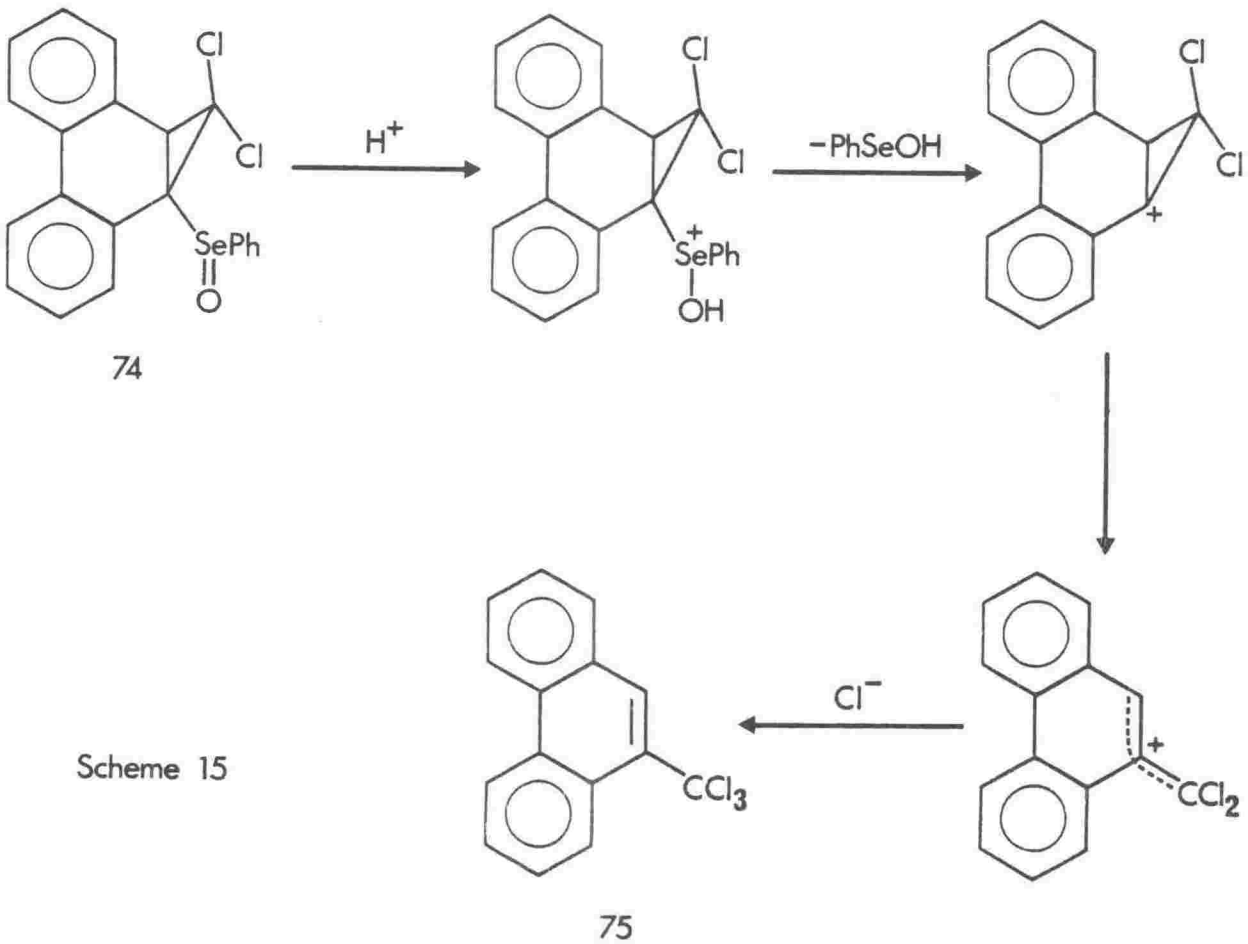


74 76 75

Scheme 14

chloride may have been derived from decomposition of the dichloromethane solvent, or the chloride ion might instead have arisen from the ionisation of another molecule of cycloproparene (76), and the proton may have been sourced from the acidic selenium-containing by-products.

As the result of a report[77] that alkyl aryl selenoxides can yield alkyl halides upon reaction with hydrogen halides, a mechanism for the formation of trichloride (75) was proposed which does not require the intermediacy of the sought-after cycloproparene (Scheme 15). Thus, protonation of selenoxide (74), loss of PhSeOH, formal cyclopropyl-allyl rearrangement



74

Scheme 15

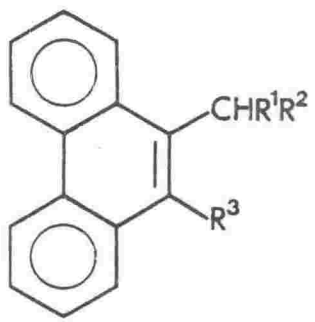
75

and interception by chloride ion accounts for the observed product. In order to establish if compound (75) might, in practice, be obtained by such a pathway (which does not involve *syn*-selenoxide elimination), a solution of selenoxide (74) was prepared and kept at -20°, at which temperature it was observed to be stable for some hours. Hydrogen chloride was bubbled slowly through the solution and after five minutes, work-up revealed the complete conversion of compound (74) to compound (75). This result shows that although trichloride (75) might have arisen through the intermediacy of cyclopropparene (76) according to Scheme 14, it could also have been formed by the direct reaction of selenoxide (74) with hydrogen chloride, perhaps as shown in Scheme 15.

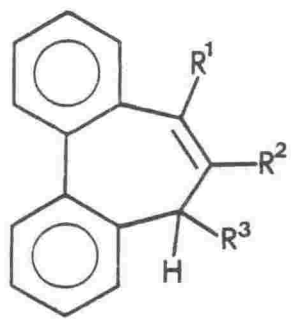
Three other discrete products were observed on tlc when selenoxide (74) was allowed to decompose in the presence of t-butyl hydroperoxide. All were isolated nearly pure through a com-

bination of column and layer chromatography.

Product A (Experimental) was obtained as an unstable gum. The proton nmr spectrum contains a nine-proton singlet at δ 1.09, which is consistent with the incorporation of a t-butyl group,[74] and a one-proton singlet at δ 5.99. The aromatic region consists of multiplets only. The carbon-13 spectrum, which was poorly resolved because of the small sample size (10 mg), exhibits signals at δ 26.4 (t-butyl methyl carbons[75]) and 80.5. The latter resonance is too intense to be due to the quaternary t-butyl carbon. The aromatic region shows only eight C-H resonances, all of similar intensity. This evidence suggests the compound to be either a disubstituted phenanthrene (77) or a 5*H*-dibenzo[*a*,*c*]cycloheptene (78). The mass spectrum has low-



77

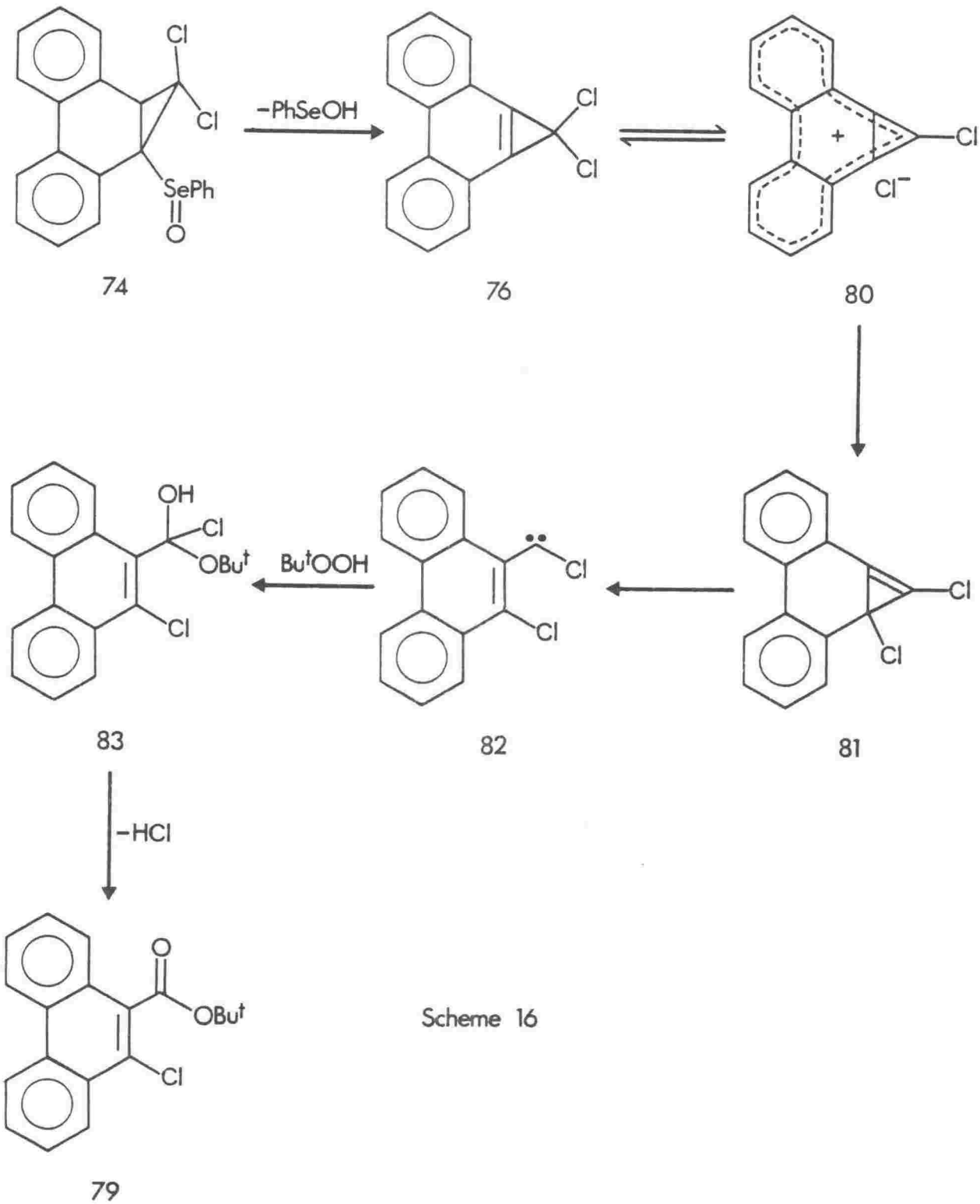


78

intensity peaks at m/z 348, 350 and 352 in a ratio of 100:62:12, which is consistent with the presence of two chlorine atoms. The most intense set of peaks is at m/z 259, 261 and 263, again in the ratio expected for two chlorine atoms. The [M-89] peak is a characteristic mass spectral fragment[78] of molecules which contain the t-butyldioxy group, $-OOBu^t$. Accordingly, although it remains unidentified, the compound is proposed to have the molecular formula $C_{19}H_{18}Cl_2O_2$ and a structure represented by either phenanthrene (77) or 5*H*-dibenzo[*a*,*c*]cycloheptene (78), where one of R^1-R^3 is the t-butyldioxy group and the other two are chlorine atoms. A yield of 1.3% was calculated from the molecular formula. The product could not be characterised further because of its instability and the small

quantity obtained.

Product B incorporates a t-butyl group with a deshielding substituent,[74,75] as evidenced by a nine-proton singlet at δ 1.73 in the proton nmr spectrum and signals at δ 28.3 and 83.4 in the carbon-13 spectrum. The remainder of the proton spectrum displays only aromatic multiplets; a singlet which might be expected for H-10 of a 9-substituted phenanthrene is absent. The aromatic region of the carbon-13 spectrum contains six C-H peaks of nearly equal height and a seventh at twice the height of the others: this was taken to be good evidence of the presence of eight unsubstituted aromatic carbon atoms. The occurrence of a small signal at δ 166.4 is consistent with the proposition that the compound is a carboxylic acid derivative.[75] The lack of other resonances on either side of the aromatic regions of the proton and carbon-13 spectra suggests that the compound is not a 5*H*-dibenzo[*a*,*c*]cycloheptene, but a 9,10-disubstituted phenanthrene. The infrared spectrum shows a carbonyl stretch at 1710 cm^{-1}. The highest-mass peaks in the mass spectrum are a pair at m/z 312 and 314 in an intensity ratio of 3:1 : this indicates the presence of only one chlorine atom. The occurrence of pairs of peaks (in 3:1 ratios) at m/z 256, 258 and 239, 241 is strongly reminiscent of the fragmentation pattern expected[79] for a t-butyl ester, with [M-56] being due to the loss of C_4H_8 (isobutene) and [M-73] being due to the loss of OBu^t. The combined spectral data, together with high-resolution mass spectral analysis, allowed the compound to be identified as t-butyl 10-chlorophenanthrene-9-carboxylate (79) (7% yield). A credible mechanism for its formation is shown in Scheme 16. *syn*-Selenoxide elimination of PhSeOH from selenoxide (74) delivers the desired 1,1-dichloro-1*H*-cyclopropa[*l*]-phenanthrene (76), which is stabilised by the equilibrium loss of chloride ion to give the charge-delocalised cation (80). There is ample precedent[1a,c] for such ionisations of 1,1-dihalocyclopropareneS. Recapture of chloride ion at the bridgehead leads to the 1a*H*-cyclopropa[*l*]phenanthrene (81). Such compounds are known[65-8] to collapse irreversibly to aryl carbenes; as a result, intermediate (82) is formed, which may be intercepted by t-butyl hydroperoxide to give compound (83). This



74 76 80

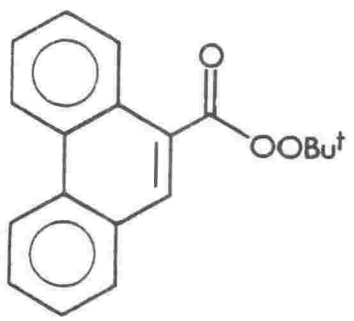
83 82 81

79

Scheme 16

latter compound loses hydrogen chloride to afford the observed t-butyl ester (79). It is hard to postulate an alternative mechanism which does not involve a 1,2-migration of chloride ion, and it is also difficult to by-pass the sought-after cyclopropparene (as was done for trichloro-compound (75)).

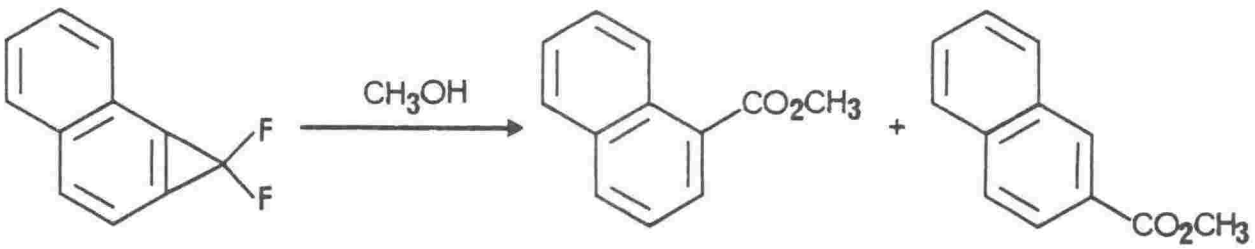
Product C was isolated as an unstable gum. The proton nmr spectrum contains a nine-proton singlet at δ 1.48 and the only other resonances are in the aromatic region, within which is a one-proton singlet at δ 8.19. This information suggested that the compound was a 9-substituted phenanthrene, and that the substituent contained a t-butyl group (again from t-butyl hydroperoxide). The carbon-13 spectrum supports these suggestions, with signals at δ 26.4 and 84.0 being consistent with the presence of a t-butyl ether or ester function.[75] The aromatic region displays nine distinct C-H resonances, as expected for a mono-substituted phenanthrene. In addition, there is a low-intensity signal in the carbonyl region at δ 165.7. The infrared spectrum shows a carbonyl vibration at 1755 cm^{-1}, and it is this information which has led to the compound being confidently proposed to be t-butyl phenanthrene-9-carboperoxoate (84) (1.7% yield). The position of the carbonyl stretch agrees



84

with that observed for other per-esters and especially with that for t-butyl benzenecarboperoxoate,[80] at 1758 cm^{-1}. Further evidence for the assignment of structure (84) to product C was provided by the mass spectrum. A low-intensity molecular ion observed at m/z 294 is consistent with the proposed structure, as is the presence of fragment ions at m/z 222 and 205, which are attributed to the loss of C_4H_8O and $C_4H_9O_2$ respectively from the parent compound.[78] The instability of this compound, coupled with the small quantity produced (11 mg), precluded the acquisition of combustion or high-resolution mass data.

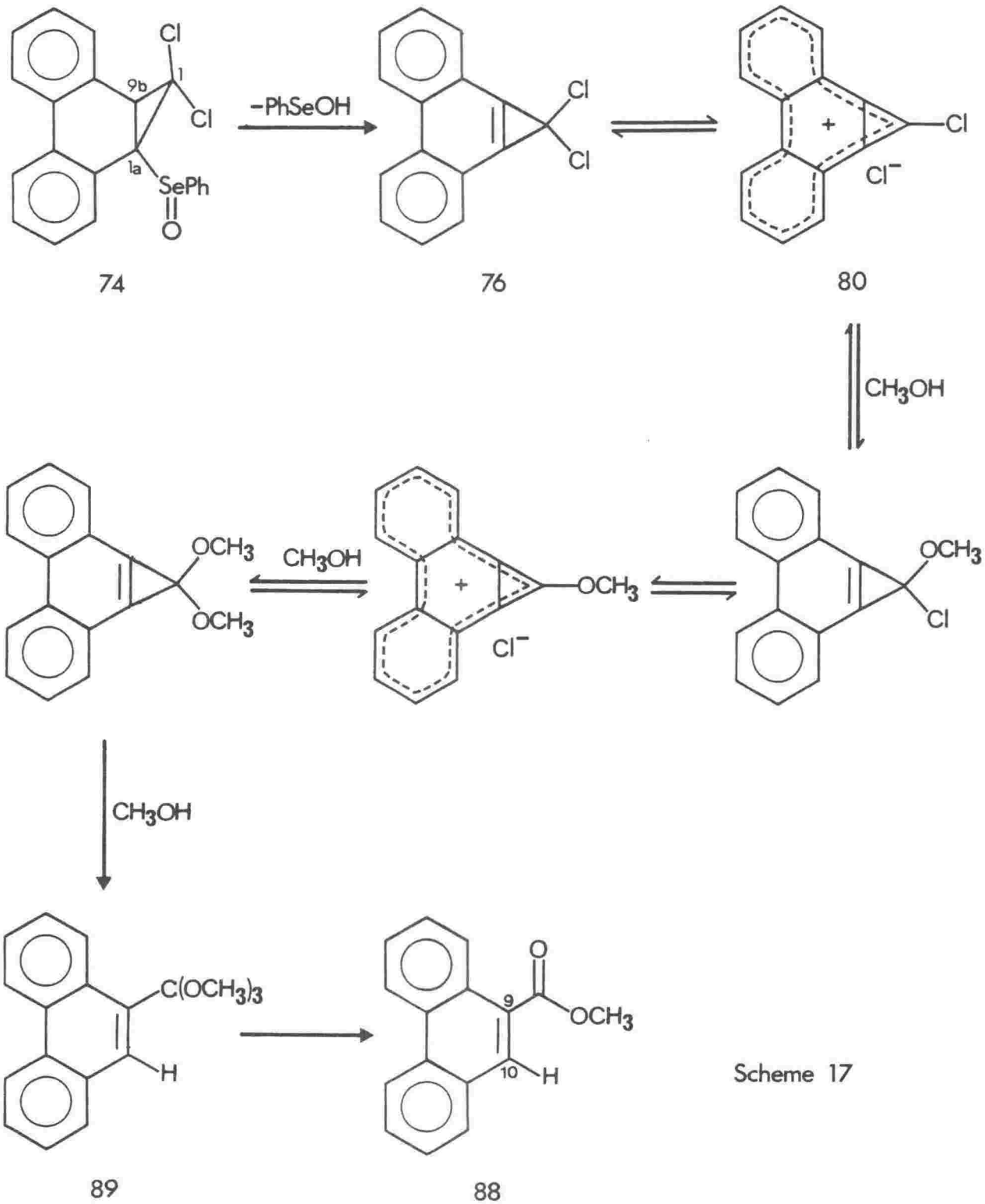
A pathway for the formation of per-ester (84) was suggested by the fact that 1,1-dihalocycloproparenes are known[52,54,81] to give esters upon reaction with alcohols. For example, Müller and Nguyen-Thi[81] were able to characterise the unstable 1,1-difluorocyclopropa[*a*]naphthalene (85) by its reaction with methanol to produce methyl esters (86) and (87). A similar



85 86 87

reaction of 1,1-dichloro-1*H*-cyclopropa[*l*]phenanthrene with t-butyl hydroperoxide to give per-ester (84) might be envisaged. It is dangerous, however, to speculate that the desired cyclopropa-rene (76) had been formed, by elimination of PhSeOH from selenoxide (74), solely on the basis of the isolation of an unstable and incompletely characterised compound (84) in a yield of 1.7%. Therefore, a sample of selenoxide (74) was allowed to decompose in pyridine-buffered methanol, in the hope that a stable methyl ester might be isolated in good yield. Methyl phenanthrene-9-carboxylate (88) was indeed obtained, in 65% yield, and it was identical to an authentic sample. A possible mechanism for its formation, which requires 1,1-dichloro-1*H*-cyclopropa[*l*]phenanthrene (76) as an intermediate and follows precisely the route proposed[52,54] for the alcoholysis of other dihalocycloproparenes, is shown in Scheme 17. Thus, *syn*-selenoxide elimination from compound (74) leads to the dichlorocyclopropa-rene (76), which is stabilised by loss of chloride ion to yield cation (80). Sequential capture and solvolysis by methanol affords methyl ester (88) by way of the orthoester (89).

Protic solvents such as methanol are thought[82] to promote the heterolysis of carbon-selenium bonds, and this led to the pro-

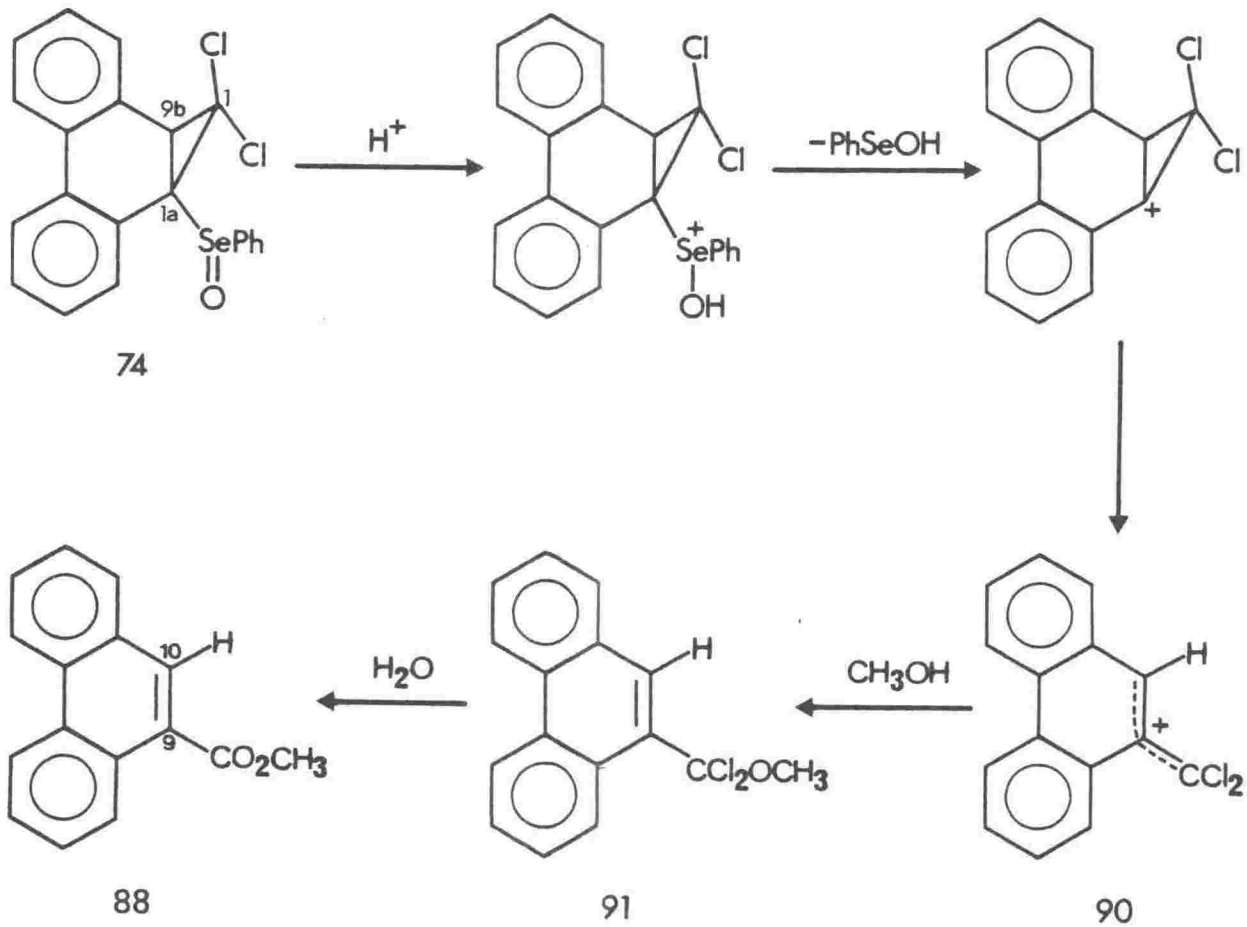


74 76 80

89 88

Scheme 17

posal of an alternative mechanism (Scheme 18) for the formation of methyl ester (88), which does **not** involve cycloproparene (76) as an intermediate and is strictly analogous to that suggested in Scheme 15 for the production of 9-trichloromethylphenanthrene (75). Again, protonation of selenoxide (74),



Scheme 18

loss of PhSeOH and formal cyclopropyl-allyl rearrangement, as in the first three steps of Scheme 15, leads to cation (90), which is intercepted by methanol to provide compound (91). Hydrolysis, either under the reaction conditions or upon work-up, leads to the observed methyl ester. This pathway must be regarded as unlikely, however, since the presence of added base should hinder protonation of the selenoxide and thus slow the reaction substantially.

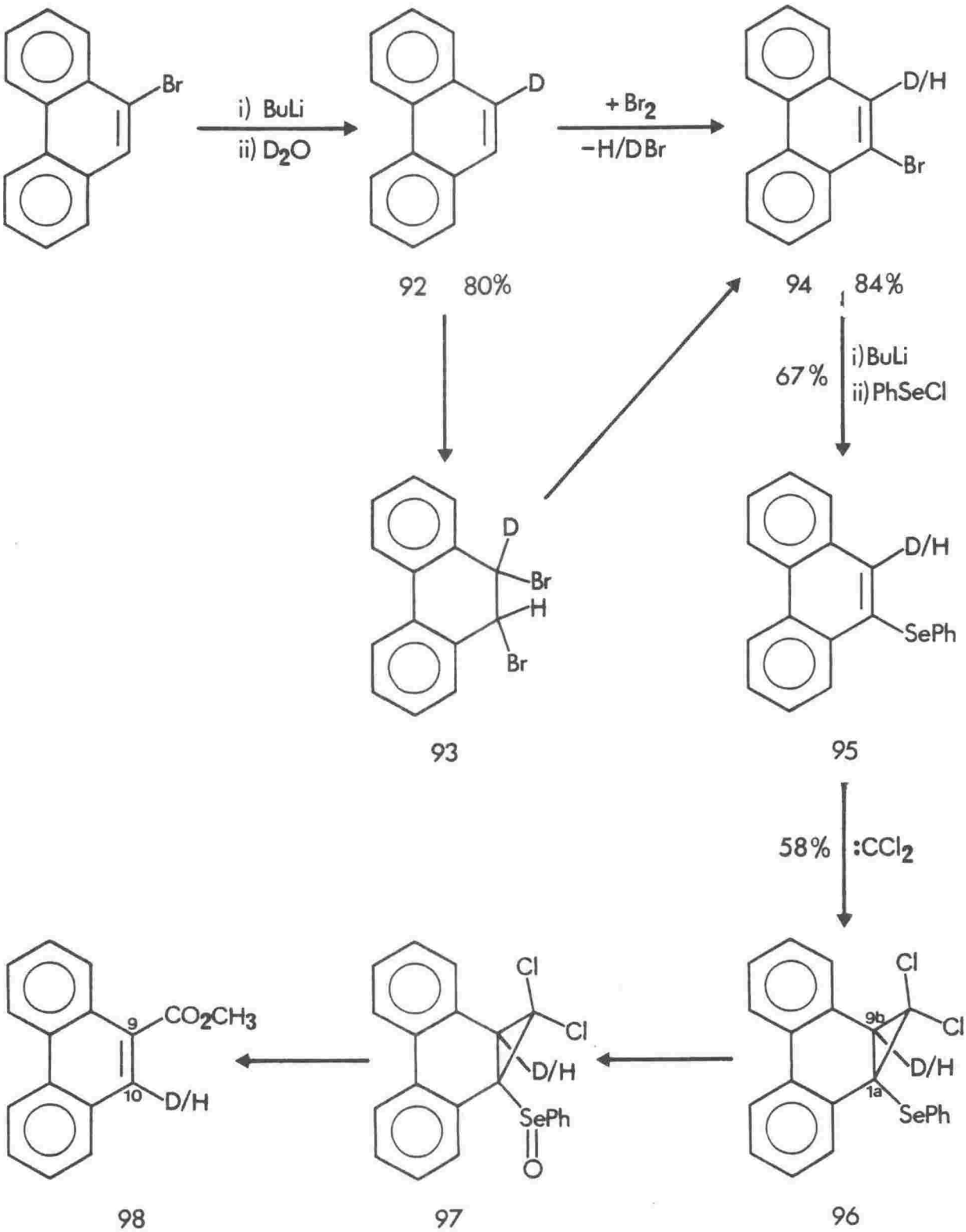
An inspection of the mechanism shown in Scheme 17 reveals that H-9b of selenoxide (74) is **not** retained in methyl ester (88), the proton at C-10 being derived instead from methanol. On the other hand it can be seen from the route depicted in Scheme 18, that H-9b of selenoxide (74) **is** retained as H-10 of ester (88). Deuterium labelling studies were performed, therefore, in order to distinguish between the two mechanisms.

If 9,10-dibromophenanthrene were readily obtainable, the synthesis of (10-^{2}H)-9-bromophenanthrene would be a trivial matter, and a 9b-deuterium-substituted selenoxide would then be prepared in the same way as was its unlabelled counterpart (74). Since the disubstituted phenanthrene was not available to us, however, advantage was taken of the hydrogen-deuterium kinetic isotope effect, as outlined in Scheme 19. Halogen-lithium exchange on 9-bromophenanthrene, followed by quenching with deuterium oxide, afforded (9-^{2}H)phenanthrene (92) in 80% yield. The product was found to be 100% deuterium-labelled at C-9 by a combination of nmr and mass spectrometry. Compound (92) was then heated with bromine in refluxing tetrachloromethane and an intermediate thought to be the dibromide (93) was observed on tlc. The isolated product was identified as [10-^{2}H]-9-bromophenanthrene (94) (84% yield). It had a deuterium content (at C-10) of 60%, which presumably reflected the readier elimination of HBr, compared with loss of DBr, from dibromide (93). Compound (94) was then converted to selenide (96) *via* compound (95) in the usual way. The deuterium content at C-9a was 60% as expected.

Labelled selenoxide (97) was allowed to decompose in methanol, either at room temperature for five days or at reflux for one day. The yield of methyl ester was higher under the latter conditions (50%), but the products of both reactions showed the same extent of deuterium incorporation within experimental error. The integral of the proton nmr spectrum showed the deuterium to be located solely at C-10 of ester (98), and the deuterium content was found by mass spectrometry to be (17±2)%, after correction for carbon-13. This meant that, provided the reaction had gone to completion, at least 70% of the deuterium label had been lost.

In another experiment, unlabelled selenoxide (74) was allowed to decompose in CH_3OD. The methyl ester (98) produced was found to contain (75±4)% deuterium at C-10.

The two labelling experiments are complementary in showing that at least 70% of the methyl ester is **not** formed by the pathway


Br
i) BuLi
ii) D2O
D
+ Br2
−H/DBr
D/H
Br
92 80%
94 84%
67%
i) BuLi
ii) PhSeCl
D
Br
H
Br
D/H
SePh
93
95
58%
:CCl2
Cl
Cl
D/H
SePh
O
9b
1a
CO2CH3
9
10
D/H
98
97
96

Scheme 19

shown in Scheme 18, and further that an intermediate is produced which is sufficiently reactive to allow a proton (deuteron) to be incorporated from the solvent at what becomes C-10 of ester (98). Indeed the ionisation-rearrangement-solvolysis pathway of Scheme 18 may not be involved in the production of the methyl ester **at all**: the selenoxide may decompose exclusively by *syn*-selenoxide elimination to deliver 1,1-dichloro-1*H*-cyclopropa[*l*]phenanthrene (76). The just-formed selenium-containing by-product, with its acidic proton (or deuteron), remains close to the cycloproparene and thus that proton (or deuteron) is able to compete quite successfully with protons (or deuterons) from the solvent bulk for incorporation at C-10 of the solvolysis product. In this way, one might explain the formation of labelled ester from labelled selenoxide and the formation of unlabelled ester in the presence of labelled solvent, while still proposing cycloproparene (76) to be an intermediate. Suffice it to say, however, that the route outlined in Scheme 18 does **not** describe the major mode of formation of methyl ester (88).

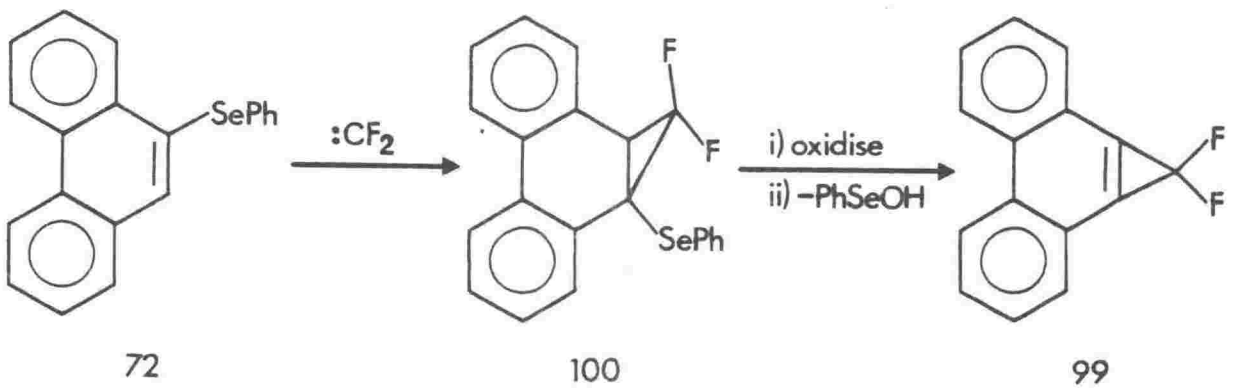
Taken with the known facility for the *syn*-elimination of PhSeOH from phenyl selenoxides which carry a β-proton and the known reactions of 1,1-dihalocycloproparenes with alcohols, these results provide convincing evidence for the formation[83] of 1,1-dichloro-1*H*-cyclopropa[*l*]phenanthrene (76) from selenoxide (74).

If a selenoxide like (74), with a carbon label located exclusively at either C-1a or C-9b, were to be allowed to decompose in methanol, then the subsequent isolation of methyl phenanthrene-9-carboxylate with the label distributed evenly between C-9 and C-10 would provide excellent evidence for the production of a symmetrical intermediate such as cycloproparene (76). Because of the convincing results obtained from the deuterium labelling studies, however, and the likely difficulty and expense associated with the synthesis of a carbon-labelled selenoxide, this idea has not been pursued further.

In separate experiments, cycloproparene (76) could not be trapped with the reactive dienes furan, 1,3-diphenylisobenzo-

furan or tetrachloro-*o*-benzoquinone (Experimental). This is perhaps not surprising if compound (76) is indeed stabilised by the rapid loss of chloride ion to give a resonance-delocalised cation (Schemes 16 and 17). Therefore, if the cyclopropa[*l*]-phenanthrene framework were to be equipped with poorly nucleofugic substituents at C-1, then it might be able to participate in a cycloaddition reaction before its destruction by ionisation and solvolysis. This proposition, coupled with the possibility that the cycloproparene might be inductively stabilised by electron-withdrawing groups at C-1, prompted an attempt to synthesise 1,1-difluoro-1*H*-cyclopropa[*l*]phenanthrene (99).

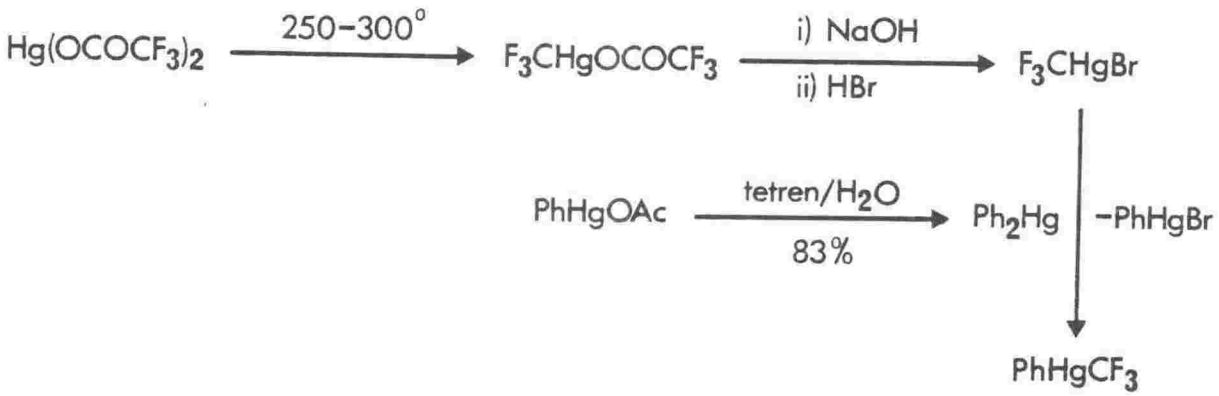
It was hoped that the addition of difluorocarbene to compound (72), oxidation of the resultant selenide (100) and *syn*-selenoxide elimination might provide cycloproparene (99), as outlined in Scheme 20.



72 100 99

Scheme 20

Although there are several literature procedures for generating difluorocarbene, the most universally applicable method[84] involves the iodide-promoted thermal decomposition of phenyltrifluoromethylmercury (101). In our hands, this compound was most easily prepared by the route shown in Scheme 21. Thermal decarboxylation of mercury(II) trifluoroacetate led to trifluoromethylmercury(II) trifluoroacetate,[85] which was then converted to the corresponding bromide.[86] Wade and Seyferth[87] have prepared diphenylmercury in 94% yield by the disproportionation of phenylmercury(II) acetate in the presence of the polyamine



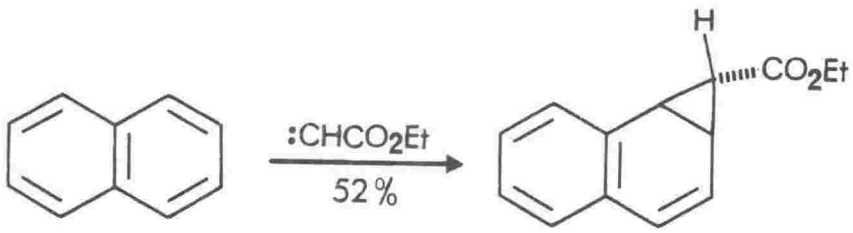
Scheme 21

101 72%

'Dow PEI-6'. This polymer was not available to us, but tetraethylenepentaamine (tetren) was found to work nearly as well, providing diphenylmercury in 83% yield on a multigram scale. Stirring of equimolar amounts of diphenylmercury and trifluoromethylmercury(II) bromide in refluxing toluene was sufficient to precipitate phenylmercury(II) bromide and allow the isolation of phenyltrifluoromethylmercury[86] (101) in 72% yield.

Phenanthrenyl selenide (72) was heated in refluxing 1,2-dimethoxyethane in the presence of tenfold excesses of phenyltrifluoromethylmercury and sodium iodide, by analogy with the method of Seyferth and Hopper.[84] The organomercurial decomposed as expected,[84] with phenylmercury(II) iodide being formed quantitatively, but unreacted selenide (72) was recovered in 100% yield. The reaction was assumed to be unsuccessful because of the low electrophilicity of difluorocarbene,[88] low electron density at the 9-10 bond of selenide (72), and also the possibility of competitive formation of ylids.[88-90] To our knowledge, there have been no successful additions of difluorocarbene to arenes.

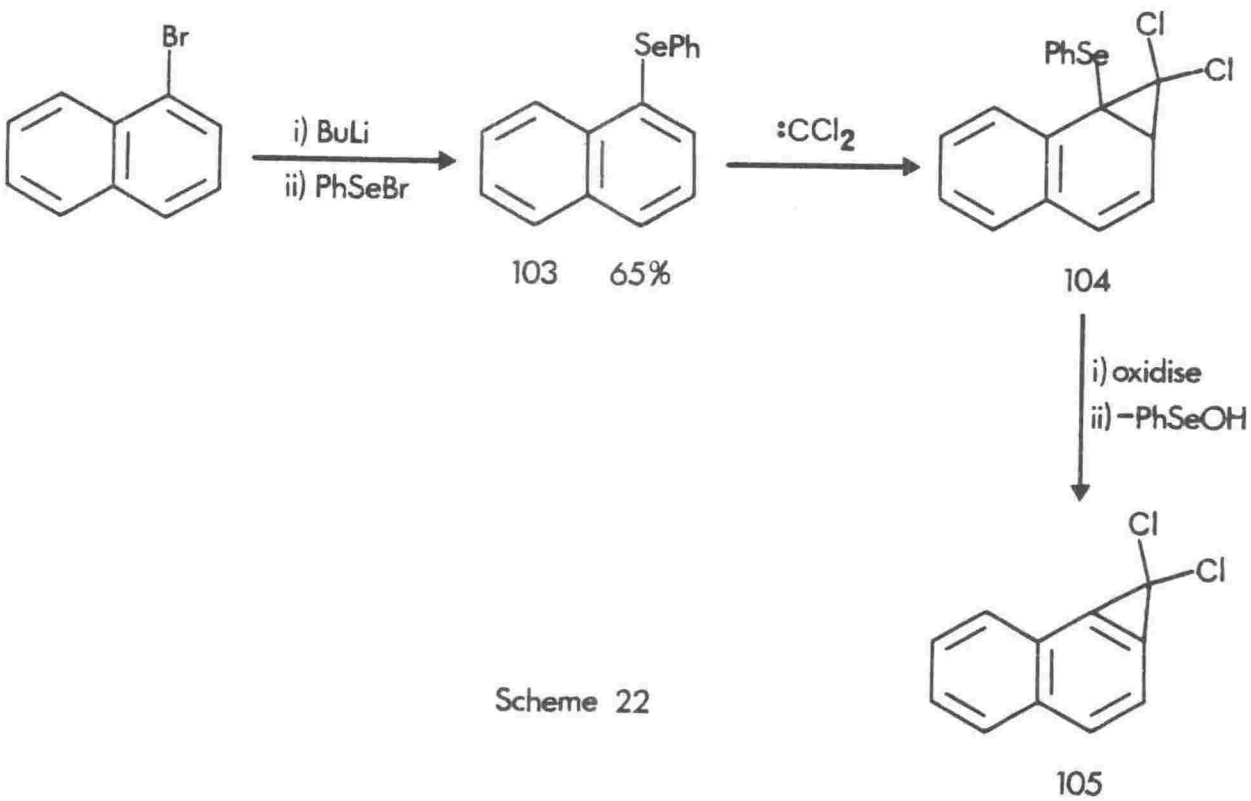
There is a lack of simple routes to cyclopropa[*a*]naphthalenes, and an attempt was made to apply to that class of compounds the selenium-based methods recounted herein. There are some examples of carbenes adding to naphthalenes with retention of the norcaradiene framework of the adduct.[88] Thus, compound (102) has been isolated from the reaction of naphthalene with



102

ethoxycarbonylcarbene.

1-Phenylselenonaphthalene (103) was prepared by a simple modification of the literature procedure,[91] and it was hoped that the dichlorocarbene adduct (104) and thence 1,1-dichloro-cyclopropa[*a*]naphthalene (105) might be synthesised through the transformations shown in Scheme 22. Unfortunately, selenide



103 65%

104

105

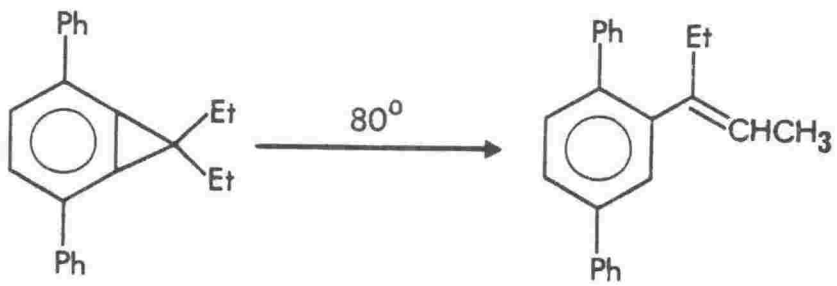
Scheme 22

(103) was found not to react with dichlorocarbene generated under phase-transfer conditions. The greater aromaticity of the naphthalene nucleus compared with that of phenanthrene may have rendered the 1-2 bond of selenide (103) too electron-deficient to permit the addition of dichlorocarbene under the conditions employed.

CHAPTER THREE

APPROACHES TO 1,1-DIALKYL-1*H*-CYCLOPROPA[*l*]PHENANTHRENES

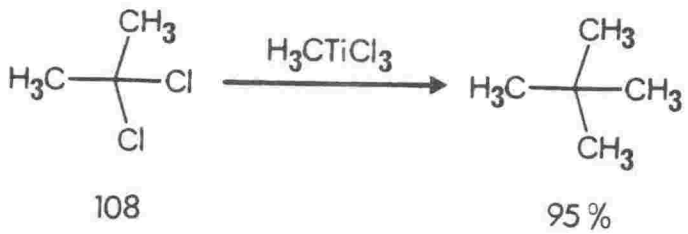
It has been suggested (Chapter Two) that 1,1-dichloro-1*H*-cyclopropa[*l*]phenanthrene (76) might be stabilised by loss of chloride ion to give a resonance-delocalised cation, a factor which may have prevented the isolation or Diels-Alder trapping of the cycloproparene. Alkyl substituents at C-1 would prevent such an ionisation but may present a new difficulty: an α-hydrogen atom on one of the substituents could allow an intramolecular hydrogen transfer through a five-membered transition state structure to give a styrene. Of the many alkyl-substituted cycloproparenes which give styrenes in this way,[1a,c] (for example, the conversion[92] of cyclopropabenzene (106) to styrene (107)) the compounds which carry smaller alkyl groups appear to



106 107

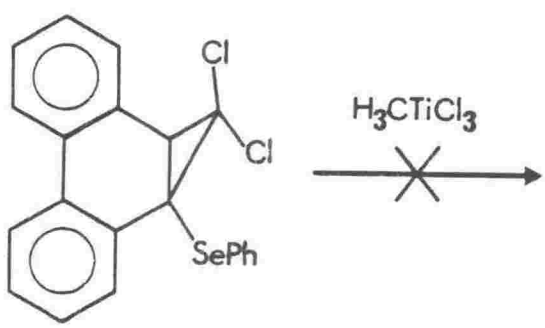
be the more stable, perhaps because such substituents are less sterically demanding. Thus, it appeared worthwhile to try to prepare 1,1-dimethyl-1*H*-cyclopropa[*l*]phenanthrene from a dihydro-precursor.

Reetz and co-workers[93] have reported the conversion of some *gem*-dichlorides to the corresponding *gem*-dimethyl compounds by use of methyltitanium reagents. For example, compound (108) was converted to 2,2-dimethylpropane in 95% yield by the action of methyltitanium trichloride. Despite the generally low propensity of cyclopropanes towards substitution, and the fact that the mechanism of such organometallic substitutions is by



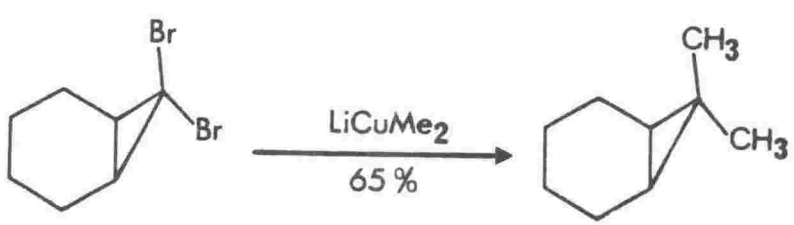
108 95 %

no means clear, dichloro-compound (73) was treated with methyltitanium trichloride. Unfortunately, compound (73) was recovered quantitatively, even after exposure to an excess of the reagent for one day at room temperature.



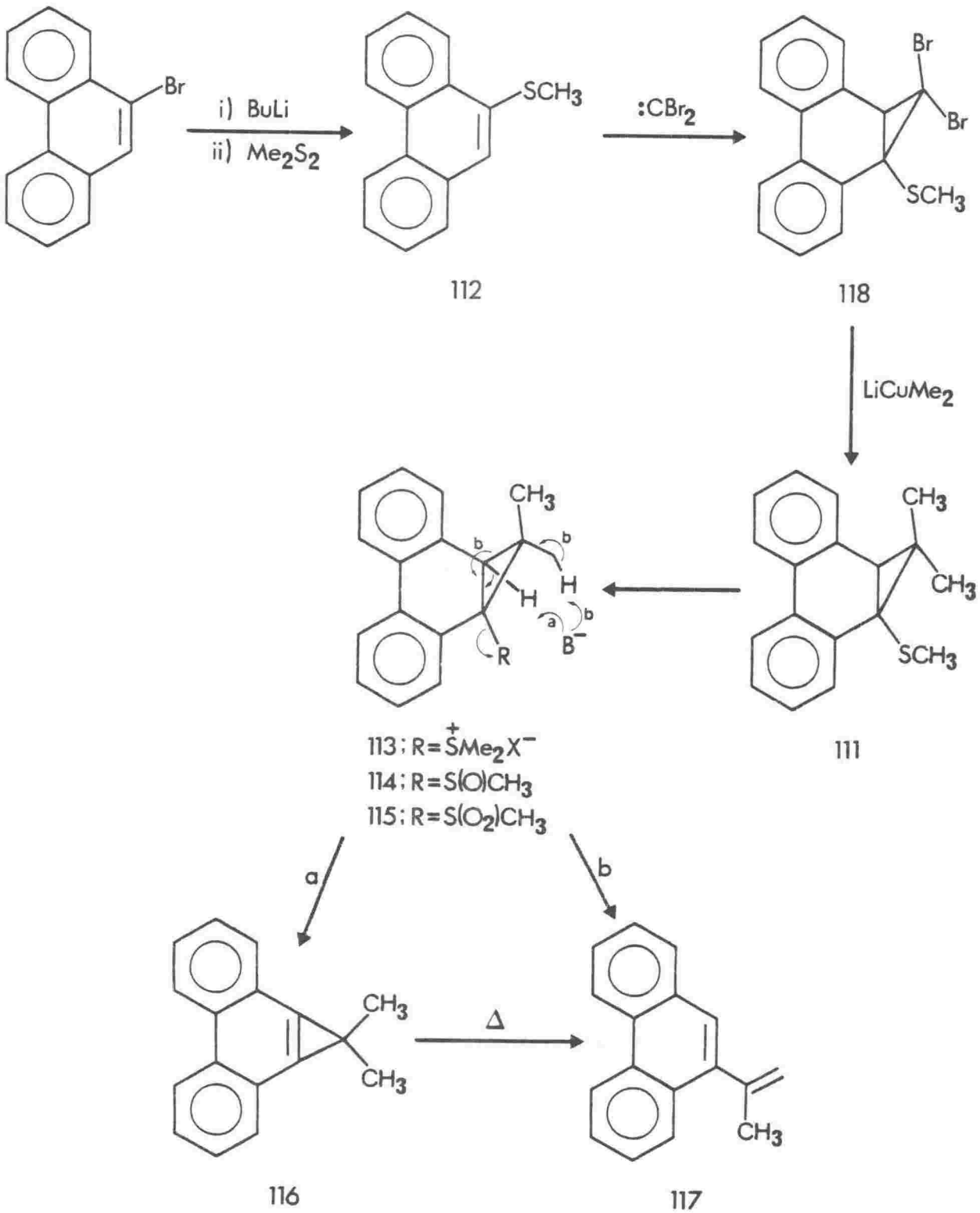
73

Corey and Posner[94] have shown that the *gem*-dibromocyclopropane (109) is converted to the *gem*-dimethyl compound (110) in 65% yield by the use of five equivalents of lithium dimethylcuprate at -15° for five days. The use of such a reaction in the syn-



109 110

thesis of a selenium-substituted 1,1-dimethyldihydrocyclopropa-[*l*]phenanthrene is questionable, since some selenides have been found[95] to react with lithium dimethylcuprate. Accordingly, methylthio compound (111) was chosen as a more appropriate target (Scheme 23).



Scheme 23

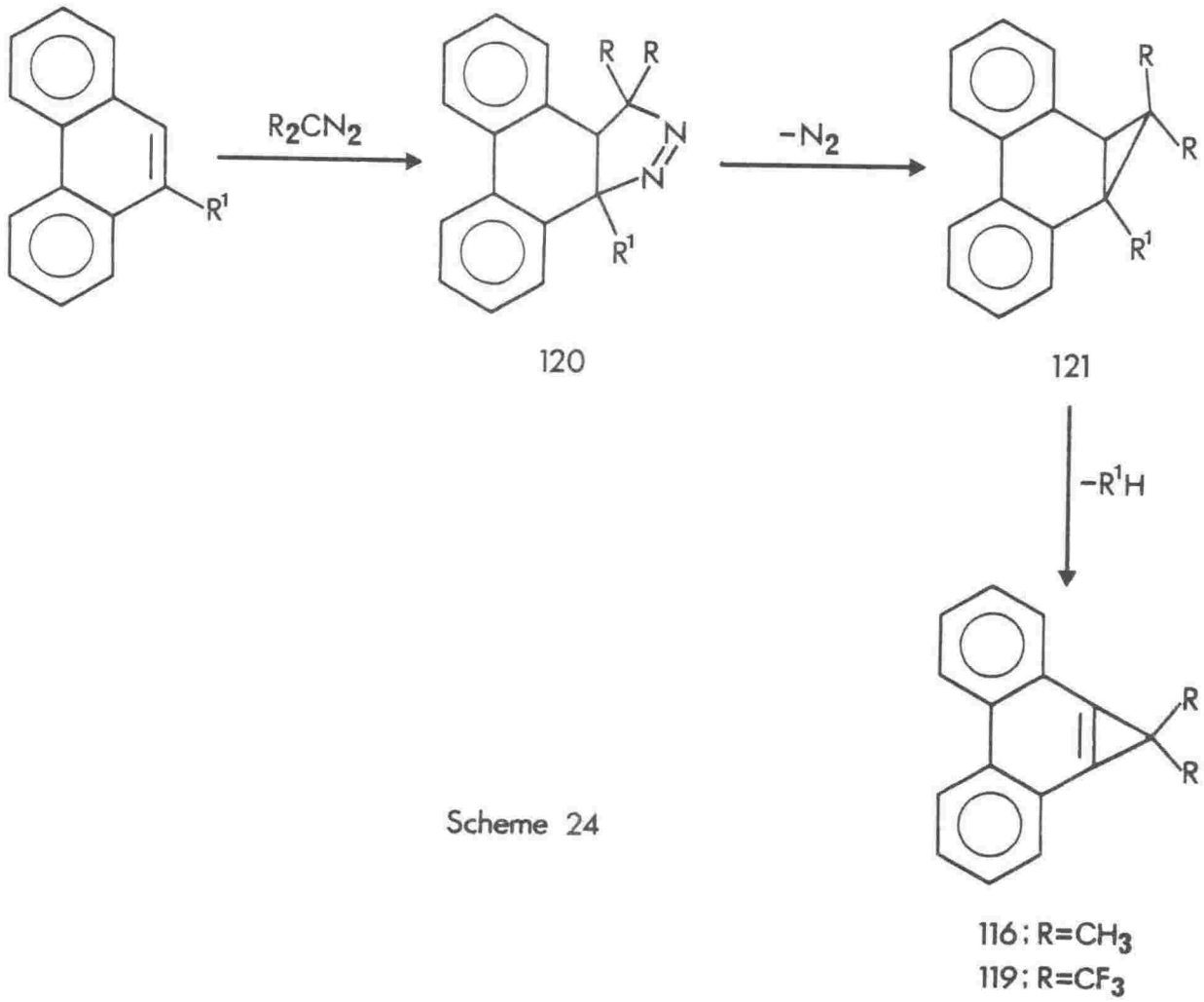
The small steric bulk of, and mesomeric electron donation from, the methylthio group should facilitate the addition of dibromocarbene to the 9,10-positions of phenanthrene (112). Furthermore, if the final elimination reaction were to be performed

with dimethylsulfonium salt (113) as the substrate, then the resultant formation of the volatile dimethyl sulfide would make purification of the products easier. Sulfoxide (114) or sulfone (115) might also be used in the elimination reaction. In any event a complication could arise, whereby elimination according to route *a* to give cyclopropa**r**ene (116) might compete with route *b*, which leads directly to styrene (117), the product also expected from intramolecular hydrogen transfer in the cyclopropa**r**ene. The acidity of the benzylic H-9b should favour route *a*, but route *b* might operate by virtue of a favourable transition state structure and a reduction in ring strain.

The previously unknown 9-methylthiophenanthrene (112) was prepared in 84% yield according to Scheme 23. Unfortunately, this compound failed to give discrete products from its reaction with dibromocarbene generated by the phase-transfer technique. Even when the reaction was stopped well before the starting material had been consumed, no evidence for the formation of dibromocarbene adduct (118) was obtained from the proton nmr spectrum of the product mixture. It is possible that compound (118) was formed but that it was too base-sensitive, compared with the dichlorocarbene adducts prepared during this work, to survive the reaction conditions.

As well as 1,1-dimethyl-1*H*-cyclopropa[*l*]phenanthrene (116), the 1,1-bis-trifluoromethyl analogue (119) was also considered a desirable target: not only should the perfluoro substituents at C-1 preclude isomerisation to a styrene, but also their inductive electron withdrawal might stabilise the cyclopropa**r**ene. Both of 1*H*-cyclopropa[*l*]phenanthrenes (116) and (119) may be accessible by the route depicted in Scheme 24, whereby 1,3-dipolar cycloaddition of the appropriate diazoalkane to the 9,10-positions of a substituted phenanthrene should provide either pyrazoline (120) or its regioisomer. Thermal or photochemical extrusion of nitrogen would lead to dihydrocyclopropa[*l*]phenanthrene (121), whence the cyclopropa**r**ene itself might be obtained by elimination of the bridgehead substituents.

In a preliminary experiment, 9-(4'-chlorophenylseleno)phenan-



Scheme 24

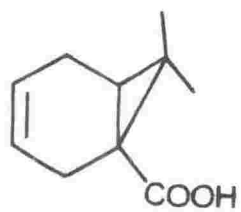
threne (71) was treated with an excess of the readily available diazomethane at ambient temperature and pressure. The starting material was recovered quantitatively after five days of reaction. Such a reaction could be facilitated by the use of high pressure, since dipolar cycloadditions have a negative volume of activation.[96] Thus, it is possible that the transformations depicted in Scheme 24 might be carried out with organoselenium substrates, but the lack of high pressure equipment suitable for preparative-scale reactions in these laboratories has meant that the idea has not been pursued.

There is a single example of the addition of a diazoalkane to a substituted phenanthrene.[97] The 9,10-bond of methyl phenanthrene-9-carboxylate (88) was found to be sufficiently activated towards the addition of diazomethane to allow the formation of pyrazoline (120;R=H,R^1=$COOCH_3$) in 7 and 45% yields after react-

ion for 49 h at 1 and 5000 atm respectively. The regiochemistry of the addition and the tautomeric integrity of the adduct were established by x-ray crystallography.[98]

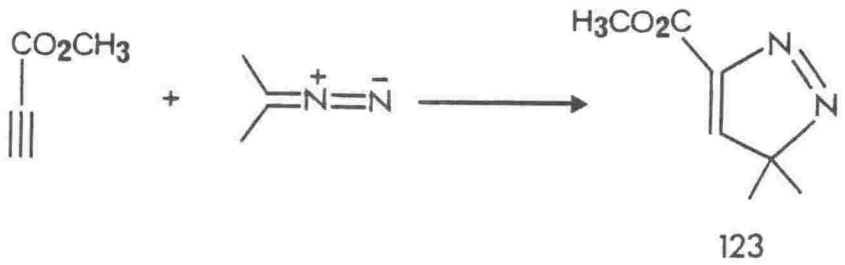
Similarly, diazopropane and hexafluorodiazopropane could be added to methyl phenanthrene-9-carboxylate (88). Extrusion of nitrogen from the resultant pyrazolines and hydrolysis of the ester functions should provide carboxylic acids (121;R=CH_3 and CF_3, R^1=COOH), and oxidative decarboxylation might then lead to cyclopropparenes (116) and (119). Diazopropane has a limited lifetime at room temperature but is easy to make,[99] whilst hexafluorodiazopropane is more stable but its synthesis[100] requires the highly toxic and difficult to obtain hexafluoroacetone. The use of either diazoalkane in a 1,3-dipolar cycloaddition with ester (88) might well require specially constructed high pressure apparatus and, because of these difficulties, it was decided first to test the utility of the oxidative decarboxylation on a model compound.

The model chosen was 7,7-dimethylbicyclo[4.1.0]hept-3-ene-1-carboxylic acid (122), a compound which has previously been



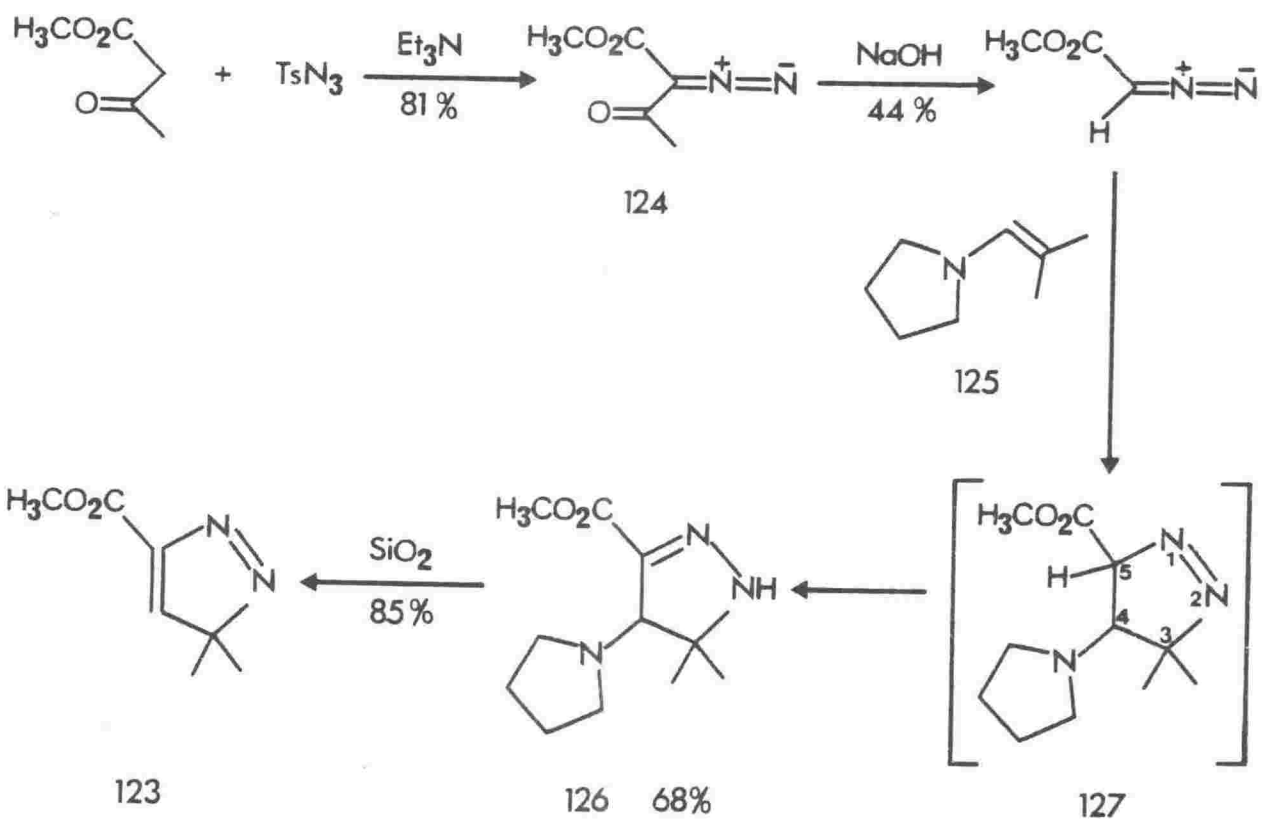
122

prepared[101] in these laboratories. A key intermediate in its synthesis is the 3*H*-pyrazole (123), which is available by the method of Franck-Neumann[102] (Scheme 25). Dipolar cycloaddition of diazopropane with methyl propynoate affords the pyrazole directly, but the need to manipulate the unstable and hazardous diazopropane and the lachrymatory acid precursor of methyl propynoate led to the method of Huisgen and Reissig[103] being employed instead (Scheme 26). Base-induced diazo transfer between *p*-toluenesulfonyl azide and methyl 3-oxobutanoate



Scheme 25

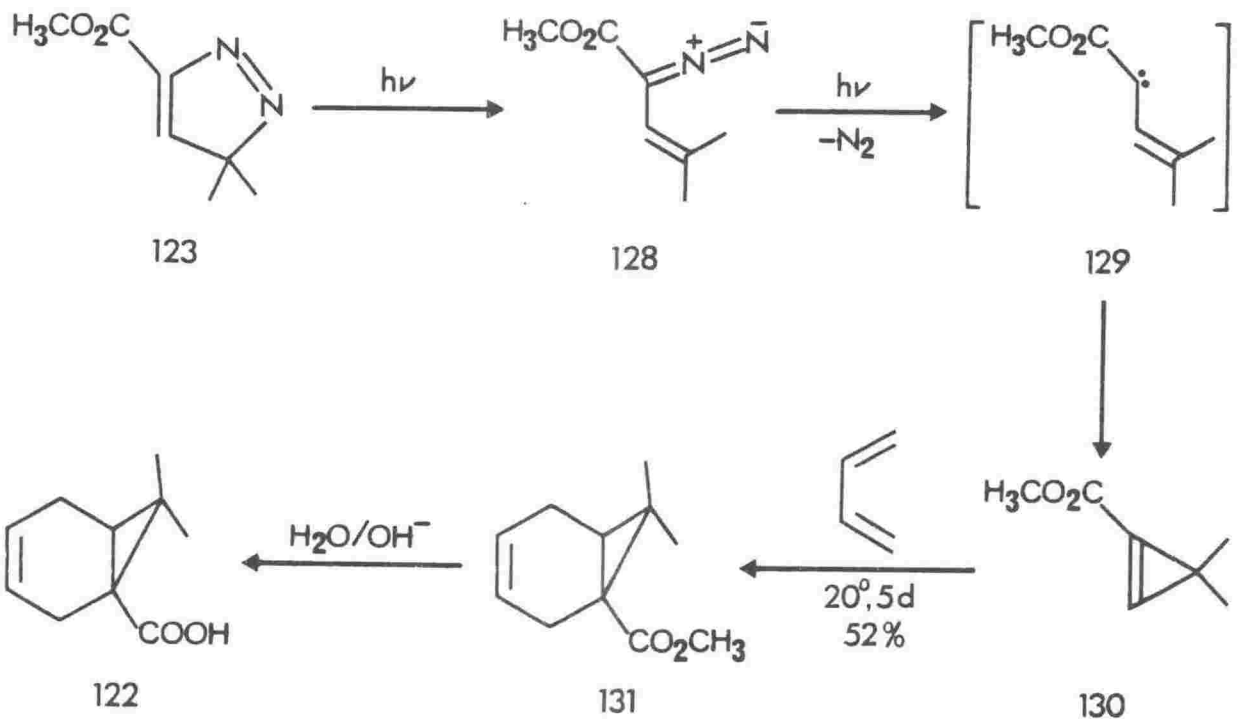
gave an 81% yield of methyl 2-diazo-3-oxobutanoate (124), which was hydrolysed with aqueous base to provide a 44% yield of methyl diazoacetate after distillation. Both of these steps involved modifications of the literature procedures[104] (Experimental). Reaction of methyl diazoacetate with the pyrrolidine-enamine (125) of 2-methylpropanal led to the isolation of the 4,5-dihydro-1*H*-pyrazole (126) in 68% yield. This product is thought to result from a [1,3]-hydrogen shift in the 4,5-dihydro-3*H*-pyrazole (127), the initial product of 1,3-dipolar cycloaddition. Chromatography on silica gel was sufficient to



Scheme 26

eliminate pyrrolidine from compound (126) and to provide the required pyrazole (123) in 85% isolated yield.

An ethereal solution of pyrazole (123) was photolysed according to the method of Franck-Neumann,[44d] and the composition of the reacting mixture was monitored by proton nmr and infrared analysis. The concentration of one component was found to increase with time, and then to decrease almost to zero by the end of the photolysis (Experimental). This component, which was observed but not characterised in the original work,[44d] is proposed to be methyl 2-diazo-4-methyl-3-pentenoate (128). The infrared spectrum exhibits an intense peak at 2090 cm^{-1} (diazo stretch), whilst the proton spectrum displays narrow multiplets at δ 1.7 and 1.9 (methyl protons), a singlet at δ 3.78 (methoxyl protons) and a narrow multiplet at δ 5.4 (vinyl proton). This spectrum is similar to those which have been recorded[44b,c] for analogous vinyl diazo compounds. It is believed that compound (128) arises from a 6π electrocyclic ring-opening of pyrazole (123). Diazo compounds such as (128) deliver vinyl carbenes such as (129) upon photolysis, and these may cyclise to produce cyclopropenes.[41,44] Indeed, the product mixture obtained



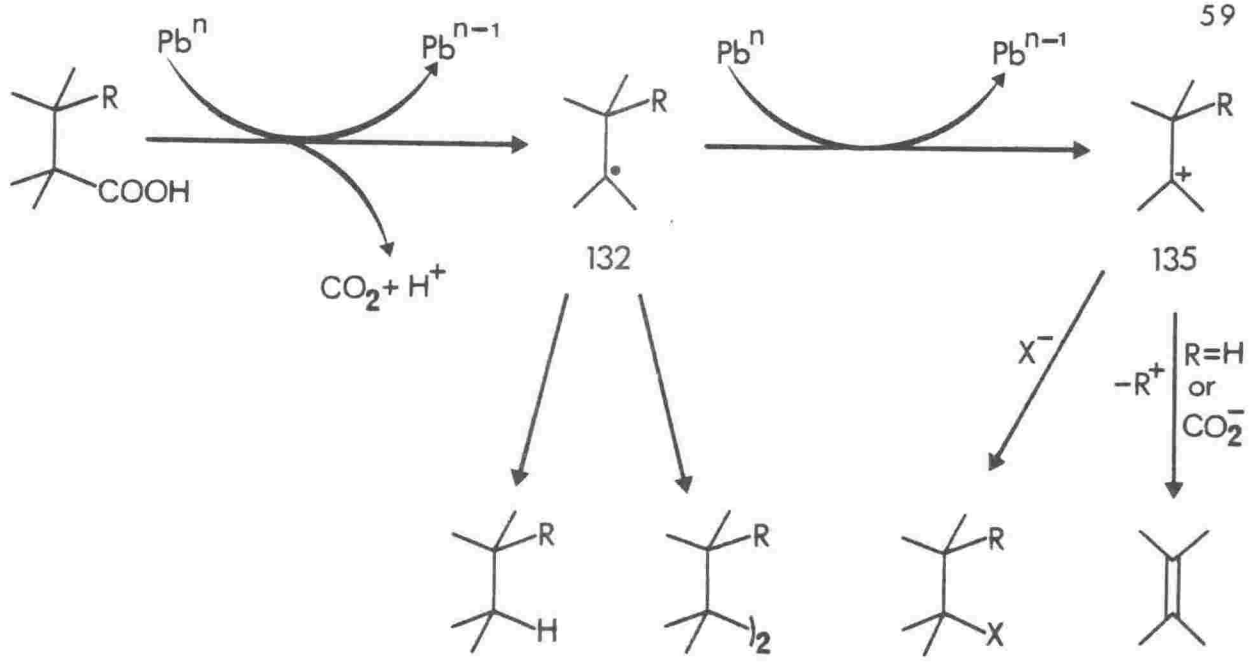
Scheme 27

after pyrazole (123) had been photolysed was found to contain mostly cyclopropene (130) (Scheme 27). The proton nmr and infrared spectra of the cyclopropene are identical to those obtained previously,[44d] and the compound was further characterised by carbon-13 nmr spectroscopy. Much of cyclopropene (130) decomposed during acquisition of the off-resonance decoupled spectrum, but the following signals were assigned: a quartet at δ 26.9 (methyl carbons), a quartet at δ 51.9 (methoxyl carbon), and a doublet at δ 133.8 (C-2).

The cyclopropene was used without purification because of its known[44d] instability, and a concentrated ethereal solution together with an excess of 1,3-butadiene was kept in a sealed tube at room temperature.[101] After five days, methyl 7,7-dimethylbicyclo[4.1.0]hept-3-ene-1-carboxylate (131), the product of [4+2] cycloaddition of the two reactants, was isolated in 52% yield (based on pyrazole (123)). The ester function in compound (131) was then hydrolysed to complete the preparation[101] of carboxylic acid (122).

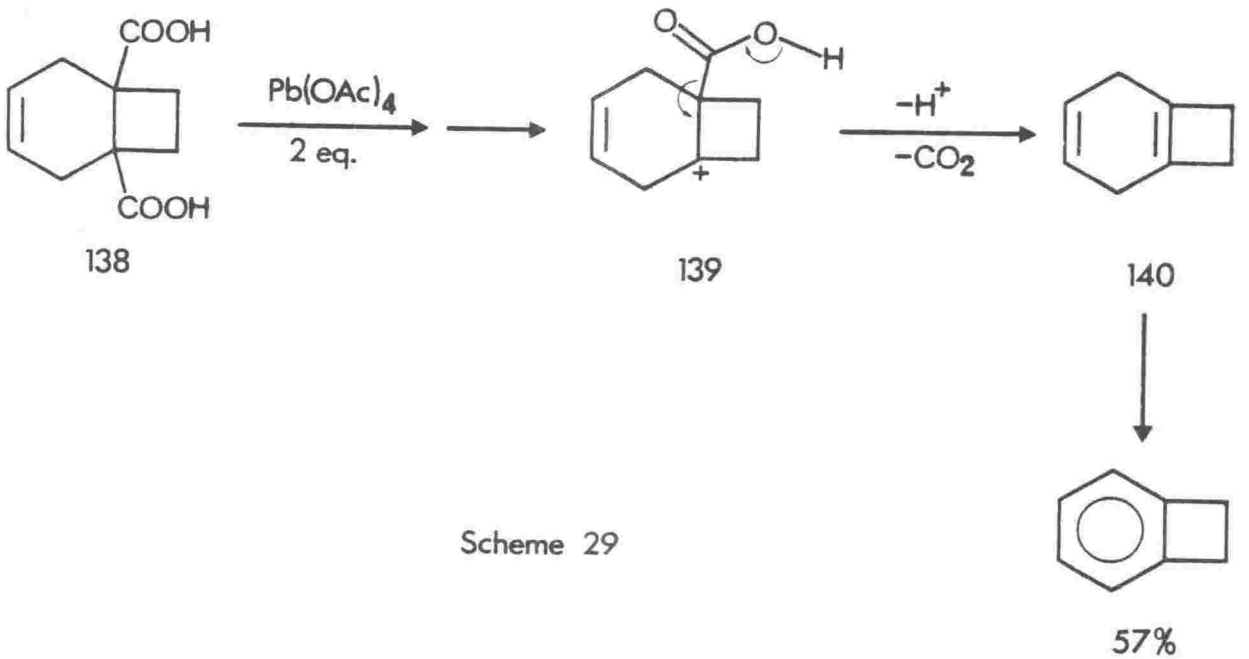
A reagent which has been widely used for the oxidative decarboxylation of both mono- and vicinal di-carboxylic acids is lead(IV) acetate.[105] It is generally accepted that decarboxylations with this reagent proceed *via* a free-radical chain mechanism such as that proposed by Kochi,[105a] the substantive effect of which is a series of one-electron transfers between the substrate and the lead reagent (Scheme 28). Thus, initial decarboxylation leads to a species represented by radical (132), which may be intercepted by solvent to give an alkane (133), or it may give other radical-derived products such as dimer (134). A further one-electron transfer from radical (132) gives a species formulated as cation (135), which may be trapped by an anionic species X^- (often acetate ion) to give a product (136) of oxidative substitution. Alternatively, the loss of an adjacent proton (for mono-decarboxylation) or a carboxylate function (for bis-decarboxylation) leads to an alkene (137).

Through the efforts of Thummel[1d] and his co-workers, cycloalkarenes have already been synthesised by oxidative decarb-



Scheme 28

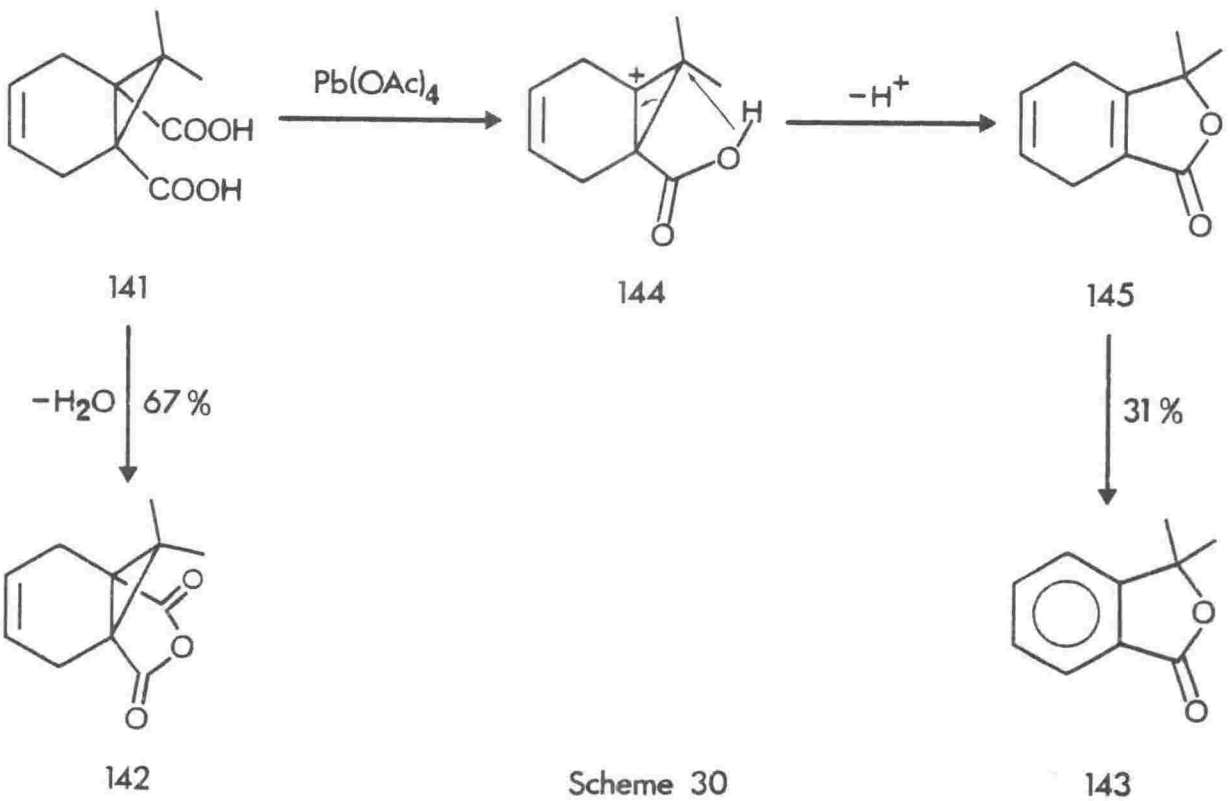
oxylation with lead(IV) acetate. For example, it was found[18a] that the vicinal dicarboxylic acid (138) was smoothly converted to cyclobutabenzene in 57% yield (Scheme 29). By analogy with



Scheme 29

the mechanism outlined in Scheme 28, an intermediate represented by cation (139) is formed. Subsequent loss of carbon dioxide provides diene (140), which aromatises under the reaction conditions to afford the observed product. Such an aromatisation has precedent[105a] in lead(IV) acetate oxidations.

Galloway and Halton[106] have tried to synthesise a cyclopropabenzene in a similar manner by oxidative decarboxylation of compound (141). Apart from the dehydrated species (142) which, like some other anhydrides,[105a] was found not to react with lead(IV) acetate, the only product to be isolated from the reaction of di-acid (141) was the isobenzofuranone (143). It



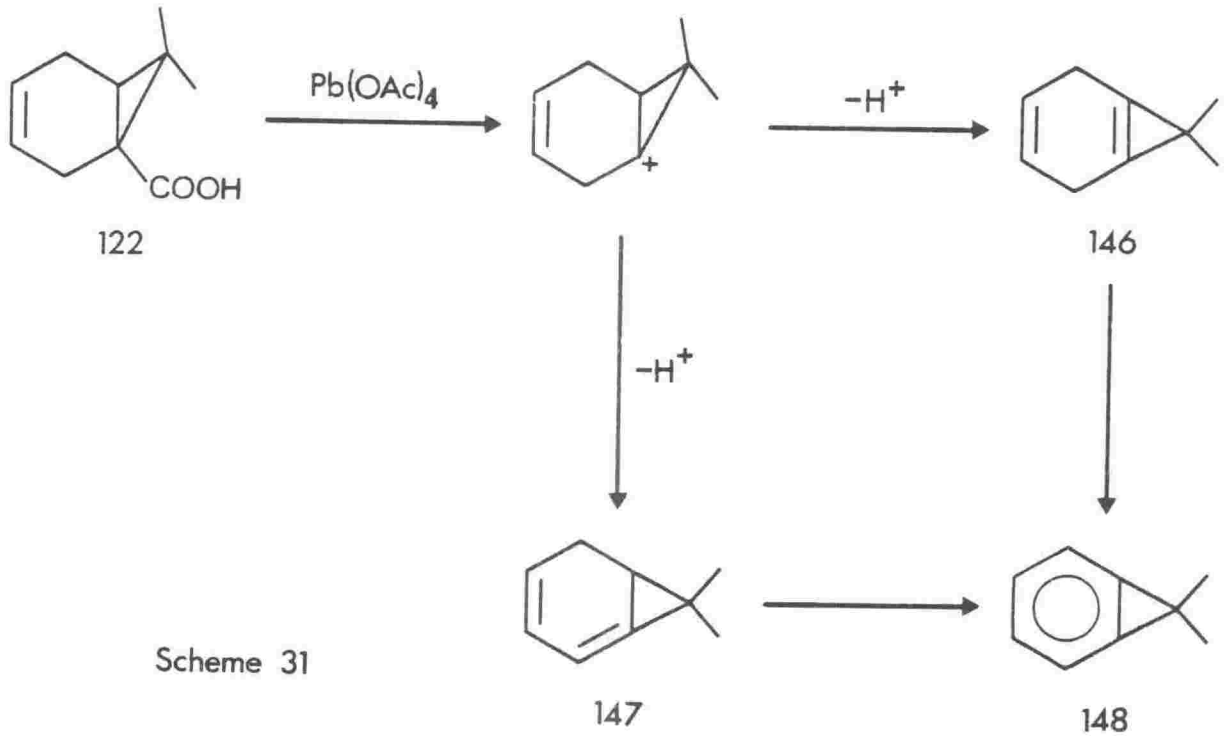
141 144 145

142 143

Scheme 30

was proposed[106] that the cationic intermediate (144) underwent carboxylate-assisted ring expansion, involving a formal cyclopropyl-allyl rearrangement, to give the dienic lactone (145), which was then aromatised to complete the sequence (Scheme 30). If the second carboxylic acid function were to be absent, as in the model compound (122), then cleavage of the three-membered ring might be avoided and dienes (146) or (147), and thence cyclopropabenzene (148), might be formed according to Scheme 31.

Oxidative decarboxylations with lead(IV) acetate proceed most readily in strongly-coordinating solvents and in the presence of organic bases such as pyridine.[105] Therefore, the decarboxylation of compound (122), with 1.7 equivalents of lead(IV)

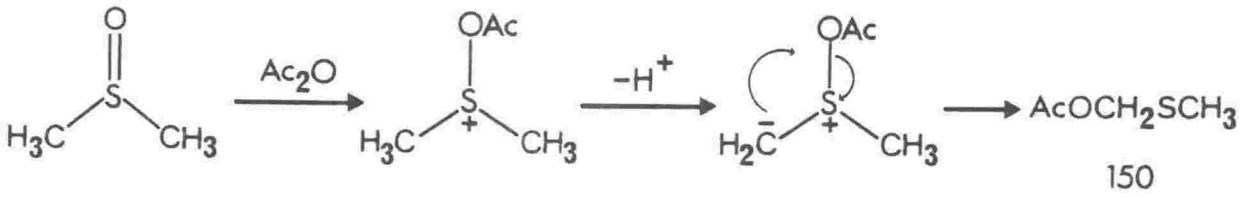


122 146 147 148

Scheme 31

acetate, was performed in dimethyl sulfoxide-pyridine.[18a] After four hours of reaction at room temperature, during which time the mixture darkened and gas was evolved, unchanged carboxylic acid (122) was recovered in 26% yield by base extraction of the product mixture. The neutral fraction which remained was found to contain several chromatographically mobile products, but most of the material was polymeric. The proton nmr spectrum showed the presence of 1-methyl-1-phenylethyl acetate (149), which was characterised, both in this work[107] and in a preliminary study[101] in these laboratories, by comparison with an independently prepared sample.[108] No other component of the product mixture was identified in the earlier study, but it was found in the present investigation that the components could be separated by preparative gas-liquid chromatography (glc), albeit with substantial mechanical losses.

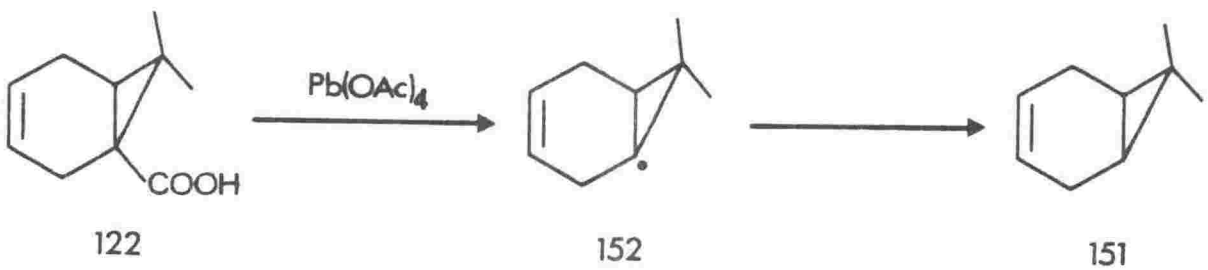
The first-eluted component was a mobile oil, whose proton and carbon-13 nmr spectra are identical to those of a sample of methylthiomethyl acetate (150), prepared independently by a Pummerer reaction of dimethyl sulfoxide with acetic anhydride[109] (Scheme 32). Compound (150) is believed to form during the oxidative decarboxylation reaction in a way similar to its



Scheme 32

preparation according to Scheme 32.

The next-eluted component was obtained in a quantity of 2 mg. Its proton nmr spectrum contains a two-proton multiplet at δ 0.55-0.70, three-proton singlets at δ 0.80 and 1.03, a four-proton multiplet at δ 1.9-2.5, and a broadened two-proton singlet at δ 5.54. This spectrum is identical to that obtained for 7,7-dimethylbicyclo[4.1.0]hept-3-ene (151) by Paquette *et al.*,[110] who synthesised the compound by a different route. The product was further characterised by glc-mass spectrometry and was found to have a molecular weight of 122, which corresponds to that of the proposed structure. A credible mechanism for the formation of compound (151) is shown in Scheme 33.

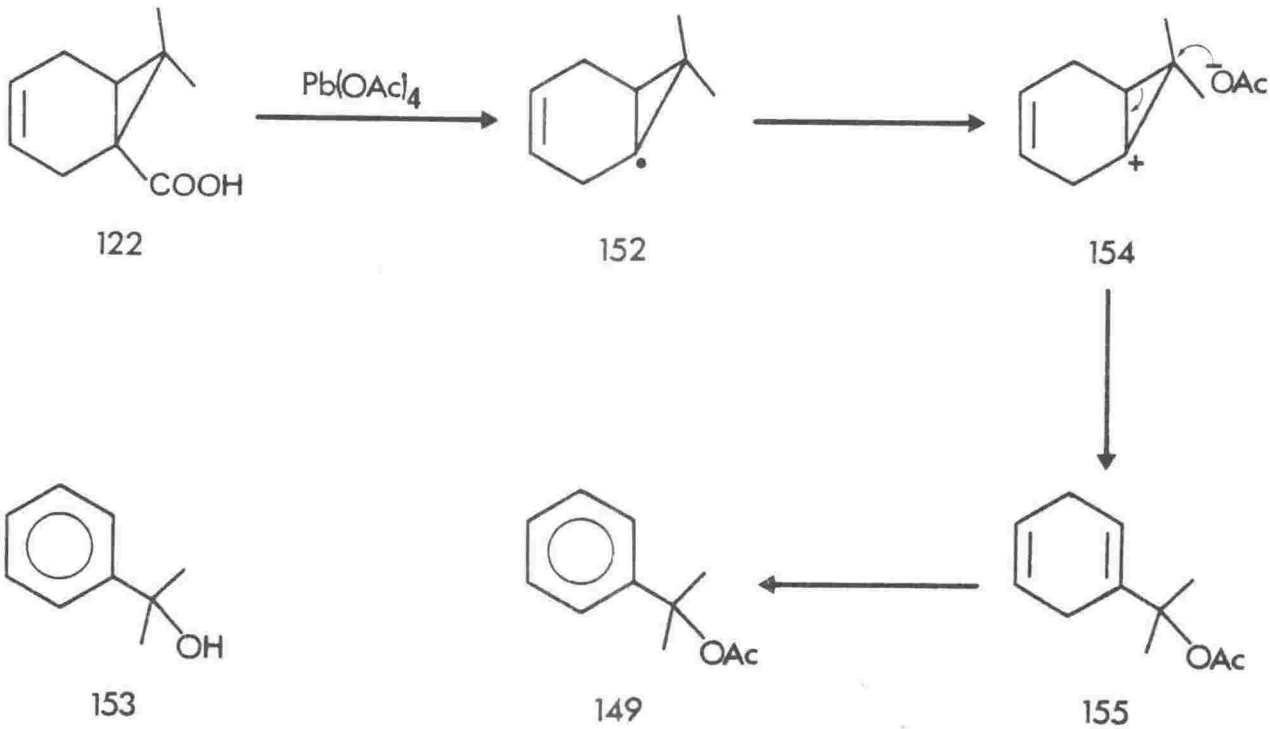


Scheme 33

Thus, acid (122) is decarboxylated as expected to provide a species formulated as radical (152), which is then intercepted by hydrogen transfer from solvent to give the observed product (0.6% yield). Such radical-derived products are often isolated from decarboxylations[105] (compare with the generalised product (133) in Scheme 28).

The last-eluted component of the product mixture was found to

be 1-methyl-1-phenylethanol (153) (2% yield), which was identical to an independently prepared sample.[111] This product is believed to arise from the hydrolysis of acetate (149) during work-up. A tenable mechanism for the formation of the acetate is shown in Scheme 34. As before, carboxylic acid (122) is



122 152 154 153 149 155

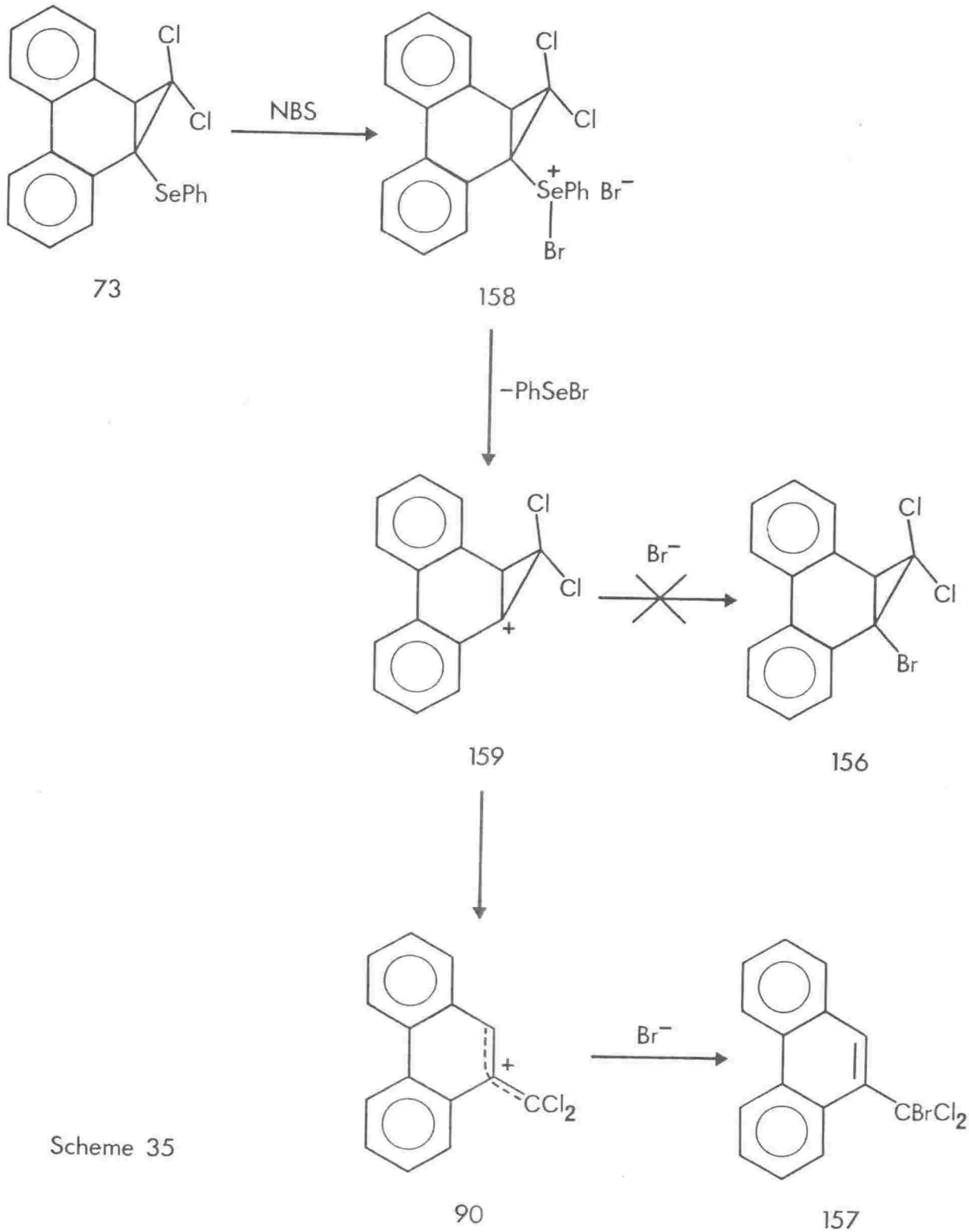
Scheme 34

decarboxylated to give radical (152), which transfers an electron to the lead reagent and affords cation (154). Instead of losing a proton to give a diene, the cation suffers formal cyclopropyl-allyl rearrangement and interception by acetate ion to provide compound (155), which is then aromatised to complete the sequence.

The extremely poor material balance of the reaction makes it impossible to generalise about the fate of the decarboxylated intermediates, but if cation (154) is intercepted as a ring-cleaved product before it can lose a proton and form a bicyclic diene (Scheme 31), then it would appear that the oxidative decarboxylation route cannot be applied to the synthesis of 1,1-dimethylcyclopropabenzene (148). From the results of this model study, it might also be reasoned that the oxidative de-

carboxylation of carboxylic acids (121;R=CH_3 and CF_3, R^1=COOH) is unlikely to represent a viable route to 1*H*-cyclopropa[*l*]-phenanthrenes (116) and (119).

The formation of the rearranged acetate (149) also casts doubt on the utility of any cyclopropa rene precursors which rely upon the formation of bridgehead cyclopropyl cations as intermediates. Indeed, within the cyclopropa[*l*]phenanthrene framework, two apparent examples of the rearrangement of such a cation have been found in the present study. The first involves the reaction of selenoxide (74) with hydrogen chloride to produce 9-trichloromethylphenanthrene (Scheme 15), while the second was found during an attempt to prepare 1a-bromo-1,1-dichloro-1a,9b-dihydrocyclopropa[*l*]phenanthrene (156). This compound was of interest because 1,1-dichloro-1*H*-cyclopropa[*l*]phenanthrene might have been prepared from it by base-induced dehydrobromination. Krief *et al.*[112] have found that various alkyl selenides could be converted to alkyl bromides by reaction with bromine or *N*-bromosuccinimide (NBS), and the analogous reaction of selenide (73) with NBS provided a single, chromatographically unstable product. The mass spectrum indicated that the molecular formula was indeed $C_{15}H_9BrCl_2$, but the product was identified not as compound (156), but as 9-bromodichloromethylphenanthrene (157) (100% yield). The proton nmr spectrum contains only aromatic resonances, including a one-proton singlet at δ 8.46 which indicates that the compound is a 9-substituted phenanthrene. In addition, the aromatic fingerprint is superimposable with that of 9-trichloromethylphenanthrene (75). The compound was also hydrolysed to phenanthrene-9-carboxylic acid, identical to an authentic sample. The chromatographic lability of compound (157), however, prevented further purification and the acquisition of combustion data. It is proposed that the first step in the reaction (Scheme 35) involves the formation of the selenide-dibromide (158), whose subsequent decomposition entails the loss of phenylselenenyl bromide and the formal rearrangement of cyclopropyl cation (159) to benzyl cation (90). The observed product results when the latter species is intercepted by bromide ion.

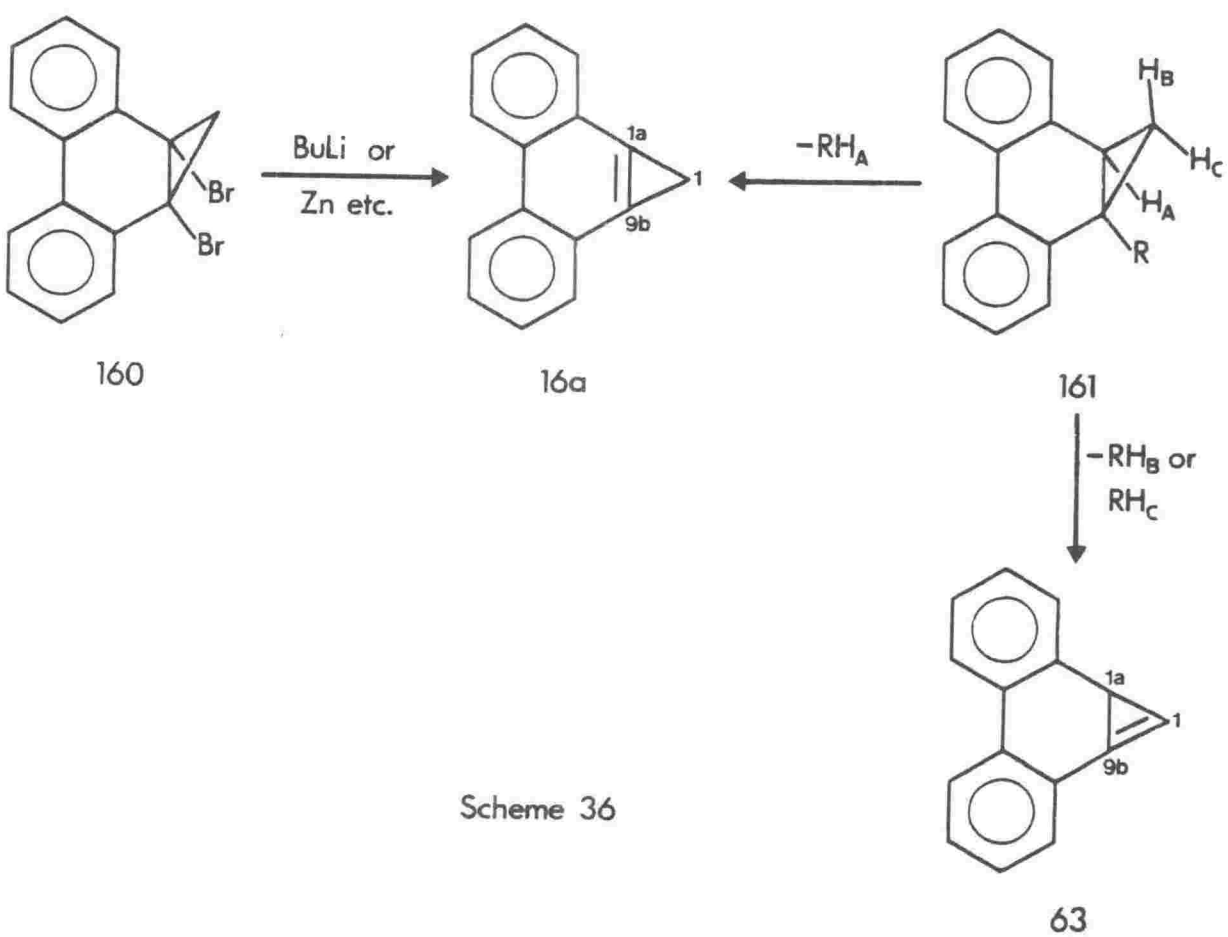

Cl
Cl
SePh
NBS
Cl
Cl
+
SePh Br⁻
Br
73
158
–PhSeBr
Cl
Cl
+
Br⁻
Cl
Cl
Br
159
156
CCl2
Br⁻
CBrCl2
90
157

Scheme 35

CHAPTER FOUR

1*H*-CYCLOPROPA[*1*]PHENANTHRENE

The ideal way of constructing the parent 1*H*-cyclopropa[*1*]-phenanthrene (16a) from a dihydro-precursor would involve the elimination of two 'non-hydrogen' substituents from the bridge-head positions. As an example, bromine could be eliminated from the unknown compound (160), but reasons have been advanced already (Chapter Two) to suggest that such precursors would be difficult to obtain. Whilst a **mono**-substituted progenitor of type (161) is likely to be more accessible, more than one direction of elimination is possible (Scheme 36): the elimination

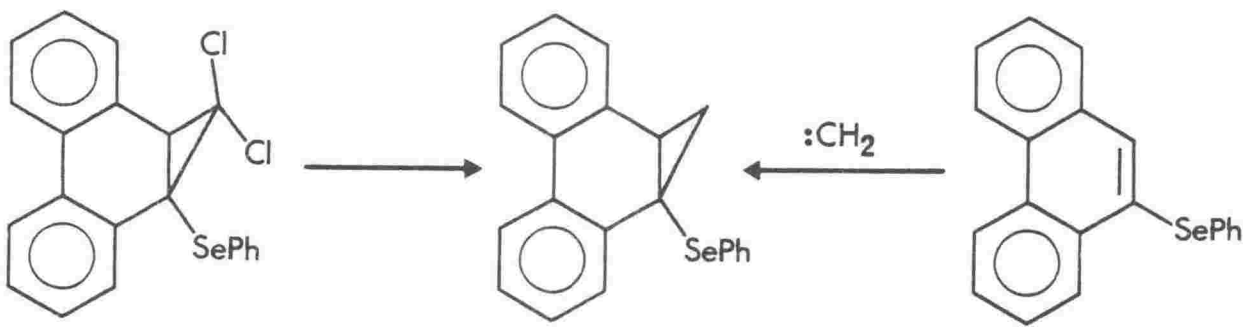


160 16a 161 63

Scheme 36

of RH_A would give the desired 1*H*-cycloproparene (16a), but the loss of RH_B or RH_C would give the 1a*H*-cycloproparene (63). The

loss of RH_A should be favoured since H_A is the most acidic proton present, but steric factors might dictate that RH_B or RH_C be lost, depending on the type of elimination involved. The possibility of an *anti*-elimination of RH_B is avoided by the use of a *syn*-elimination, and a method of choice would again appear to be the *syn*-selenoxide elimination of PhSeOH. This route requires the synthesis of selenide (162) (Scheme 37).



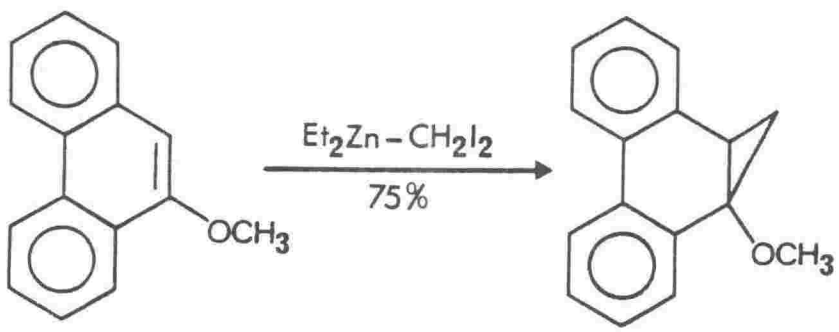
73 162 72

Scheme 37

The direct reduction of dichloro-selenide (73) (available from earlier studies - see Chapter Two) to compound (162) was not expected to succeed, because the phenylseleno group is itself easily reduced.[71] Indeed, the treatment of compound (73) with either lithium in t-butanol or lithium triethylborohydride produced only complex mixtures of products which did not contain the desired selenide (162).

The synthesis of compound (162) by the direct addition of methylene to 9-phenylselenophenanthrene (72) was also investigated. Compound (72) was treated with a large excess of methylene produced by the copper-catalysed decomposition of diazomethane,[113] but was recovered unchanged. Preliminary experiments showed that selenide (72) was also unaffected by the ultrasound-promoted variation[114] of the Simmons-Smith reaction, and so it was exposed to the potent reagent system diethylzinc-diiodomethane.[115] Diethylzinc was prepared, according to the literature procedure,[116] from iodoethane and a zinc-copper alloy made in these laboratories (Experimental). The efficacy of the

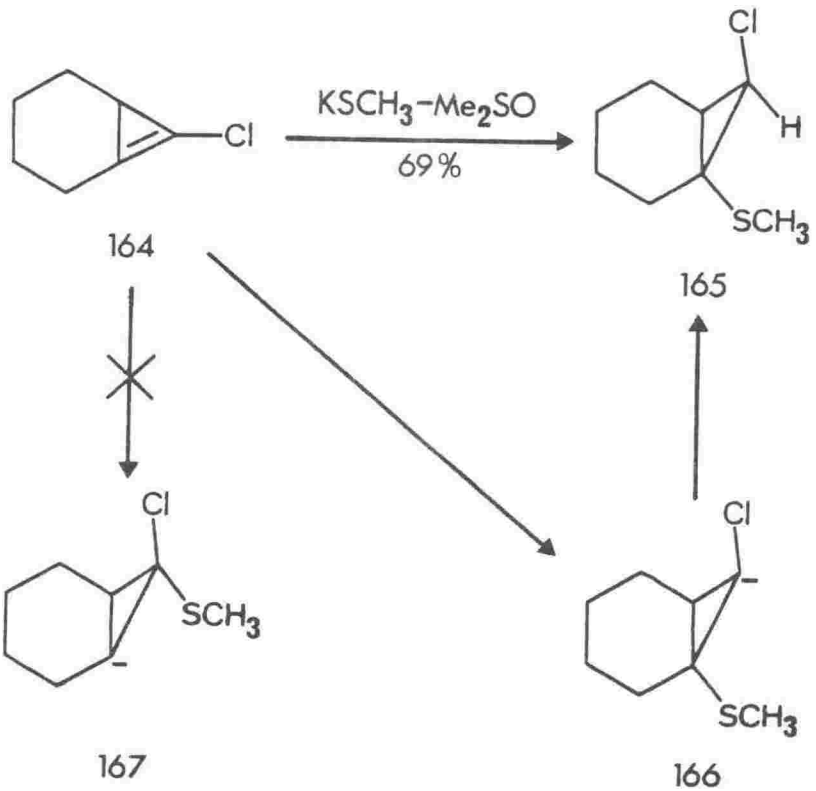
reagent system was checked by its reaction with cyclohexene in benzene-d_6. Proton nmr spectra of the reacting mixture showed the disappearance of cyclohexene and the appearance of high-field multiplets which were fully compatible with the presence of bicyclo[4.1.0]heptane. Furthermore, dihydro-compound (163) was isolated in 75% yield from the reaction of diethylzinc-diiodomethane with the electron-rich 9-methoxyphenanthrene.



163

Compound (163) was identified from its proton nmr spectrum which, in addition to aromatic and methoxyl resonances, displays three one-proton doublets of doublets at high field, due to H-1α, H-1β and H-9b. The carbon-13 and high-resolution mass spectra are also consistent with the assigned structure. Selenide (72), however, was found not to react with diethylzinc-diiodomethane, either under the conditions used for the formation of compound (163) (10 equiv. of reagent, toluene, 60°), at reflux temperature, or at 60° in the presence of oxygen[117] (to promote the formation of the radicaloid intermediates).

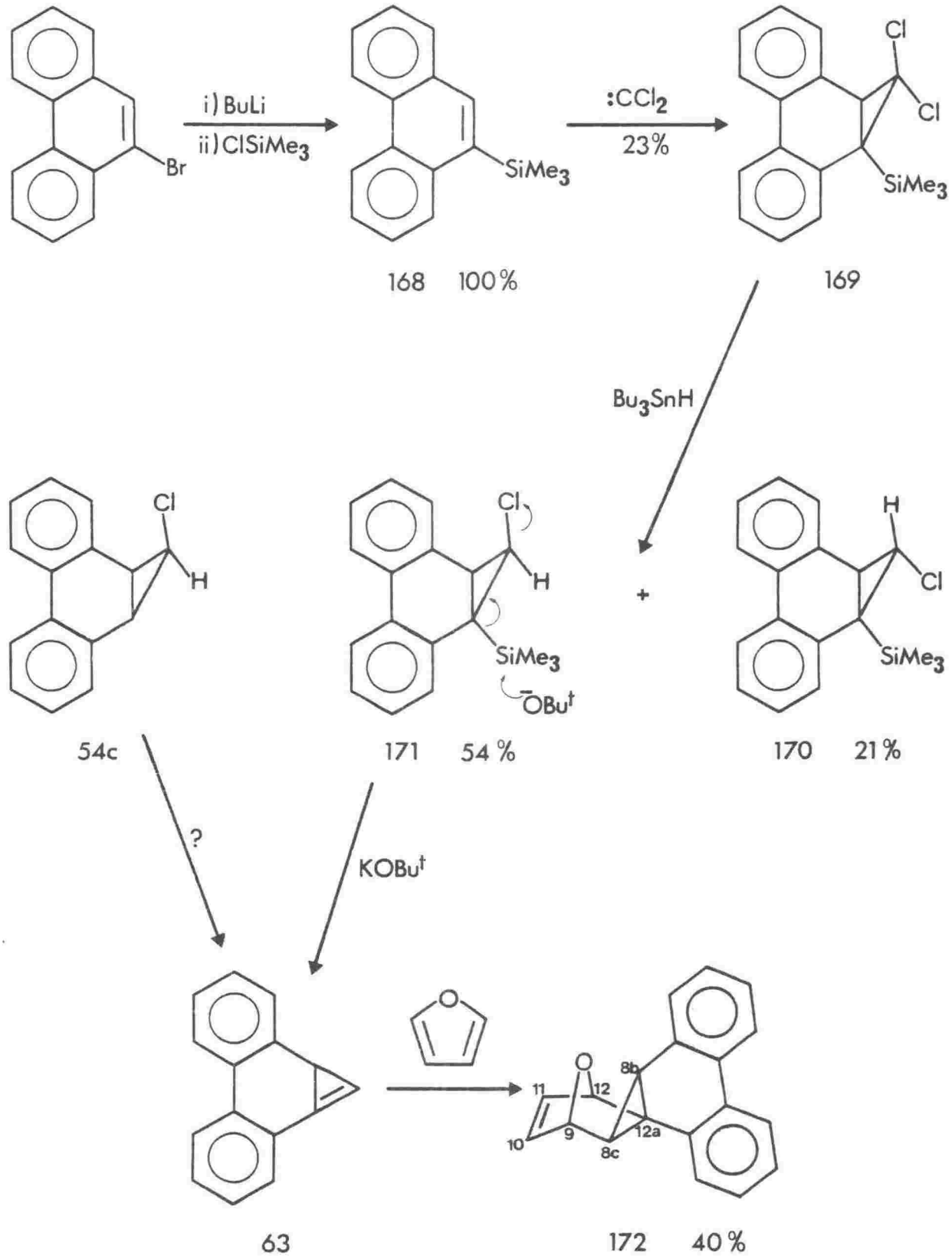
Alternative routes to 1a-substituted dihydrocyclopropa[*l*]phenanthrenes are severely restricted, but it was decided nevertheless to take advantage of the known[65,118] addition of nucleophiles to strained multiple bonds. In this way compound (164) has been intercepted[118a] with methylsulfide ion to give compound (165). The *syn*-geometry of addition is typical[65,118a,c,d] of such reactions, as is the high regioselectivity, which reflects the greater stability of anion (166) compared with its isomer (167) (Scheme 38). For this type of reaction to be useful in the synthesis of 1*H*-cyclopropa[*l*]phenanthrene, a nucleophile is needed which could cleanly intercept 1a*H*-cyclopropa[*l*]phenan-



Scheme 38

threne (63), and then be converted to a group which may be eliminated with H-9b. Organoselenium chemistry again appears the most useful: phenylselenide anion could be used to trap the strained cycloalkene, and *syn*-selenoxide elimination could then provide 1*H*-cyclopropa[*l*]phenanthrene.

1a*H*-Cyclopropa[*l*]phenanthrene (63) has been obtained[67] previously by a cycloheptatrienylidene-bicycloheptatriene rearrangement (Scheme 8), but the route to the carbene precursor was lengthy. An alternative precursor of compound (63) is the 1-chloro-dihydrocyclopropa[*l*]phenanthrene (54c), but since this compound is dehydrochlorinated only sluggishly[66] (or not at all[65]) with strong base, another route was sought (Scheme 39). Thus, 9-bromophenanthrene was reacted sequentially with butyllithium and chlorotrimethylsilane to provide crude 9-trimethylsilylphenanthrene (168) quantitatively.[119] This compound was then reacted with a large excess of chloroform-sodium hydroxide under phase transfer catalysis. After five days the mixture had become too viscous to be stirred efficiently and the reaction was stopped. A considerable amount of starting material


i) BuLi
ii) ClSiMe3
Br
SiMe3
168 100%
:CCl2
23%
Cl
Cl
SiMe3
169
Bu3SnH
Cl
H
54c
Cl
H
SiMe3
OBut
171 54%
+
H
Cl
SiMe3
170 21%
?
KOBut
O
11
12
8b
10
9
8c
12a
63
172 40%

Scheme 39

remained but it could not be recovered pure despite repeated chromatography. The major product was identified as 1,1-dichloro-1a-trimethylsilyl-1a,9b-dihydrocyclopropa[*l*]phenanthrene (169) (23% yield). The proton and carbon-13 nmr spectra are consistent with those obtained for the other dichlorodihydro-compounds synthesised in the present study, with signals due to H-9b at δ 3.12, C-1a at δ 32.5, C-9b at δ 38.8 and C-1 at δ 64.9. The compound was also characterised by mass spectral and elemental analysis.

Compound (169) was reduced with tributyltin hydride and the two products which resulted were separated by column chromatography. The mass spectrum of the more mobile compound shows the presence of only one chlorine atom, with molecular ions at m/z 298 and 300 in an intensity ratio of 3:1. The proton nmr spectrum displays a pair of one-proton spin-coupled doublets, J=3.5 Hz, at δ 2.77 and 3.08, in addition to resonances due to trimethylsilyl and aromatic protons. By virtue of the small coupling constant[120] between the high-field protons, the compound was identified as (1α,1aα,9bα)-1-chloro-1a-trimethylsilyl-1a,9b-dihydrocyclopropa[*l*]phenanthrene (170) (21% yield). As expected, the carbon-13 spectrum shows an upfield shift of C-1 compared with the same resonance in the dichloro-precursor (169). The compound was characterised by elemental analysis.

The less mobile product from the reaction of compound (169) with tributyltin hydride was identified as (1α,1aβ,9bβ)-1-chloro-1a-trimethylsilyl-1a,9b-dihydrocyclopropa[*l*]phenanthrene (171) (54% yield). The proton nmr spectrum contains one-proton doublets, J=7.3 Hz, at δ 2.70 and 3.60, and the large coupling constant establishes the stereochemistry.[120] The carbon-13, mass spectral and combustion data are also consistent with the assigned structure. The dominant formation of the (1α,1aβ,9bβ)-product may well reflect the preferential interception of the radical intermediate from its least hindered side.

Treatment of compound (171) with potassium t-butoxide led to the formation of the unstable[67] 1a*H*-cyclopropa[*l*]phenanthrene (63) which was trapped by Diels-Alder reaction with furan to

provide compound (172)† in 40% yield. This compound has also been reported by Coburn and Jones,[67] who assigned the *exo*-geometry of addition because of the negligible coupling[44d,121] between H-8c and H-9, and the low-field position of H-8b (δ 3.61) which requires its proximity to the bridging oxygen.[122,123] The spectral data obtained in this study are identical to those of Coburn and Jones. The *endo*-adduct was not observed in either study and although this result is not predicted by maximisation of secondary orbital overlap, it might be explained on steric grounds. Indeed, there have been a number of reports of cyclopropenes reacting with furans to give solely the *exo*-adducts.[44d,122-4]

Having established that 1a*H*-cyclopropa[*l*]phenanthrene (63) can be obtained by elimination of the elements of chlorotrimethylsilane from compound (171), it remained to intercept the ring-fused cyclopropene with phenylselenide anion. Therefore, a solution of silane (171) in dimethyl sulfoxide was treated with excesses of selenophenol and potassium t-butoxide. The reaction mixture decomposed considerably, but two products were isolated. Product A (Experimental) was identified as 1a-phenylseleno-1a,9b-dihydrocyclopropa[*l*]phenanthrene (162) (10% yield). The proton nmr spectrum contains three one-proton doublets of doublets due to H-1α, H-1β and H-9b, and there are thirteen aromatic protons. The low-resolution mass spectrum (18 eV) shows an envelope of molecular ions consistent with the presence of a selenium atom, with the most intense peak at m/z 348 ($C_{21}H_{16}{}^{80}Se$). The most abundant fragment has m/z 191, corresponding to [M-PhSe]. The compound was characterised by high-resolution mass measurement.

Product B has identical low- and high-resolution mass spectra to those of compound (162), but the high-field region of the proton spectrum contains a one-proton triplet at δ 1.84 and a

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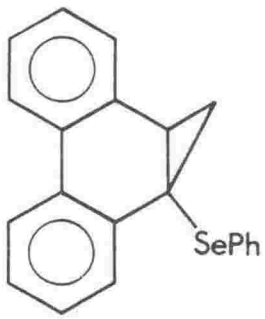
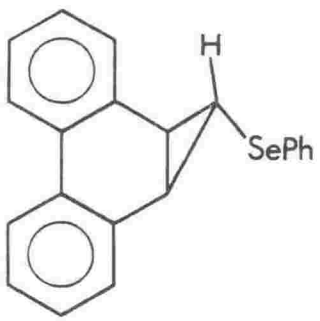
† Compound (172) may be named as (8bα,8cβ,9α,12α,12aR*)-8b,8c,9,12-tetrahydro-9,12-epoxybenzo[1,3]cyclopropa[1,2-*l*]phenanthrene.



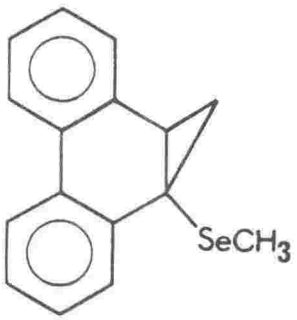
162



173

two-proton doublet at δ 2.90, J=3.9 Hz. The size of the coupling constant[120] establishes the compound to be (1α,1aα,9bα)-1-phenylseleno-1a,9b-dihydrocyclopropa[*l*]phenanthrene (173) (15% yield), with the triplet being due to H-1β and the doublet being due to the magnetically equivalent H-1a and H-9b. Such a lack of regioselectivity of addition has not been previously observed in the reaction of bridgehead cyclopropenes with nucleophiles, but presumably compound (173) is formed, *via* a less stable tertiary anion, because the bulky phenylselenide nucleophile is more hindered in its attack of the cyclopropene at the bridgehead than are other less sterically demanding trapping agents. The stereochemistry of compound (173) indicates a *syn*-addition[65,118a,c,d] of selenophenol, and the alternative (1α,1aβ,9bβ)-product of *anti*-addition was not detected.

The non-regioselective addition of phenylselenide anion to compound (63) makes this an inefficient route to a bridgehead-substituted precursor of 1*H*-cyclopropa[*l*]phenanthrene. In contrast, the addition of methylselenide anion was regiospecific. When a mixture of silanes (170) and (171) was reacted with excesses of lithium methylselenide and freshly-dried tetrabutylammonium fluoride, a single product was formed and it was identified as 1a-methylseleno-1a,9b-dihydrocyclopropa[*l*]phenanthrene (174) (80% yield). The proton nmr spectrum contains, in addition to one-proton doublets of doublets due to H-1α, H-1β and H-9b, a three-proton singlet ($-SeCH_3$) at δ 2.00 with selenium-77 satellites,[125] $^2J_{Se-H}$=10.7 Hz. Compound (174) was isolated as a gum which slowly polymerised on standing, and it was characterised by high-resolution mass spectral analysis. The synthe-

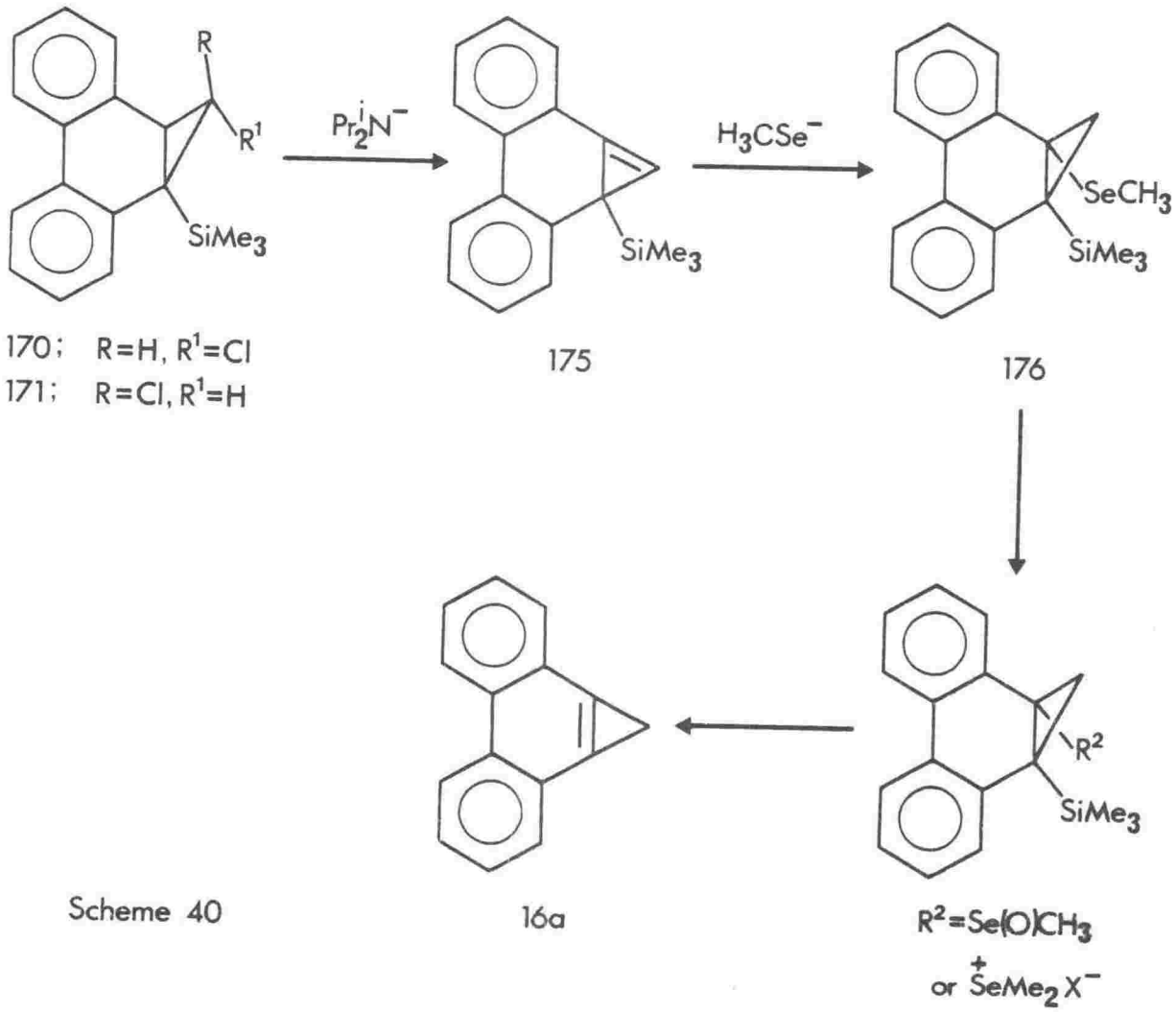


174

ses of compounds (162), (173) and (174) are the first examples of the addition of selenium nucleophiles to a cyclopropene.

Whereas the treatment of silanes (170) and (171) with oxygen or fluoride nucleophiles causes elimination of the elements of chlorotrimethylsilane, the same compounds might be dehydrochlorinated with a nitrogenous base, which will not attack silicon readily. The resultant cyclopropene (175) could be trapped with a nucleophile, such as methylselenide ion, to give compound (176). Alkylation or oxidation of the selenium substituent would provide a leaving group β to silicon, and then reaction with a fluoride or an oxygen nucleophile should give solely the desired cyclopropparene (Scheme 40). In preliminary experiments, however, silanes (170) and (171) failed to give discrete products from reaction with lithium diisopropylamide-lithium methylselenide.

Since methyl selenoxides undergo *syn*-selenoxide elimination only slowly,[71] the selenoxide derived from compound (174) is unlikely to be a good progenitor of 1*H*-cyclopropa[*l*]phenanthrene. Halazy and Krief[126] have reported, however, a facile, base-induced conversion of dimethyl- and methylphenyl-selenonium salts to olefins whereby, for example, the 1-dodecylselenonium salts (177a,b) gave 1-dodecene in good yield upon treatment with potassium hydroxide or potassium t-butoxide. A methylene selenurane (178) was proposed to be an intermediate in the reaction (Scheme 41), since the diphenylselenonium salt (177c) failed to give any 1-decene under comparable conditions. Were a simple E2 mechanism to operate, then compound (177c)



170; R=H, R^1=Cl
171; R=Cl, R^1=H

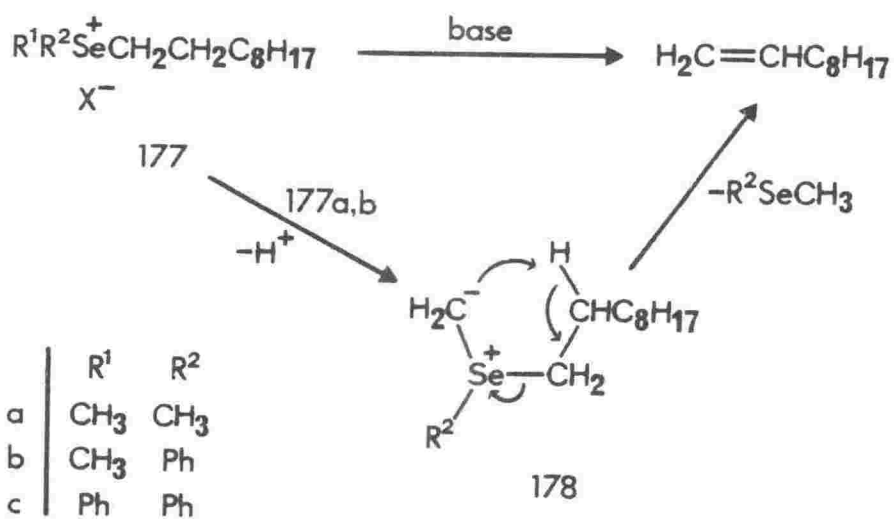
175

176

16a

R^2=Se(O)CH_3
or $\overset{+}{S}eMe_2X^-$

Scheme 40



	R^1	R^2
a	CH_3	CH_3
b	CH_3	Ph
c	Ph	Ph

178

Scheme 41

should be an olefin precursor equally as good as compounds (177a,b) (diphenyl selenide should be at least as good a leaving group as dimethyl or methylphenyl selenide). A similar, ylid-based mechanism has been proposed[89] for elimination reactions of some sulfonium salts.

By analogy with the method of Halazy and Krief,[126] compound (174) was methylated with iodomethane-silver tetrafluoroborate and the crude product, the dimethylselenonium tetrafluoroborate (179), was treated with excesses of potassium t-butoxide and furan (Scheme 42). After 20 h of reaction at 20°, three compounds were isolated from the multicomponent product mixture. Product A (Experimental) was obtained as white prisms, m.p. 178-9°. The proton nmr spectrum (Fig.1) contains two one-proton spin-coupled doublets, J=4.6 Hz, at δ 0.58 and 2.56, broadened two-proton singlets at δ 5.26 and 6.34, and resonances due to eight aromatic protons. The compound was characterised by its carbon-13 and high-resolution mass spectra, and was identified as the *endo*-adduct* (180) (20% yield) of 1*H*-cyclopropa[*l*]phenanthrene and furan. The geometry is assigned by the chemical shifts of the protons at C-13: the proton at δ 0.58 is *anti* to the oxygen bridge and above the dihydrophenanthrene π-system, while the deshielded proton at δ 2.56 is *syn* to the oxygen bridge.[122,123]

Product B was identical to the previously synthesised *exo*-adduct (172) of 1a*H*-cyclopropa[*l*]phenanthrene and furan. The yield was 7%.

Product C was obtained as white prisms, m.p. 183-90° (decomp.). The proton nmr spectrum (Fig.2) is similar to that of compound (180), except that the high-field doublets are at δ 0.78 and 1.98. These doublets are assigned to the protons at C-13 of the *exo*-adduct* (181) (13% yield) of 1*H*-cyclopropa[*l*]phenan-

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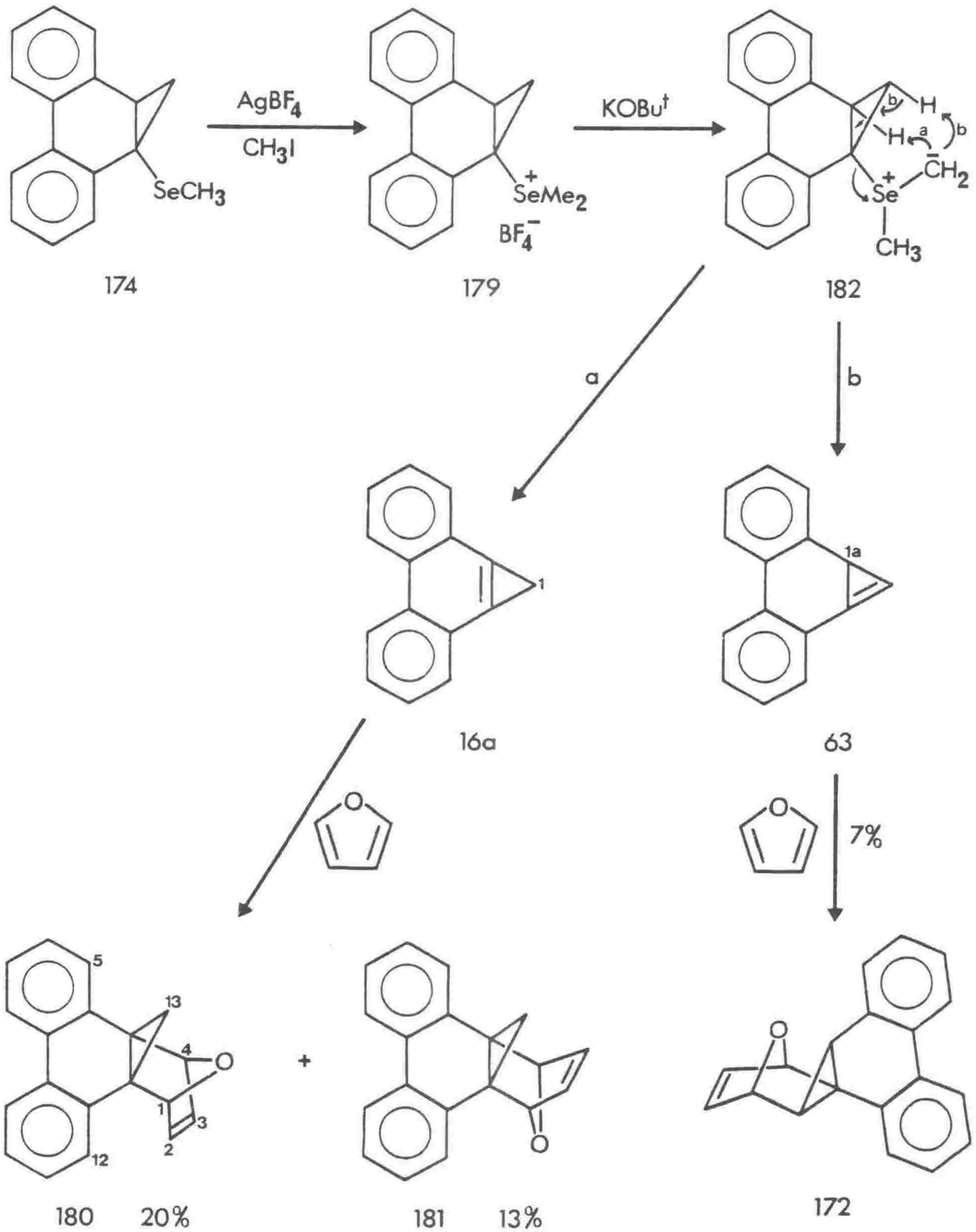
* Compounds (180) and (181) may be named as (1α,4α,4aα,12bα)- and (1α,4α,4aβ,12bβ)-1,4,4a,12b-tetrahydro-1,4-epoxy-4a,12b-methanotriphenylene respectively.



174 179 182

16a 63

180 20% 181 13% 172

Scheme 42

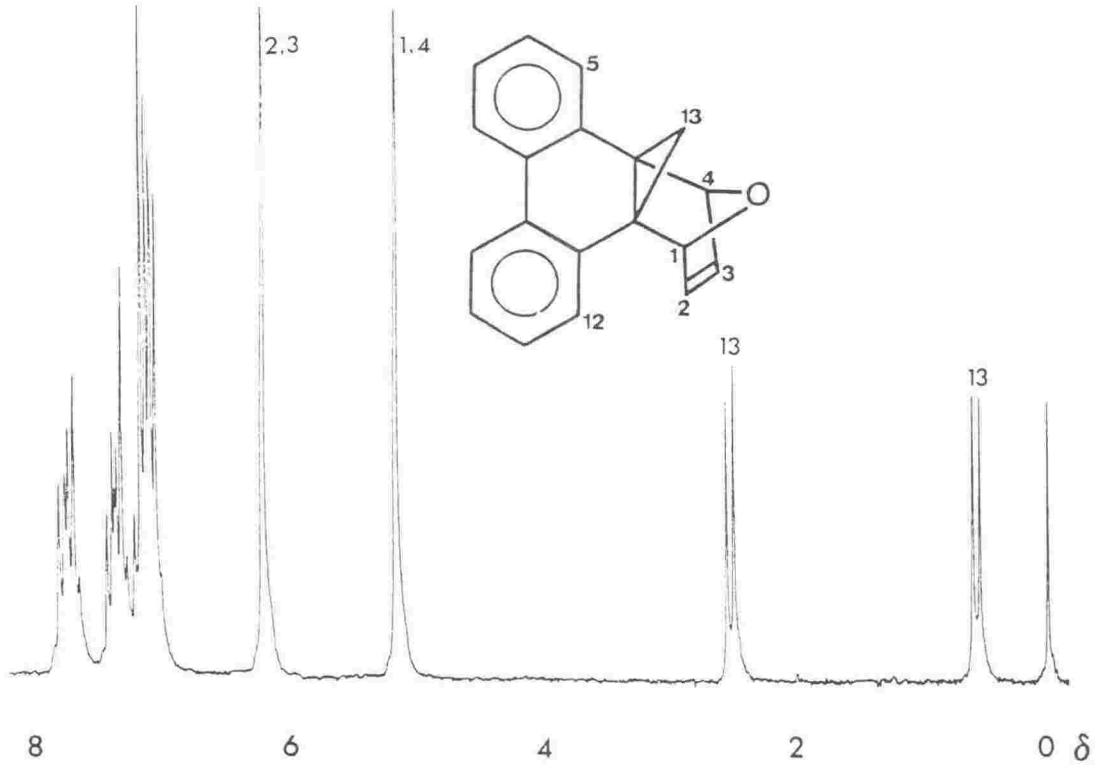


Fig. 1. Proton Nmr Spectrum of Compound (180)

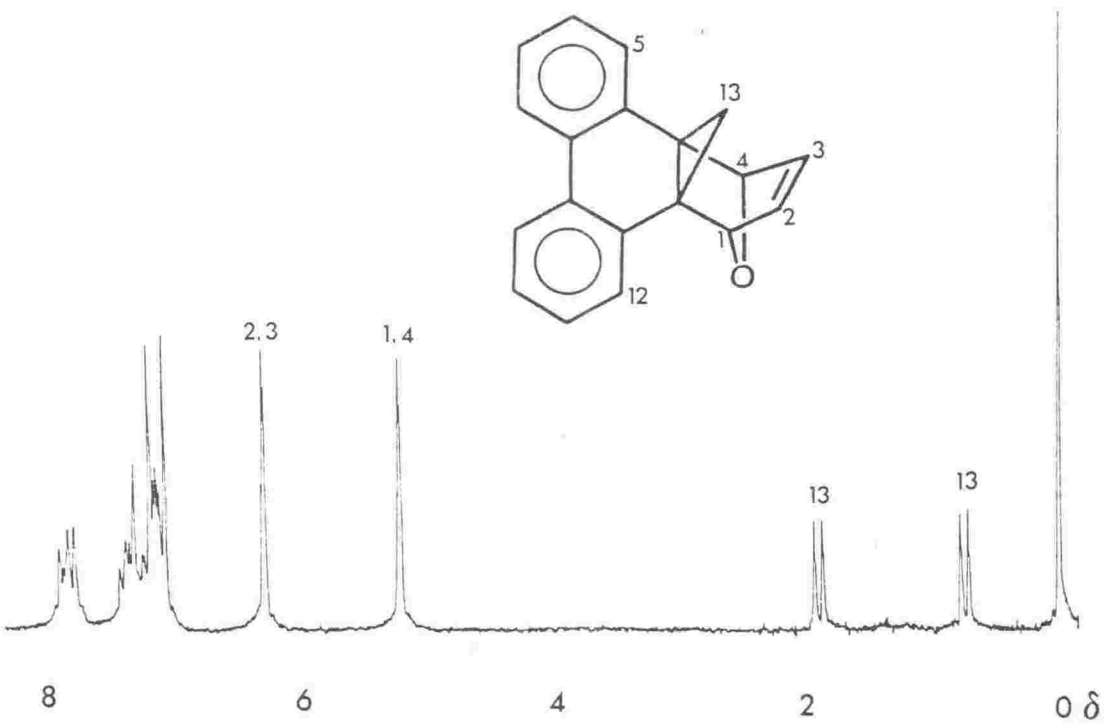


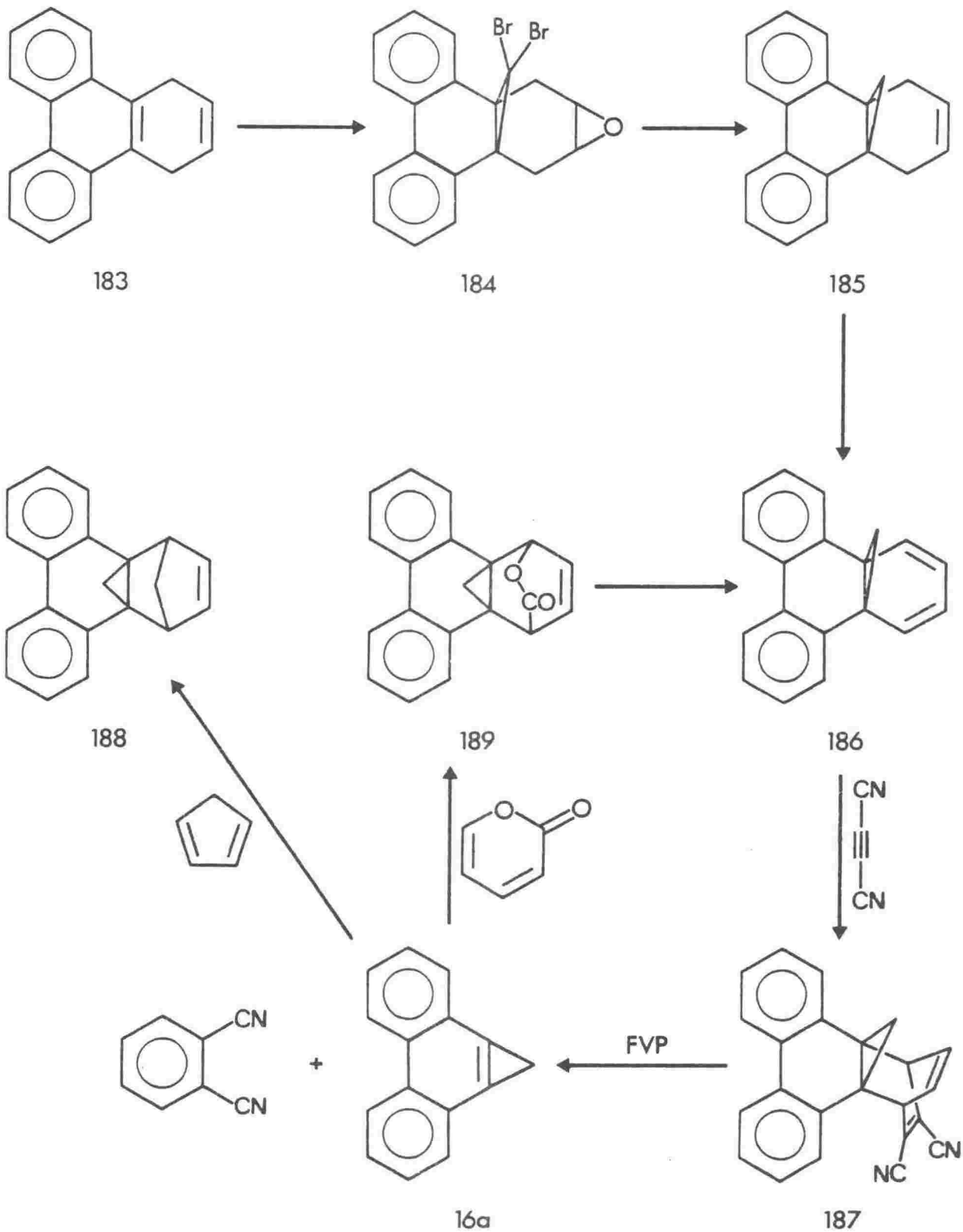
Fig. 2. Proton Nmr Spectrum of Compound (181)

threne and furan. The doublet at higher field is again due to the proton which is above the dihydrophenanthrene π-system, and the doublet at δ 1.98 (0.58 ppm higher field than the corresponding proton in the *endo*-adduct) is due to the proton which is *syn* to, and shielded by, the C-2,3 'etheno bridge'. The compound was again characterised by its carbon-13 and high-resolution mass spectra.

The isolation of compounds (180) and (181) provides conclusive evidence that the long sought-after 1*H*-cyclopropa[*l*]phenanthrene (16a) is generated under the conditions described. The formation of both *endo*- and *exo*-furan adducts is not surprising, since Alder's *endo* rule is often violated for [4+2] cycloadditions with cyclopropenes, perhaps because of steric factors in the transition state structure.[127] Preliminary experiments have shown that no discrete products are obtained when the selenonium salt (179) is treated with base in the absence of a trapping agent, and this may give an indication of the thermal and/or chemical instability of the cyclopropa rene.

Provided that 1*H*- and 1a*H*-cyclopropa[*l*]phenanthrene are trapped by furan equally efficiently, these results show that route *a* (Scheme 42) for the elimination of dimethyl selenide from compound (182) is favoured by a factor of five over route *b*. The pathway depicted in Scheme 42, therefore, is a way of selectively generating 1*H*-cyclopropa[*l*]phenanthrene from a bridgehead-substituted dihydrocyclopropa[*l*]phenanthrene. (An ylid-based mechanism is shown in Scheme 42, but an E2 mechanism might operate instead; the argument is not affected)

Simultaneously with the work in these laboratories, and in collaboration with us, Vogel *et al.*[33] have prepared 1*H*-cyclopropa[*l*]phenanthrene in milligram quantities by the route shown in Scheme 43. Thus, the mono-epoxidation of dihydrotriphenylene (183) followed by the addition of dibromocarbene led to compound (184), which was reductively debrominated and the double bond deprotected to afford compound (185). Bromination and subsequent bis-dehydrobromination gave the norcaradiene (186), which was reacted with dicyanoacetylene to provide the



183 184 185

188 189 186

16a 187

Scheme 43

[4+2] cycloadduct (187). Retrodiene cleavage of this compound at 400° and 2×10^{-3} torr gives a product mixture whose low-temperature (-90°) proton nmr spectrum shows the presence of phthalodinitrile and 1*H*-cyclopropa[*l*]phenanthrene. There is a singlet due to H-1 at δ 3.47, which is within the range of chemical shifts reported for the methylene protons of other cycloproparenes.[1] The compound is unstable above -70° and thus far has not been isolated pure. The cyclopentadiene adduct(s) (188), of undefined stereochemistry, was also prepared by Vogel's group, and the formation of an α-pyrone addition product (189) was inferred from the isolation of the norcaradiene product (186) of carbon dioxide expulsion. Vogel *et al*. have since trapped the cycloproparene with furan: the products isolated and the ratio of *endo*- to *exo*-addition are the same as those obtained in these laboratories. In the present study, no evidence has been obtained for the formation of compound (186) from the reaction of selenonium salt (179) with potassium t-butoxide in the presence of α-pyrone. Despite variations in the amount of base used and in the order of addition of the reagents (Experimental), a procedure has not yet been devised to enable the cycloproparene to be formed in the presence of, and be trapped by, this base-sensitive[128] diene.

The instability of 1*H*-cyclopropa[*l*]phenanthrene will probably preclude its isolation from solution-phase reaction mixtures by conventional extractive work-up. The selenonium salt route (Scheme 42) might be adapted, however, to provide the cycloproparene if the salt were to be passed through solid-supported potassium t-butoxide under vacuum pyrolytic conditions.[129] A lack of appropriate equipment in these laboratories has precluded such an experiment.

The pathways of Schemes 42 and 43 constitute two routes to the hitherto elusive 1*H*-cyclopropa[*l*]phenanthrene, and the properties of this latest addition to the class of cycloproparenes can now be investigated in detail.

CHAPTER FIVE

EXPERIMENTAL

General Methods

Melting points were determined by use of a Reichert hot stage apparatus and were not corrected. Elemental analyses were performed by Professor A. Campbell and associates, University of Otago. High-resolution mass spectra were recorded by Dr. G. Wright and associates, University of Canterbury, on an A.E.I. MS902 instrument. Glc-mass spectra were recorded by Dr. R. Furneaux and Ms J. Mason, Chemistry Division, D.S.I.R., Petone, on a Shimadzu QP-1000 instrument, in Chemical Ionisation (CI) mode. Low-resolution mass spectra were recorded on a Micromass 12F instrument, operating at 70 eV unless stated otherwise. Infrared spectra were recorded for Nujol mulls or for thin films on a Pye-Unicam SP3-100 or a Perkin-Elmer 599B spectrophotometer. Nuclear magnetic resonance spectra were recorded on a Varian FT-80A instrument at 79.56 MHz for H-1 and 20.00 MHz for C-13; deuterochloroform was used as the solvent unless stated otherwise; chemical shifts are expressed in ppm downfield from internal tetramethylsilane and nmr resonance multiplicities are defined by the usual notation.

Solvents were purified and dried according to the methods given by Perrin, Armarego and Perrin.[130] The 'hexanes' used throughout this work are the fraction of light petroleum, b.p. 66-68°. Tetrahydrofuran and 1,2-dimethoxyethane were distilled from sodium benzophenone ketyl immediately before use. Reactions performed 'under nitrogen' were carried out in apparatus equipped with rubber septa and syringe needle inlets and outlets for oxygen-free nitrogen which had been passed through a sulfuric acid-sodium hydroxide drying tower. Air- and moisture-sensitive reagents were transferred by syringe techniques. Where possible, reactions were followed by tlc, on commercially prepared plates coated with Merck Kieselgel 60 F_{254} to a thickness of 0.2 mm. Components were detected under an ultraviolet lamp (254 and 350 nm), in an iodine chamber, or by spraying with anisaldehyde-

sulfuric acid and heating. Preparative layer chromatography (plc) was performed on glass plates (1000x200 mm) coated with Merck Kieselgel GF_{254} to a thickness of 0.75 mm; the separated components were extracted with ethyl acetate (50 cm^3). Riedel de Haën Silica Gel S (0.063-0.1 mm) was used for column chromatography, and flash chromatography was performed with Riedel de Haën Silica Gel S (0.032-0.063 mm). Preparative glc was performed on a Pye Series 105 instrument, with columns and conditions as stated.

Organic solutions obtained by extractive work-up were dried with magnesium sulfate, which was then removed by filtration under vacuum. Solvents were removed by use of a rotary evaporator and then an oil pump. Unless stated otherwise, the quoted yields refer to recrystallised or (for gums) chromatographically homogeneous material.

Tetrabutylammonium fluoride was 'dried' by co-evaporation of a commercial tetrahydrofuran solution with toluene, on a rotary evaporator equipped with a water bath maintained below 30°; it was used immediately. (For a discussion of the drying of tetrabutylammonium fluoride, the reader is referred to Ref. 131)

The following materials were prepared by the literature procedures: diazomethane[132]; 4,4'-dichlorodiphenyl diselenide (73% yield, lit.[133] 75%); diphenyl diselenide (75%, m.p. 62-65°, lit.[133] 75%, 63-65°); lithium methylselenide[134]; mercury(II) trifluoroacetate[85]; 9-methoxyphenanthrene[135]; 1-methyl-1-phenylethanol (153) (60%, b.p. 60-61°/1.2 mm, lit.[111] 50%, 60-65°/4 mm); 1-methyl-1-phenylethyl acetate[108] (149); *N*-(2-methyl-1-propenyl)pyrrolidine (125) (80%, b.p. 49°/12 mm, lit.[136] 89%, 46°/11 mm); methylthiomethyl acetate (150) (b.p. 50°/15 mm, lit.[109] 48.5°/12 mm); phenylselenenyl bromide[137]; phenylselenenyl chloride[137,138]; phenyltrifluoromethylmercury (101) (72%, m.p. 140-142°, lit.[86] 77%, 141-143°); selenophenol (78%, b.p. 78-80°/20 mm, lit.[139] 86%, 60-63°/30 mm); *p*-toluenesulfonyl azide[140]; trifluoromethylmercury(II) bromide[86]; trifluoromethylmercury(II) trifluoroacetate (55%, lit.[85] 53%).

9-Phenylthiophenanthrene (68)

To a stirred solution of 9-bromophenanthrene (3.54 g, 13.8 mmol) in dry ether (40 cm^3), under nitrogen, was added a solution of butyllithium in hexane (1.6 mol dm^{-3}, 10 cm^3, 1.2 mol. equiv.), dropwise over 5 min. The suspension which resulted was allowed to settle and the supernatant was removed by syringe. The remaining slurry of 9-phenanthrenyllithium was stirred and a solution of diphenyl disulfide (3.00 g, 13.8 mmol) in ether (15 cm^3) was added by dropping funnel over 10 min. The mixture was stirred 10 min more, then quenched with water (50 cm^3); the whole was transferred to a separatory funnel, toluene (200 cm^3) was added, the layers were separated and the organic phase was washed with water (1x30 cm^3), dried and concentrated to a yellow solid. Recrystallisation (toluene/ethanol) gave pale yellow crystals of 9-phenylthiophenanthrene (68) (3.36 g, 85%), m.p. 143-144° (lit.[72] 134-136°, 141-143°) (Found: C, 83.4; H, 4.5; S, 11.0. Calc. for $C_{20}H_{14}S$: C, 83.9; H, 4.9; S, 11.2%). C-13 δ 122.6, 123.0, 126.2, 126.5, 126.9, 127.0, 127.1, 127.3, 128.4, all C-H; 129.0, 4 C-H; 129.9, 130.6, 131.1, 131.7, all quaternary; 133.8, C-10; 136.7, quaternary.

1,1-Dichloro-1a-phenylthio-1a,9b-dihydrocyclopropa[l]phenanthrene (69)

To a solution of 9-phenylthiophenanthrene (68) (1.00 g, 3.50 mmol) in chloroform (100 cm^3) was added benzyltriethylammonium chloride (30 mg, 4 mol %) and aqueous sodium hydroxide (50% w/v, 120 cm^3). The resultant two-phase mixture was stirred at 20° until no starting material remained (tlc, 2 d); the layers were separated and the organic phase was washed with water (100 cm^3), dried and concentrated. The residue was column chromatographed (15:1 hexanes:ether) to give a yellow solid, which was recrystallised from toluene/hexanes to provide white prisms of *1,1-dichloro-1a-phenylthio-1a,9b-dihydrocyclopropa[l]phenanthrene* (69) (1.06 g, 82%), m.p. 126-128°. A sample from ether/hexanes had m.p. 127.5-128.5° (Found: C, 68.3; H, 3.9; Cl, 19.5; S, 8.4. $C_{21}H_{14}Cl_2S$ requires C, 68.3; H, 3.8; Cl, 19.2; S, 8.7%). H-1 δ 3.45, s, 1H, H-9b; 6.9-7.1, m, 5H; 7.2-8.2, m, 8H. C-13 δ

43.6, C-1a; 46.0, C-9b; 64.6, C-1; 122.5, 123.3, 126.4, all C-H; 127.4, quaternary; 128.2, 128.4, 128.7, 128.9, 130.6, 130.6, all C-H; 132.3, 134.6, both quaternary. m/z 372, 370, 368 (10:65:100, M).

9-(4'-Chlorophenylseleno)phenanthrene (71)

To a stirred solution of 9-bromophenanthrene (4.93 g, 19.2 mmol) in dry ether (20 cm^3), under nitrogen, was added a solution of butyllithium in hexane (1.6 mol dm^{-3}, 14 cm^3, 1.1 mol. equiv.), dropwise over 5 min. The resultant white suspension was allowed to settle and the supernatant was removed by syringe. The residue was re-suspended in ether (20 cm^3) and a solution of 4,4'-dichlorodiphenyl diselenide (7.30 g, 19.2 mmol) in ether (20 cm^3) was added dropwise during 15 min. The mixture was stirred 10 min more; water (50 cm^3) was added, followed by toluene (100 cm^3). The layers were separated and the organic phase was dried and concentrated. The residue was column chromatographed (hexanes) and the eluate, after concentration, was crystallised from ethanol to afford off-white *9-(4'-chlorophenylseleno)phenanthrene* (71) (4.18 g, 59%). A sample provided white needles from dichloromethane, m.p. 144-145° (Found: C, 65.6; H, 4.1; Cl, 9.9. $C_{20}H_{13}ClSe$ requires C, 65.3; H, 3.6; Cl, 9.6%). C-13 δ 122.7, 123.0, 127.0, 127.1, 127.3, 127.5, 128.5, 128.5, 129.4, all C-H; 130.1, 130.9, 131.0, 131.9, 132.1, all quaternary; 132.6, C-H; 133.0, quaternary; 135.7, C-H.

1,1-Dichloro-1a-(4'-chlorophenylseleno)-1a,9b-dihydrocyclopropa[l]phenanthrene (70)

To a solution of 9-(4'-chlorophenylseleno)phenanthrene (71) (1.49 g, 3.30 mmol) in chloroform (20 cm^3) was added benzyltriethylammonium bromide (36 mg, 4 mol %) and aqueous sodium hydroxide (50% w/v, 10 cm^3). The two-phase mixture which resulted was stirred at 20°. Portions of chloroform (10 cm^3) and aqueous sodium hydroxide (50% w/v, 10 cm^3) were added at five-day intervals until, after 20 days, the layers were separated and the organic phase was washed with water (40 cm^3), dried and concentrated to a yellow-brown gum. This residue was subjected to plc (pentane, 2 developments). Band A, Rf

0.6-0.7, gave a white solid identified as starting material (110 mg, 7%), having, after recrystallisation from dichloromethane, m.p. and m.m.p. 143-144°. Band B, R_f 0.4-0.5, provided a yellow gum (380 mg) which was crystallised from toluene/ethanol to afford white leaflets of *1,1-dichloro-1a-(4'-chlorophenylseleno)-1a,9b-dihydrocyclopropa[l]phenanthrene* (70) (300 mg, 20%), m.p. 132.0-133.5°. A sample from the same solvent mixture had m.p. 132.5-133.5° (Found: C, 56.1; H, 3.1; Cl, 23.6. $C_{21}H_{13}Cl_3Se$ requires C, 56.0; H, 2.9; Cl, 23.6; Se, 17.5%). H-1 δ 3.50, s, 1H, H-9b; 6.9-7.4, m, 9H; 7.8-8.1, m, 3H. C-13 δ 40.6, C-1a; 46.4, C-9b; 64.3, C-1; 122.6, 123.3, both C-H; 127.5, 127.9, both quaternary; 128.1, 128.2, 128.5, 128.7, all C-H; 129.3, C-3' and C-5'; 130.7, C-H; 131.2, 132.1, both quaternary; 132.3, C-H; 133.5, quaternary; 133.8, C-2' and C-6'; 134.1, quaternary. m/z 450 ($C_{21}H_{13}{}^{35}Cl_3{}^{80}Se$).

9-Phenylselenophenanthrene (72)

To a stirred solution of 9-bromophenanthrene (32.20 g, 0.125 mol) in dry ether (150 cm^3), under nitrogen, was added a solution of butyllithium in hexane(1.6 mol dm^{-3}, 85 cm^3, 1.1 mol. equiv.), dropwise over 20 min. The resultant suspension was allowed to settle and then the supernatant was removed by syringe. The residue was re-suspended in ether (50 cm^3) and a solution of phenylselenenyl chloride (24.00 g, 0.126 mol) in ether (150 cm^3) was added by dropping funnel over 1 h. The resultant slurry was stirred for 10 min and then the reaction was quenched with water; the slurry was filtered and the filter cake washed with ether (50 cm^3). The solid remaining was partitioned between toluene (500 cm^3) and water (300 cm^3); the toluene layer was dried and concentrated, and the residue was crystallised from toluene/ethanol to provide off-white crystals of 9-phenylselenophenanthrene (72) (31.25 g, 75%), m.p. 158.5-160.5° (lit.[73] 158-159°). C-13 δ 122.7, 123.0, both C-H; 126.8-127.3, 5 C-H; 128.2, quaternary; 128.4, 128.7, 129.3, all C-H; 130.8, 130.9, both quaternary; 131.7, C-H; 132.0, 132.3, both quaternary; 135.3, C-10.

1,1-Dichloro-1a-phenylseleno-1a, 9b-dihydrocyclopropa[1]-phenanthrene (73)

To a solution of 9-phenylselenophenanthrene (72) (5.00 g, 15.0 mmol) in chloroform (600 cm^3) was added benzyltriethylammonium chloride (0.68 g, 20 mol %) and aqueous sodium hydroxide (50% w/v, 400 cm^3). The resultant two-phase mixture was stirred at 20° until no starting material remained (tlc, 5d); the layers were separated and the organic phase was washed with water (300 cm^3), dried and concentrated to a thick brown oil, which was column chromatographed (30:1 hexanes: ether) to provide a yellow gum. Crystallisation from toluene/ethanol afforded off-white prisms of *1,1-dichloro-1a-phenylseleno-1a, 9b-dihydrocyclopropa[1]phenanthrene* (73) (2.20 g, 35%), m.p. 110-112°. A recrystallisation from the same solvent mixture gave white prisms, m.p. 113-114°, which yellowed on standing (Found; C, 60.6; H, 3.6; Cl, 17.3. $C_{21}H_{14}Cl_2Se$ requires C, 60.6; H, 3.4; Cl, 17.0; Se, 19.0%). H-1 δ 3.49, s, 1H, H-9b; 6.9-7.4, m, 10 H; 7.7-8.2, m, 3H. C-13 δ 40.4, C-1a; 46.2, C-9b; 64.6, C-1; 122.5, 123.1, 127.4, all C-H; 128.0, 2 C-H; 128.3, 128.5, 129.0, all C-H; 129.7, quaternary; 130.6, C-H; 131.6, 131.9, both quaternary; 132.3, 132.5, both C-H. m/z 416 ($C_{21}H_{14}{}^{35}Cl_2{}^{80}Se$).

Synthesis of Selenoxide (74) from Selenide (73)

m-Chloroperbenzoic acid (1.3 mol. equiv.) was added in one portion to a solution of selenide (73) (0.1-3.0 mmol) in dichloromethane (5-50 cm^3) at -10°. When formation of the *selenoxide* (74) was complete (tlc, 1-5 min), the solution was washed with cold aqueous sodium hydroxide (2 mol dm^{-3}, 5-20 cm^3) and filtered through a pad of magnesium sulfate into a flask suitable for further reaction. On one occasion the filtrate was concentrated, then dissolved in deuterochloroform. The H-1 nmr spectrum showed a singlet at δ 4.21 (H-9b), together with aromatic multiplets.

Decomposition of Selenoxide (74) in Dichloromethane-Pyridine

To a solution of selenoxide (74), derived from selenide (73) (1.03 g, 2.47 mmol), in dichloromethane (20 cm^3), prepared as described (p. 87), was added pyridine (2 cm^3). The mixture was stirred at 20° until selenoxide (74) could no longer be observed (tlc, 18 h), whereupon it was filtered and column chromatographed (neutral alumina, pentane followed by ether). The pentane-mobile fraction was an inseparable mixture of diphenyl diselenide and 9-trichloromethylphenanthrene (75) (5-7% by nmr), characterised as described on p. 90. The ether-mobile fraction was concentrated to a yellow gum (34 mg), which showed 3-4 spots on tlc. The H-1 nmr spectrum was recorded, and no significant change in it was noticed after methanol (0.1 cm^3) had been added. Characterisation of this product mixture was not pursued. The rest of the product was dark brown and remained at the top of the column.

Reaction of Selenoxide (74) with Hydrogen Chloride

Hydrogen chloride was bubbled slowly for 5 min through a solution of selenoxide (74) (prepared in the usual way from selenide (73) (58 mg, 0.139 mmol) in toluene (10 cm^3), maintained at -20°. The reaction mixture was diluted with toluene (10 cm^3), washed with aqueous sodium hydroxide (2 mol dm^{-3}), water (1x15 cm^3), dried and concentrated to leave crude 9-trichloromethylphenanthrene (75) (48 mg, 110%). The proton nmr and mass spectra were identical to those obtained below (p.90).

Decomposition of Selenoxide (74) in Dichloromethane-Pyridine-t-Butyl Hydroperoxide

To a solution of selenoxide (74), derived from selenide (73) (926 mg, 2,226 mmol), in dichloromethane (20 cm^3), prepared as outlined previously (p. 87), was added pyridine (0.5 g, 3 mol. equiv.) and t-butyl hydroperoxide (3.0 g, 15 mol. equiv.). The mixture was stirred at 20° until selenoxide (74) could no longer be detected (tlc, 30 h). The reaction mixture was filtered, concentrated and column chromatographed (pentane

followed by ether). A large amount of polymeric material was left on the column.

The pentane-mobile fraction was a colourless gum (< 5 mg) which showed tlc characteristics identical to those of 9-trichloromethylphenanthrene (75) (see below).

The ether eluate was washed with hydrochloric acid (1 mol dm^{-3}, 50 cm^3) to remove pyridine, then with water (50 cm^3). It was dried and concentrated to a yellow-brown gum (120 mg), which was subjected to plc (20:1 hexanes:ether). There were three mobile bands (A, R_f 0.6-0.7; B, R_f 0.3-0.5; C, R_f 0.1-0.2) and a brown baseline.

Band A gave a pale yellow unidentified gum (77) or (78) (10 mg, 1.3%), H-1 δ 1.09, s, 9H, $-C(CH_3)_3$; 5.99, s, 1H; 7.2-7.5, m, 5H; 7.6-8.0, m, 3H. C-13 δ 26.4, $-CH_3$; 80.5, C-H; 124.0, 124.1, 127.4, 128.0, 129.2, 130.3, 130.4, 130.9, all C-H. m/z (18 eV) 352, 350, 348 (M, 12:62:100). 278 (8, $M-Cl_2$); 263, 261, 259 (10:64:100, $M-C_4H_9O_2$); 222 (32, $M-Cl_2-C_4H_8$); 205 (10%, $M-Cl_2-C_4H_8O$).

Band B furnished a white solid identified as *t-butyl 10-chlorophenanthrene-9-carboxylate* (79) (50 mg, 7%), pure by tlc and nmr (Found: m/z 312.0899. $C_{19}H_{17}O_2{}^{35}Cl$ requires 312.0917). ν_{max} 1710 cm^{-1}. H-1 δ 1.73, s, 9H, $-C(CH_3)_3$; 7.6-7.8, m, 5H; 8.4-8.5, m, 1H; 8.6-8.7, m, 2H; C-13 δ 28.3, $-CH_3$; 83.4, $-C(CH_3)_3$; 122.8, 123.0, 125.3, 125.7, 127.2, 127.7, 128.1, 8 C-H; 166.4, $-COOBu^t$. m/z 314, 312 (2.1:6.0, M); 258, 256 (32:100, $M-C_4H_8$); 241, 239 (10:36, $M-C_4H_8-OH$); 213, 211 (7:16, $M-C_4H_8-OH-CO$); 176 (34%, $M-C_4H_8-OH-CO-Cl$).

Band C provided an unstable pale yellow gum proposed to be *t-butyl phenanthrene-9-carboperoxoate* (84) (11 mg, 1.7%). ν_{max} 1755 cm^{-1}. H-1 δ 1.48, s, 9H, $-C(CH_3)_3$; 7.5-8.0, m, 5H; 8.19, s, 1H, H-10; 8.5-8.8, m, 3H. C-13 δ 26.4, $-CH_3$; 84.0, $-C(CH_3)_3$; 122.7, 122.9, 126.3, 127.2, 127.3, 127.6, 129.1, 129.8, 131.0, all C-H; 165.7, $-C(O)OOBu^t$. m/z 294 (6, M); 222 (26, $M-C_4H_8O$); 205 (100%, $M-C_4H_9O_2$).

In separate experiments the pentane eluates yielded slightly impure colourless gums, identified as *9-trichloromethylphenanthrene* (75) (2-15% by nmr) (Found: m/z 293.9772. $C_{15}H_9{}^{35}Cl_3$ requires 293.9770). H-1 δ 7.5-7.8, m, 4H; 7.8-8.0, m, 1H; 8.57, s, 1H, H-10; 8.6-8.9, m, 3H. C-13 δ 80.5, $-CCl_3$; 122.5, 123.4, 126.3, 126.9, 127.0, 127.4, 127.7, 129.0, 130.4, all C-H. m/z 298, 296, 294 (3.5:10.7:11.0, M); 263, 261, 259 (9.8:63:100, M-Cl); 225, 223 (4.7:12, M-Cl-HCl); 189 (31, M-$Cl-Cl_2$); 187 (15%, M-Cl-2HCl). Compound (75) was found to be unstable to chromatography on neutral alumina or silica gel.

Decomposition of Selenoxide (74) in Methanol and in Methanol-d_1.

To a cold solution in dichloromethane (20 cm^3) of selenoxide (74) derived from selenide (73) (400 mg, 0.962 mmol), prepared as described previously (p. 87), was added methanol (2 cm^3) and pyridine (150 mg, ∿2 mol. equiv.). The mixture was stirred at 20° until the selenoxide could no longer be observed (tlc, 2 d); the solvent was removed in vacuum and the residue was dissolved in dichloromethane (20 cm^3). This solution was washed with hydrochloric acid (2 mol dm^{-3}, 15 cm^3), aqueous sodium hydroxide (2 mol dm^{-3}, 15 cm^3), water (15 cm^3), dried and concentrated to a yellow solid (320 mg), which was subjected to plc (10:1 hexanes:ether). The band at R_f 0.3-0.5 gave an off-white solid (147 mg, 65%), which was crystallised from methanol (3 cm^3) to provide colourless needles of methyl phenanthrene-9-carboxylate (88) (123 mg, 54%), m.p. and m.m.p. 113-114°C. All spectroscopic data were identical with those of an authentic sample.[35]

Selenoxide (74) was allowed to decompose in methanol-d_1 in a manner analogous to that described above. The methyl phenanthrene-9-carboxylate was isolated in the same manner. The integrated H-1 nmr spectrum showed the incorporation of 75% D (at C-10), and the mass spectrum showed a deuterium content (after correction for C-13) of (74±4)%.

(9-^{2}H)Phenanthrene (92)

A suspension of 9-phenanthrenyllithium in dry ether (100 cm^3) was prepared, exactly as described previously (p. 85), from 9-bromophenanthrene (9.03 g, 35.1 mmol) and butyllithium (1.1 mol. equiv.). To this stirred suspension, maintained under nitrogen and cooled to 0-5°, was added deuterium oxide (4 cm^3). After 1 h, water (50 cm^3) was added, the layers were separated and the organic phase was washed with water (1x50 cm^3), dried and concentrated to leave an off-white solid. Recrystallisation (ethanol) afforded white plates of (9-^{2}H)phenanthrene (92) (5.01 g, 80%), m.p. 97-99°. m/z 179 (100%, M).

[10-^{2}H]-9-Bromophenanthrene (94)

To a solution of (9-^{2}H)phenanthrene (92) (4.30 g, 24.0 mmol) in refluxing tetrachloromethane (50 cm^3) was added, dropwise during 1 h, a solution of bromine (8.1 g, 51 mmol) in tetrachloromethane (20 cm^3). After the addition was complete, the mixture was maintained at gentle reflux. The reaction was monitored by tlc, which showed the presence of starting material and two products, one at lower and one at higher R_f than the starting material. When the starting material and the product at lower R_f had both disappeared (4 h), the reaction mixture was cooled to 20° and diluted with dichloromethane (100 cm^3). The resultant solution was washed with 10% aqueous sodium metabisulfite (1x50 cm^3), aqueous sodium hydroxide (2 mol dm^{-3}, 1x50 cm^3), water (1x50 cm^3), dried and concentrated to an off-white solid. Recrystallisation (ethanol, two crops) provided white crystals, identified as [10-^{2}H]-9-bromophenanthrene (94) (5.23 g, 84%), m.p. 62-63.5°. δ 7.4-7.8, m, relative intensity 12.5; 8.02, s, relative intensity 1.0; 8.2-8.7, m, relative intensity 7.5. m/z 259 (97.8, $C_{14}H_8{}^{81}BrD$); 258 (77.1, $C_{14}H_9{}^{81}Br$); 257 (100.0, $C_{14}H_8{}^{79}BrD$); 256 (65.8%, $C_{14}H_9{}^{79}Br$). The deuterium content was calculated from the integrated proton nmr spectrum to be 60% D (at C-10), and from the mass spectrum (after correction for C-13) to be 58% D.

[10-^{2}H]-9-Phenylselenophenanthrene (95)

The title compound was prepared in the same way as its unlabelled analogue (72), from [10-^{2}H]-9-bromophenanthrene (94) (5.03 g, 19.5 mmol), butyllithium (1.1 mol. equiv.) and phenylselenenyl chloride (4.40 g, 23.0 mmol). The reaction mixture was processed as described for selenide (72), (p.86) to provide lustrous off-white crystals of [10-^{2}H]-9-phenylselenophenanthrene (95) (4.35 g, 67%), m.p. 161-3°. The deuterium content was calculated from the integrated proton nmr spectrum to be 60% D (at C-10).

[9b-^{2}H]-1,1-Dichloro-1a-phenylseleno-1a,9b-dihydrocyclopropa[l]phenanthrene (96)

The title compound was prepared in the same way as its unlabelled analogue (73) (p. 87), from [10-^{2}H]-9-phenylselenophenanthrene (95) (4.09 g, 12.3 mmol). The quantities of reagents used were: chloroform, 400 cm^3; 50% aqueous sodium hydroxide (400 cm^3); benzyltriethylammonium chloride (0.7 g, 25 mol %). The reaction was stopped after 3 d and processing of the reaction mixture, as described for selenide (73) (p. 87), afforded pale yellow prisms of [9b-^{2}H]-1,1-dichloro-1a-phenylseleno-1a,9b-dihydrocyclopropa[*l*]phenanthrene (96) (2.95 g, 58%), m.p. 111.5-113°. The deuterium content was found from the integrated proton nmr spectrum to be 60% D (at C-9b).

Decomposition of Labelled Selenoxide (97) in Methanol

The title reaction was performed in a manner analogous to that of unlabelled selenoxide (74) (p. 90), except that the reaction was allowed to proceed at 20° for 5 d (Method A) or, alternatively, in refluxing toluene/methanol for 1 d (Method B). The reaction mixtures were processed in the same way as for the unlabelled material. Within experimental error, the methyl phenanthrene-9-carboxylate (98) (Method A:15%. Method B:50%) obtained from either set of reaction conditions showed the same extent of deuterium incorporation: (20±5)% at C-10 by H-1 nmr, and (17±2)% from the mass spectra.

Decomposition of Selenoxide (74) in the Presence of Reactive Dienes

Solutions of selenoxide (74) in the appropriate solvent were prepared by oxidation of selenide (73) with a slight excess of *m*-chloroperbenzoic acid. An excess of diene was then added. The dienes (with solvents, temperatures and reaction times) used were: tetrachloro-*o*-benzoquinone (dichloromethane, 20°, 2 d), 1,3-diphenylisobenzofuran (toluene, 110°, 2 h) and furan (toluene, 20°, 3 d). In all cases the product mixtures were complex, with there being no evidence for the presence of the desired adducts. The only product isolated was *o*-dibenzoylbenzene, m.p. and m.m.p. 144-145°, from the reaction with 1,3-diphenylisobenzofuran.[141]

Diphenylmercury

The procedure of Wade and Seyferth[87] was modified. To a suspension of phenylmercury(II) acetate (106 g, 0.315 mol) in water (1000 cm^3, was added tetraethylenepentaamine (technical grade, 300 g). The resultant mixture was stirred vigorously (mechanical stirrer) at 20° for 2 h, and then filtered. The filter cake was taken up in dichloromethane (500 cm^3) and the solution was washed with hydrochloric acid (2 mol dm^{-3}, 2x300 cm^3), water (300 cm^3), dried and concentrated to leave diphenylmercury (46.4 g, 83%), m.p. 116-121° (lit.[87] 120-124°), suitable for further use.

Attempted Reaction of 9-Phenylselenophenanthrene (72) with Phenyltrifluoromethylmercury (101) and Sodium Iodide

A solution of 9-phenylselenophenanthrene (72) (193 mg, 0.580 mmol), phenyltrifluoromethylmercury (101) (2.00 g, 5.77 mmol) and dried sodium iodide (2.15 g, 14.3 mmol) in dry 1,2-dimethoxyethane (15 cm^3) was heated at reflux under nitrogen for 18 h. The reaction mixture was filtered to remove crude phenylmercury(II) iodide (>90%), and unreacted selenide (72) was recovered from the filtrate in quantitative yield.

1-Phenylselenonaphthalene (103)

To a stirred solution of 1-bromonaphthalene (15.0 g, 72.5 mmol) in dry ether (100 cm^3), under nitrogen, was added a solution of butyllithium in hexane (1.35 mol dm^{-3}, 60 cm^3, 1.1 mol. equiv.), dropwise over 10 min. After 20 min, a solution of phenylselenenyl bromide (made[138] *in situ* from diphenyl diselenide (11.3 g, 36.3 mmol) and bromine (5.81 g, 36.3 mmol) in dry ether (60 cm^3) was added dropwise during 30 min. The mixture was stirred for an additional 30 min, then water (100 cm^3) was added cautiously. The whole was transferred to a separatory funnel, the layers were separated and the organic phase was dried and concentrated to a brown oily residue. Vacuum distillation of this oil provided 1-phenylselenonaphthalene (103) (13.3 g, 65%) as a red oil, b.p. 178-180°/ 0.7 mm Hg (lit.[91] 180°/1mm Hg).

Attempted Reaction of 1-Phenylselenonaphthalene (103) with Dichlorocarbene

To a solution of 1-phenylselenonaphthalene (103) (7.06 g, 24.9 mmol) in chloroform (400 cm^3) was added benzyltriethylammonium chloride (1.2 g, 20 mol %) and aqueous sodium hydroxide (50% w/v, 400 cm^3). The mixture was stirred vigorously; tlc analysis during 5 d showed no discrete products to have been formed. After a total reaction time of 5 d, an aliquot was removed from the organic phase and filtered over a pad of silica gel. The proton nmr spectrum of the residue obtained after concentration showed no evidence for the formation of products. Selenide (103) was recovered in high yield from the reaction mixture.

Attempted Reaction of Selenide (73) with Methyltitanium Trichloride

To a solution of titanium tetrachloride (0.1 cm^3) in dry tetrahydrofuran (15 cm^3), under nitrogen and maintained at -75°, was added a solution of methyllithium (1.4 mol dm^{-3}, 0.40 cm^3, 0.56 mmol). The resultant purple solution was warmed to 20° and

a solution of selenide (73) (75 mg, 0.18 mmol) in dichloromethane (5 cm^3) was added by syringe. After being stirred for one day, the mixture was quenched with water (15 cm^3). Dichloromethane (30 cm^3) was added, the layers were separated and the organic phase was washed with water (15 cm^3), dried and concentrated. Plc (20:1 hexanes:ether) of the residue gave a single mobile band, R_f 0.7-0.8, which furnished unchanged selenide (73) (72 mg, 96%).

9-Methylthiophenanthrene (112)

To a stirred suspension of 9-phenanthrenyllithium (prepared in the usual way from 9-bromophenanthrene (19.35 g, 75.3 mmol) and butyllithium (1.1 mol. equiv.)) in ether (100 cm^3), maintained under nitrogen, was added dimethyl disulfide (8 cm^3), dropwise over 15 min. After a further hour the reaction mixture was partitioned between toluene (200 cm^3) and water (200 cm^3). The organic phase was washed with water (100 cm^3), dried and concentrated. The residue was crystallised (toluene/ethanol) to provide white needles, identified as *9-methylthiophenanthrene* (112) (14.16 g, 84%), m.p. 92-93° (Found: C, 80.4; H, 5.4; S, 14.0. $C_{15}H_{12}S$ requires C,80.3; H, 5.4; S, 14.3%). H-1 δ 2.51, s, 3H, $-SCH_3$; 7.4-7.7, m, 6H; 8.3-8.6, m, 3H. C-13 δ 15.8, $-SCH_3$; 122.5, 122.9, 123.6, 124.8, 125.9, 126.6, all C-H; 126.7, 2 C-H; 127.4, C-H; 128.9, 130.3, 130.5, 131.9, 134.4, all quaternary. m/z (18 eV) 224 (100, M); 209 (35%, $M-CH_3$).

Attempted Reaction of 9-Methylthiophenanthrene (112) with Dibromocarbene

To a solution of 9-methylthiophenanthrene (112) (4.00 g, 17.9 mmol) and benzyltriethylammonium bromide (0.30 g, 6.1 mol %) in bromoform (150 cm^3) was added aqueous sodium hydroxide (50% w/v, 160 cm^3). The mixture was stirred vigorously (mechanical stirrer) at 20°. An aliquot of the organic phase was removed after 12 h; analysis by tlc and H-1 nmr showed some starting material to remain, but there was no evidence for the formation of the desired product (118). After two days, the entire reaction mixture was processed to give a black gum (4 g). No

discrete products were observed on tlc, and characterisation was not pursued.

Attempted Reaction of 9-(4'-Chlorophenylseleno)phenanthrene (71) with Diazomethane

To a solution of 9-(4'-chlorophenylseleno)phenanthrene (71) (1.00 g, 2.7 mmol) in toluene (30 cm^3) was added an excess of ethereal diazomethane (~5 mol. equiv.). The homogeneous mixture was kept in a stoppered flask at 25° for five days. The solvents and diazomethane were removed under vacuum; column chromatography (10:1 hexanes:ether) of the residue and evaporation of the eluate afforded unchanged starting material (0.95 g, 95%), m.p. and m.m.p. 143-145°.

Methyl 2-Diazo-3-oxobutanoate (124)

A mixture of triethylamine (82.6 g, 0.818 mol) and *p*-toluenesulfonyl azide (161.0 g, 0.817 mol) was added to a stirred solution of methyl 3-oxobutanoate (94.8 g, 0.817 mol) in acetonitrile (900 cm^3), at such a rate that the temperature did not exceed 50°. After the addition was complete, the mixture was stirred for 3 h. The solvent was removed in vacuum and ether (200 cm^3) was added to the residue, which was then filtered (to remove *p*-toluenesulfonyl amide), concentrated and distilled to afford yellow methyl 2-diazo-3-oxobutanoate (124) (93.6 g, 81%), b.p. 45°/0.16 mm Hg (lit.[104] 60%). ν_{max} 2150, 1725, 1660 cm^{-1}. δ 2.47, s, 3H, H_3C-CO-; 3.84, s, 3H, -$COOCH_3$.

Methyl Diazoacetate

Methyl 2-diazo-3-oxobutanoate (124) (80.0 g, 0.563 mol) was stirred with a solution of potassium hydroxide (38 g, ~1 mol. equiv.) and benzyltriethylammonium bromide (0.8 g, 0.5 mol %) in water (800 cm^3) for 1 h. The resultant solution was extracted with ether (9x100 cm^3). The combined extracts were washed with water (300 cm^3), dried, concentrated and distilled to give methyl diazoacetate (24.9 g, 44%), as a yellow liquid, b.p. 34°/12 mm Hg (lit.[104] 52%, 36°/12 mm Hg). ν_{max} 2120,

1695 cm^{-1}. δ 3.75, s, 3H, $-OCH_3$; 4.78, s, 1H, H-2. In a separate preparation, the distillation was omitted, and spectroscopically pure product was obtained in 55% yield.

Methyl 5,5-Dimethyl-4-(pyrrolidin-1-yl)-4,5-dihydro-1H-pyrazole-3-carboxylate (126)

Methyl diazoacetate (17.8 g, 178 mmol) and *N*-(2-methyl-1-propenyl)pyrrolidine[137] (22.3 g, 178 mmol) in chloroform (100 cm^3) were heated under reflux for 8 h. The solvent was removed in vacuum and the residue was crystallised (ether) to provide methyl 5,5-dimethyl-4-(pyrrolidin-1-yl)-4,5-dihydro-1*H*-pyrazole-3-carboxylate (126) (27.1 g, 68%), as colourless prisms, m.p. 64-66° (lit.[103] 73%, 64-66°). ν_{max} 3270, 1700 cm^{-1}. δ 1.12 and 1.28, both s, 3H, $-CH_3$; 1.59-1.75, m, 4H; 2.45-2.95, m, 4H; 3.81, s, 1H, H-4; 3.83, s, 3H, $-OCH_3$; 6.35, s, 1H, H-1.

Methyl 3,3-Dimethyl-3H-pyrazole-5-carboxylate (123)

Dihydropyrazole (126) (11.0 g, 49 mmol) was chromatographed on silica gel (300 g), with ether as eluent. The eluate was evaporated and the residue recrystallised from ether to provide white needles of methyl 3,3-dimethyl-3*H*-pyrazole-5-carboxylate (123) (6.4 g, 85%), m.p. 94-95° (lit.[103] 92%, 93.5-95°). ν_{max} 1725, 1605 cm^{-1}. H-1 δ 1.50, s, 6H, 2 $-CH_3$; 3.98, s, $-OCH_3$; 7.69, s, 1H, H-4. C-13 δ 19.8, q, $-CH_3$; 52.4, q, $-OCH_3$; 95.2, s, C-3; 146.9, s, C-5; 154.3, d, C-4; 161.4, s, $-COOCH_3$.

Photolysis of 3H-Pyrazole (123)

A solution of 3*H*-pyrazole (123) (3.14 g, 20.4 mmol) in dry ether (300 cm^3) was photolysed (Hanovia medium pressure mercury lamp, pyrex filter) at 20° for 80 min. After this time the reaction mixture was concentrated to a volume of 20 cm^3. The solvent was removed completely from a small sample, and the residue was found to be mostly methyl 3,3-dimethylcyclopropene-1-carboxylate (130). ν_{max} 1755, 1715 cm^{-1}. H-1 δ 1.29, s, 6H, 2 $-CH_3$; 3.81, s, $-OCH_3$; 7.97, s, 1H, H-2. C-13 δ 26.9, q, $-CH_3$; 51.9, q, $-OCH_3$; 133.8, d, C-2.

In a separate experiment, aliquots were removed at intervals from the photolysis mixture; they were concentrated and H-1 nmr and infrared spectra were taken. Apart from 3*H*-pyrazole (123) and cyclopropene (130), a third component was found to be present, whose concentration was found initially to increase with time, then to decrease gradually almost to zero at the end of the photolysis. This component was proposed to be *methyl 2-diazo-4-methyl-3-pentenoate* (128). ν_{max} 2090 cm^{-1}. δ 1.7 and 1.9, both m, 3H, $-CH_3$; 3.78, s, $-OCH_3$; 5.4, m, 1H, H-3.

Methyl 7,7-Dimethylbicyclo[4.1.0]hept-3-ene-1-carboxylate (131)

A solution of cyclopropene (130) (prepared from 3*H*-pyrazole (123) (3.14 g, 20.4 mmol)) in ether (20 cm^3) was sealed in a Carius tube with 1,3-butadiene (12 g, 0.2 mol) and catechol (0.5 g). The resultant mixture was kept, in the dark, for 5 d, after which time the solvent and excess of diene were removed in vacuum. The residue was distilled to provide methyl 7,7-dimethylbicyclo[4.1.0]hept-3-ene-1-carboxylate (131) (1.91 g, 52% from 3*H*-pyrazole (123)), as a colourless oil, b.p. 63°/0.8 mm Hg (lit.[101] 62-64°/0.5 mm Hg). ν_{max} 1725, 1670 cm^{-1}. H-1 δ 0.95 and 1.10, both, s, 3H, $-CH_3$; 1.2-2.8, m, 5H, H-2,5,6; 3.67, s, 3H, $-OCH_3$; 5.55, br s, 2H, H-3,4. C-13 δ 15.0, $-CH_3$; 20.0, 22.4, C-2,5; 22.4, 23.7, $-CH_3$ and C-6; 26.7, 27.9, C-1,7; 51.6, $-OCH_3$; 124.2, 124.3, C-3,4; 175.0, $-COOCH_3$.

7,7-Dimethylbicyclo[4.1.0]hept-3-ene-1-carboxylic acid (122)

Methyl ester (131) (1.88 g, 10.4 mmol) and potassium hydroxide (1.8 g) were heated in refluxing aqueous methanol (90% v/v, 30 cm^3) for 2 d. The reaction mixture was concentrated to a volume of 15 cm^3 and then diluted with water (80 cm^3). The resultant solution was extracted with dichloromethane (2x40 cm^3, discarded), acidified with conc. hydrochloric acid and re-extracted with dichloromethane (3x40 cm^3). The latter extracts were combined, washed with water (50 cm^3), dried and concentrated to leave an off-white solid, which was crystallised from water to give white crystals of 7,7-dimethylbicyclo[4.1.0]hept-3-ene-1-carboxylic acid (122) (1.20 g, 70%), m.p. 126-7°

(lit.[101] 75%, 126-7°). ν_{max} 1665 cm^{-1}. H-1 δ 0.98, 1.21, both s, 3H, $-CH_3$; 1.6-2.9, m, 5H, H-2,5,6; 5.57, br s, 2H, H-3,4; 10.97, br s, 1H, -COOH. C-13 δ 15.3, q, $-CH_3$; 20.1, t, C-2(5); 22.1, overlapping t and q, C-2(5) and $-CH_3$; 24.8, d, C-6; 27.6, 28.4, both s, C-1,7; 124.0, 124.4, both d, C-3,4; 181.5, s, -COOH.

Oxidative Decarboxylation of 7,7-Dimethylbicyclo[4.1.0]hept-3-ene-1-carboxylic Acid (122)

To a stirred solution of carboxylic acid (122) (491 mg, 2.96 mmol) in dry dimethyl sulfoxide (5 cm^3) and pyridine (0.8 cm^3), maintained under nitrogen, was added lead(IV) acetate (3.3 g, 5.0 mmol). Stirring was continued for 4 h, during which time gas was evolved. The reaction mixture was cooled in ice-water and nitric acid (2 mol dm^{-3}, 20 cm^3) was added. The mixture was extracted with dichloromethane (4x15 cm^3), and the combined extracts were washed with aqueous sodium hydroxide (2 mol dm^{-3}, 2x15 cm^3), water (15 cm^3), hydrochloric acid (2 mol dm^{-3}, 2x15 cm^3) and water (2x15 cm^3), then dried and concentrated to a brown oil (151 mg). The alkaline washings were acidified and extracted with dichloromethane to provide a brownish solid, which was recrystallised (water) to furnish unreacted carboxylic acid (122) (129 mg, 26%), m.p. and m.m.p. 126-7°. The H-1 nmr spectrum of the brown oil showed the presence of the previously-observed and independently prepared[101,108] 1-methyl-1-phenylethyl acetate (149). δ 1.74, s, 6H, 2 $-CH_3$; 1.94, s, 3H, $-COCH_3$; 7.2, br s, 5H. This brown oil was subjected to preparative glc (25% E-30 on Celite, glass column (2.1 m x 8 mm o.d.), 102°, N_2 at 100 cm^3 min^{-1}), with substantial mechanical losses. The components obtained, in order of elution were: methylthiomethyl acetate (150) (17 mg, R_t 19 min), identical to an authentic sample.[109] H-1 δ 2.09, s, 3H, $-CH_3$; 2.24, s, 3H, $-CH_3$; 5.12, s, 2H, $-CH_2-$. C-13 δ 15.3, q, $-CH_3$; 20.8, q, $-CH_3$; 68.1, t, $-CH_2-$; 170.3, s, $-OCOCH_3$; 7,7-dimethylbicyclo[4.1.0]-hept-3-ene (151) (2 mg, 0.6%, R_t 31 min), having an identical H-1 nmr spectrum to that reported.[110] δ 0.55-0.70, m, 2H, H-1,6; 0.80, 1.03, both s, 3H, $-CH_3$; 1.9-2.5, m, 4H, H-2,5; 5.54, br s, 2H, H-3,4. m/z (glc-ms, CI mode) 123 (100%, M+H);

1-methyl-1-phenylethanol (153) (7 mg, 2%, R_t 75 min), identical to an authentic sample.[111] δ 1.53, s, 6H, 2 $-CH_3$; 2.2, br s, 1H, -OH; 7.2-7.4, m, 5H. All five products, in varying proportions, were observed in the product mixtures obtained from six separate experiments.

Reaction of Selenide (73) with N-Bromosuccinimide

N-Bromosuccinimide (263 mg, 2.02 mol. equiv.) was added all at once to a stirred solution of selenide (73) (305 mg, 0.733 mmol) in dichloromethane (20 cm^3), maintained at 0-5°. The mixture went red, then paled to yellow. When nothing of selenide (73) remained (tlc, 10 min), the solution was transferred to a separatory funnel and washed with warm water (2x15 cm^3), dried and concentrated to leave an off-white, chromatographically unstable residue of *9-bromodichloromethylphenanthrene* (157) (254 mg, 102%), pure by nmr. H-1 δ 7.4-7.8, m, 5H; 8.46, s, 1H; 7.8-8.4, m, 3H. C-13 δ 77.7, $-CBrCl_2$; 122.3, 123.1, 125.8, all C-H; 126.7, 2 C-H; 127.2, 127.7, 128.8, 130.2, all C-H. m/z 344, 342, 340, 338 (15:80:150:100, M). 307, 305, 303 (35:135:100, M-Cl). 263, 261, 259 (12:70:100, M-Br). A sample was hydrolysed with acetic acid in aqueous acetone to provide, after recrystallisation from ethanol, needles of phenanthrene-9-carboxylic acid, m.p. and m.m.p. 252-254°.

Phenanthrene-9-carboxylic acid

To a suspension of 9-phenanthrenyllithium in dry ether (50 cm^3) (prepared from 9-bromophenanthrene (9.41 g, 36.6 mmol) and butyllithium (1.1 mol. equiv.)), maintained under nitrogen, was added an excess of powdered solid carbon dioxide. The resultant mixture was diluted with ether. Base extraction of the ethereal solution, followed by acidification, extraction with dichloromethane, drying and concentration of the organic extracts gave an off-white solid, which was recrystallised (ethanol) to provide phenanthrene-9-carboxylic acid (4.19 g, 52%), m.p. 252-254.5° (lit.[142] 256-256.5°).

Reduction of Selenide (73)

When samples of selenide (73) were reduced under standard conditions with either lithium in t-butanol or lithium triethylborohydride (2 mol. equiv.), mixtures of at least five products were observed on tlc. Proton nmr spectra of the product mixtures did not indicate the presence of the desired selenide (162).

Attempted Reaction of 9-Phenylselenophenanthrene (72) with Diazomethane-Copper(II) Acetylacetonate

In a 100 cm^3 round-bottomed flask equipped with a magnetic follower was prepared a solution of 9-phenylselenophenanthrene (72) (407 mg, 1.22 mmol) in toluene (50 cm^3). Copper(II) acetylacetonate (0.4 g) was added and the flask was fitted with a rubber septum and outlet for gas. To a similar 250 cm^3

Nitrogen was bubbled through the melt and the temperature was raised to 780°. After 2 h at that temperature the alloy was allowed to cool, and then was turned on a lathe.

A one-litre, three-necked round-bottomed flask was equipped with a mechanical stirrer, reflux condenser and a septum for inlet of nitrogen. The flask was charged with turnings of zinc/copper alloy (130 g, ∿2 mol) and several crystals of iodine, and the whole was flamed out under a stream of dry, oxygen-free nitrogen. Iodoethane (156 g, 1.00 mol) was added all at once; the mixture was stirred vigorously and heated to reflux. The reaction began after 5 min; external heating was required to maintain reflux. After 2 h the condensate had become viscous and was fuming. Stirring was discontinued and the mixture was allowed to cool thoroughly; the black reaction mass solidified. The apparatus was set up for vacuum distillation, and the receiving flask was cooled in ice-water. The pressure was reduced to 8 mm Hg and the reaction flask was heated with a bunsen flame until there was no more distillate (40 min). The vacuum pump was disconnected and nitrogen was admitted to the system. The colourless distillate of diethylzinc weighed 25.1 g (41%). Solutions in benzene-d_6 and toluene were prepared by standard techniques.

WARNING. When diethylzinc is manipulated by syringe,the operator should expect a drop to fall from the end of the syringe needle. The neat diethylzinc ignited instantaneously upon exposure to the atmosphere, and burned vigorously. The prepared solutions (2-3 mol dm^{-3}) smoked but did not catch fire.

Reaction of Cyclohexene with Diethylzinc-Diiodomethane

An oven-dried nmr tube was equipped with a rubber septum and an inlet for dried oxygen-free nitrogen. Cyclohexene (0.13 cm^3, 1.3 mmol), a solution of diethylzinc in benzene-d_6 (3.2 mol dm^{-3}, 0.40 cm^3, 1.0 mol. equiv.), and diiodomethane (0.10 cm^3, 1.0 mol. equiv.) were introduced consecutively by syringe. The proton nmr spectrum of the clear, colourless solution was recorded and then the mixture was kept overnight at 60°, under positive nitro-

gen pressure. The nmr spectrum of the resultant white suspension was recorded: the signal due to the vinylic protons of cyclohexene had almost disappeared, and the presence of high-field multiplets (δ 0-1) was fully compatible with bicyclo-[4.1.0]heptane having been formed.

Reaction of 9-Methoxyphenanthrene with Diethylzinc-Diiodomethane

To a 5 cm^3 round-bottomed flask containing 9-methoxyphenanthrene (100 mg, 0.481 mmol) was fitted a rubber septum and inlet for dried oxygen-free nitrogen. A toluene solution of diethylzinc (2.2 mol dm^{-3}, 2.0 cm^3, 4.4 mmol) was added, followed by diiodomethane (0.36 cm^3, 4.5 mmol). The clear, colourless solution was stirred at 60° until the starting material had disappeared (tlc, 2 d). Pyridine (2 cm^3) was added to the cloudy mixture, which was then filtered. The filtrate was diluted with dichloromethane (30 cm^3) and the resultant solution was washed with hydrochloric acid (2 mol dm^{-3}, 2x15 cm^3), water (1x15 cm^3), dried and concentrated. Plc (20:1 hexanes:ether) of the residue gave a band, R_f 0.4-0.5, which afforded chromatographically pure *1a-methoxy-1a,9b-dihydrocyclopropa[1]phenanthrene* (163) (80 mg, 75%), as a gum (Found: m/z 222.1040. $C_{16}H_{14}O$ requires 222.1045). H-1 δ 0.04-0.20, dd, 1H, H-1β; 1.81-2.00, dd, 1H, H-1α; 2.66-2.86, dd, 1H, H-9b; 3.31, s, 3H, $-OCH_3$; 7.3-7.6, m, 5H; 7.8-8.2, m, 3H. C-13 δ 20.2, t, C-1; 26.2, d, C-9b; 55.5, q, $-OCH_3$; 62.7, s, C-1a; 123.1, 123.3, both C-H; 126.1, 3 C-H; 126.8, 127.7, 128.7, all C-H; 129.0, 130.0, 134.1, 136.2, all quaternary. m/z 222 (100, M); 207 (35, $M-CH_3$); 191 (73%, $M-OCH_3$).

Attempted Reaction of 9-Phenylselenophenanthrene (72) with Diethylzinc-Diiodomethane

To each of three 5 cm^3 round-bottomed flasks containing 9-phenylselenophenanthrene (72) (100 mg, 0.30 mmol) and equipped with a rubber septum and inlet for dried oxygen-free nitrogen, was added a solution of diethylzinc in toluene (2.2 mol dm^{-3}, 2.0 cm^3, 4.4 mmol) and diiodomethane (0.36 cm^3, 4.4 mmol), consecutively by syringe. The clear, almost colourless contents of the first flask were kept under positive nitrogen pressure

and were magnetically stirred at 60° for 60 h. The nitrogen atmosphere of the contents of the second flask was replaced with a flow (~0.1 cm^3 s^{-1}) of dried air, and the mixture was magnetically stirred at 60° for 2 h. A reflux condenser was fitted to the third flask and the material within was maintained under positive nitrogen pressure and heated at gentle reflux for 40 h.

After the specified reaction time heavy white precipitates had formed in all three flasks, and the supernatants were almost colourless. Dilute hydrochloric acid was added to the three mixtures and after the precipitates had disappeared, the organic phases were analysed by tlc. In every case a single spot was observed and it had the same R_f as the starting material. From one reaction mixture was recovered unchanged 9-phenylseleno-phenanthrene (72) (100 mg, 100%), m.p. and m.m.p. 156-160°.

In another experiment, a mixture of 9-phenylselenophenanthrene and the stoichiometric amounts of diiodomethane and diethylzinc (solution in benzene-d_6) was prepared as described (p.102) for the reaction of cyclohexene with diethylzinc-diiodomethane. The nmr tube and contents were kept at 60° overnight; a white suspension had been formed. There was no visible difference in the aromatic regions of proton nmr spectra taken before and after heating.

1,1-Dichloro-1a-trimethylsilyl-1a,9b-dihydrocyclopropa[l]phen-anthrene (169)

A solution of 9-phenanthrenyllithium in dry ether (150 cm^3) was prepared by reaction of 9-bromophenanthrene (16.3 g, 63.4 mmol) with butyllithium as described previously (p. 85). Chlorotri-methylsilane (25 cm^3) was added dropwise with cooling and the mixture was stirred overnight under nitrogen. Saturated sodium bicarbonate (100 cm^3) was added slowly; the layers were separ-ated and the organic phase was washed with water (100 cm^3), dried and concentrated to provide 9-trimethylsilylphenanthrene (168) (15.9 g, 100%), pure by nmr. δ (C_6D_6) 0.43, s, 9H, $-Si(CH_3)_3$; 7.25-7.45, m, 4H; 7.60-7.75, m, 1H; 7.94, s, 1H,

H-10; 8.10-8.25, m, 1H; 8.30-8.55, m, 2H.

To a 3 dm^3 round-bottomed flask, equipped with a mechanical stirrer and cooled in ice-water, was added chloroform (1100 cm^3), aqueous sodium hydroxide (50% w/v, 1500 cm^3) and benzyltriethylammonium chloride (3.0 g, 20 mol %). The stirrer was started and after 5 min was added crude 9-trimethylsilylphenanthrene (15.9 g, 63.6 mmol), prepared as described. The mixture was stirred vigorously and the temperature was allowed to rise to 25° over several hours. After five days the extremely thick, brown reaction mixture was filtered through celite. The filtrate was diluted with hexanes (1500 cm^3) and water (1000 cm^3). The organic phase was separated, filtered through celite and silica gel, and concentrated to a brown gum. Column chromatography (hexanes) gave two fractions: the first (6.4 g) was found by nmr to contain unreacted 9-trimethylsilylphenanthrene; the second was a white solid, which was recrystallised from methanol to provide prisms of *1,1-dichloro-1a-trimethylsilyl-1a,9b-dihydrocyclopropa[l]phenanthrene* (169) (4.92 g, 23%), m.p. 120-122° with prior softening. The analytical sample (methanol) had m.p. 123-123.5° with prior softening (Found: C,65.1; H, 5.5; Cl, 21.3. $C_{18}H_{18}Cl_2Si$ requires C, 64.9; H, 5.4; Cl, 21.3; Si, 8.4%). H-1 δ 0.27, s, 9H, $-Si(CH_3)_3$; 3.12, s, 1H, H-9b; 7.1-7.6, m, 6H; 7.8-8.0, m, 2H. C-13 δ 0.3, $-Si(CH_3)_3$; 32.5, C-1a; 38.8, C-9b; 64.9, C-1; 122.8, 123.1, 127.3, 127.8, 128.1, all C-H; 130.9, 3 C-H; 131.7, 133.1, both quaternary. m/z (18 eV) 226, 224 (35:100%, $M-(CH_3)_3SiCl$).

Half-reduction of 1,1-Dichloro-1a-trimethylsilyl-1a,9b-dihydrocyclopropa[l]phenanthrene (169)

To a magnetically-stirred solution of silane (169) (2.423 g, 7.28 mmol) in toluene (25 cm^3), maintained at 80°, was added azobisisobutyronitrile (80 mg) and tributyltin hydride (2.8 cm^3, 1.4 mol. equiv.). When nothing of silane (169) remained (tlc, 2 h), the reaction mixture was concentrated, and flash chromatography (30:1 hexanes:ethyl acetate) gave two product-containing fractions.

The first-eluted product was a white solid, which was recrystallised (methanol) to afford plates of *(1α,1aα,9bα)-1-chloro-1a-trimethylsilyl-1a,9b-dihydrocyclopropa[l]phenanthrene* (170) (456 mg, 21%), m.p. 97-99°. A second recrystallisation from the same solvent provided material with m.p. 99.5-100.5° (Found: C, 72.8; H, 6.4; Cl, 11.9. $C_{18}H_{19}ClSi$ requires C, 72.3; H, 6.4; Cl, 11.9; Si, 9.4%). H-1 δ 0.30, s, 9H, $-Si(CH_3)_3$; 2.77, 3.08, both d, both *J*=3.5 Hz, both 1H, H-1 and H-9b; 7.1-7.6, m, 6H; 7.8-8.0, m, 2H. C-13 δ 0.4, $-Si(CH_3)_3$; 24.6, C-1a; 33.7, 47.9, C-1 and C-9b; 123.1, 123.7, 126.4, 127.3, 127.6, 127.8, all C-H; 129.5, quaternary; 129.6, 130.0, both C-H; 130.2, 132.1, 136.5, all quaternary. m/z (18 eV) 300, 298 (37:100, M).

The second-eluted product, obtained as a colourless gum, furnished after crystallisation (methanol) white prisms of *(1α,1aβ,9bβ)-1-chloro-1a-trimethylsilyl-1a,9b-dihydrocyclopropa[l]phenanthrene* (171) (1.186 g, 54%), m.p. 78-80°. The analytical sample (methanol) had m.p. 81-81.5° (Found: C, 72.7; H, 6.5; Cl, 12.0. $C_{18}H_{19}ClSi$ requires C, 72.3; H, 6.4; Cl, 11.9; Si, 9.4%). H-1 δ 0.17, s, 9H, $-Si(CH_3)_3$; 2.70, 3.60, both d, both *J*=7.3 Hz, both 1H, H-1 and H-9b; 7.1-7.6, m, 6H; 7.8-8.1, m, 2H. C-13 δ -1.5, $-Si(CH_3)_3$; 22.2, C-1a; 28.6, 31.9, C-1 and C-9b; 122.6, 122.9, 126.6, all C-H; 127.3, 2 C-H; 127.6, C-H; 129.6, quaternary; 130.4, 130.7, both C-H; 132.1, 132.8, 133.0, all quaternary. m/z (18 eV) 300, 298 (37:100, M).

Reaction of (1α,1aβ,9bβ)-1-Chloro-1a-trimethylsilyl-1a,9b-dihydrocyclopropa[l]phenanthrene (171) with Potassium t-Butoxide in the Presence of Furan.

Silane (171) (52 mg, 0.174 mmol) was dissolved in a mixture of dry tetrahydrofuran (2 cm^3) and freshly distilled furan (3 cm^3). To this solution, maintained under nitrogen and magnetically stirred, was added all at once a solution of potassium t-butoxide (186 mg, 1.66 mmol) in tetrahydrofuran (2 cm^3). When nothing of silane (171) remained (tlc, 3 h), the reaction was quenched with water (5 cm^3) and diluted with dichloromethane (25 cm^3). The organic phase was washed with water (1x15 cm^3),

dried and concentrated. Plc (10:1 hexanes:ethyl acetate) gave a major band at R_f 0.4-0.5, which furnished a white solid identified as (8bα,8cβ,9α,12α,12aR*)-8b,8c,9,12-tetrahydro-9,12-epoxybenzo[1,3]cyclopropa[1,2-*l*]phenanthrene (172) (18 mg, 40%), pure by nmr. Recrystallisation (toluene/hexanes) provided white needles, m.p. 186-186.5° with prior sublimation (lit.[67] 157-158°) (Found: C, 88.3; H, 5.4. Calc. for $C_{19}H_{14}O$: C, 88.3; H, 5.5; O, 6.2%). δ 0.43, d, *J*=2.6 Hz, 1H, H-8c; 3.60, d, *J*=2.6 Hz, 1H, H-8b; 4.99-5.08, dd, 2H, H-9,12; 6.51-6.60, 7.04-7.13, both dd, both 1H, H-10,11; 7.2-7.5, m, 6H; 7.9-8.1, m, 2H. m/z 258 (2, M); 191 (100%).

Reaction of (1α,1aβ,9bβ)-1-Chloro-1a-trimethylsilyl-1a,9b-dihydrocyclopropa[l]phenanthrene (171) with Potassium t-Butoxide-Potassium Selenophenolate

To a stirred solution of potassium t-butoxide (0.47 g, 4.2 mmol) in dry dimethyl sulfoxide (5 cm^3), maintained under nitrogen, was added selenophenol (0.19 cm^3, 1.8 mmol). To the resultant colourless solution was added, all at once, a solution of silane (171) (100 mg, 0.335 mmol) in dimethyl sulfoxide (3 cm^3). The mixture darkened immediately; it was stirred for 3 h and then poured into a separatory funnel which contained water (30 cm^3) and toluene (30 cm^3). The layers were separated and the organic phase was washed with water (3x15 cm^3), dried and concentrated to an oil, which was subjected to plc (hexanes, 2 developments). Apart from diphenyl diselenide, and some brown material on the baseline, there were two products.

Band A, R_f 0.25-0.3, furnished nearly pure *1a-phenylseleno-1a,9b-dihydrocyclopropa[l]phenanthrene* (162) (12 mg, 10%) (Found; m/z 348.0429. $C_{21}H_{16}{}^{80}Se$ requires 348.0416). δ 0.47-0.59, dd, 1H, H-1β; 1.99-2.16, dd, 1H, H-1α; 2.93-3.12, dd, 1H, H-9b; 7.0-7.4, m, 10H; 7.8-8.2, m, 3H. m/z (18 eV) 348 (2,$C_{21}H_{16}{}^{80}Se$); 191 (100%, M-C_6H_5Se).

Band B, R_f 0.2-0.25, provided a white solid identified as *(1α,1aα,9bα)-1-phenylseleno-1a,9b-dihydrocyclopropa[l]phenanthrene* (173) (18 mg, 15%) (Found: m/z 348.0423. $C_{21}H_{16}{}^{80}Se$

requires 348.0416). δ 1.84, t, *J*=3.9 Hz, 1H, H-1β; 2.90, d, *J*=3.9 Hz, 2H, H-1a,9b; 7.1-7.6, m, 11H; 7.8-8.1, m, 2H. m/z (18 eV) 348 (4, $C_{21}H_{16}{}^{80}Se$); 191 (100%, M-C_6H_5Se).

*1a-Methylseleno-1a,9b-dihydrocyclopropa[*l]phenanthrene (174)

A suspension of lithium methylselenide[135] was prepared by careful addition of ethereal methyllithium (3.9 mmol) to a stirred suspension of selenium powder (308 mg, 3.90 mmol) in dry tetrahydrofuran (2 cm^3). To the resultant white suspension, maintained under nitrogen, was added a solution of a mixture of silanes (170) and (171) (217 mg, 0.727 mmol) in tetrahydrofuran (2 cm^3). A freshly dried solution of tetrabutylammonium fluoride (∿5 mmol) in tetrahydrofuran (2 cm^3) was added all at once; the mixture turned light green and reaction was complete by tlc after 5 min. Water (5 cm^3) was added and the mixture was transferred to a separatory funnel with dichloromethane (30 cm^3). The organic phase was washed with water (1x15 cm^3), hydrochloric acid (2 mol dm^{-3}, 1x15 cm^3), water (1x15 cm^3), aqueous sodium hydroxide (2 mol dm^{-3}, 1x15 cm^3), water (1x15 cm^3), dried and concentrated. Plc (100:1 hexanes:ethyl acetate) gave a band, R_f 0.5-0.6, which furnished *1a-methylseleno-1a,9b-dihydrocyclopropa[*l*]phenanthrene* (174) (165 mg, 80%), as a pale yellow gum (Found: m/z 286.0245. $C_{16}H_{14}{}^{80}Se$ requires 286.0259). δ 0.30-0.42, dd, 1H, H-1β; 1.85-2.02, dd, 1H, H-1α; 2.00, s with d, $^2J_{^{77}Se-H}$=10.7 Hz, 3H, -$SeCH_3$; 2.78-2.97, dd, 1H, H-9b; 7.1-7.4, m, 5H; 7.8-8.0, m, 2H; 8.1-8.3, m, 1H. m/z (18 eV) 286 (8, $C_{16}H_{14}{}^{80}Se$); 189 (100%).

*Methylation of 1a-Methylseleno-1a,9b-dihydrocyclopropa[*l*]phenanthrene (174) and Reaction of the Selenonium Tetrafluoroborate (179) with Potassium t-Butoxide in the Presence of Furan*

A solution of silver(I) tetrafluoroborate in dry ether (1 cm^3) was prepared from silver(I) fluoride (145 mg, 1.16 mmol) and boron trifluoride etherate (0.22 cm^3, 1.7 mmol). To this solution was added a solution of selenide (174) (165 mg, 0.579 mmol) and iodomethane (0.19 cm^3, 3.0 mmol) in ether (2 cm^3). A yellow precipitate formed immediately; after 10 min the sol-

vent was removed under vacuum and the residue was triturated with dichloromethane (5 cm^3). The triturate was concentrated to leave the crude *selenonium tetrafluoroborate* (179) (203 mg, 91%). Of this, 188 mg (0.486 mmol) was dissolved in a mixture of tetrahydrofuran (4 cm^3) and furan (5 cm^3), which solution was cooled to -5° and treated with a solution of potassium t-butoxide (0.14 g, 1.3 mmol) in tetrahydrofuran (2 cm^3). The mixture, maintained under nitrogen and magnetically stirred, was allowed to warm to 20°. After 20 h the solvents were removed under vacuum and the residue was partitioned between dichloromethane (25 cm^3) and water (15 cm^3). The organic phase was washed with water (2x15 cm^3), hydrochloric acid (2 mol dm^{-3}, 1x15 cm^3), water (1x15 cm^3), aqueous sodium hydroxide (2 mol dm^{-3}, 1x15 cm^3), water (1x15 cm^3), dried and concentrated. The multicomponent residue was separated into two fractions by flash chromatography (10:1 hexanes:ethyl acetate). The more mobile fraction was subjected to plc (18:1 hexanes:ethyl acetate). The bands were located by spraying of a small section of the plate with anisaldehyde-sulfuric acid and heating; the two most strongly-coloured bands were extracted.

Band A, R_f 0.35-0.4, coloured brown after spraying, furnished a white solid identified as *(1α,4α,4aα,12bα)-1,4,4a,12b-tetrahydro-1,4-epoxy-4a,12b-methanotriphenylene* (180) (25 mg, 20% from crude selenonium salt). Recrystallisation (ethyl acetate) gave white prisms, m.p. 178-179° (Found: m/z 258.1042. $C_{19}H_{14}O$ requires 258.1045). H-1 δ 0.58, d, *J*=4.6 Hz, 1H, H-13 *anti*; 2.56, d,*J*=4.6 Hz, 1H, H-13 *syn*; 5.26, br s, 2H, H-1,4; 6.34, br s, 2H, H-2,3; 7.2-7.4, m, 4H; 7.4-7.6, m, 2H; 7.8-8.0, m, 2H. C-13 δ 25.6, 35.8, C-4a,12b,13; 79.6, C-1,4; 123.7, 126.8, 127.9, 129.0, all C-H; 130.7, 134.7, both quaternary; 139.5, C-2,3. m/z (18 eV) 258 (39,M); 229 (100%).

Band B, R_f 0.3-0.35, coloured grey after spraying, provided chromatographically and spectroscopically homogeneous (8bα,8cβ, 9α,12α,12aR*)-8b,8c,9,12-tetrahydro-9-12-epoxybenzo[1,3]cyclopropa[1,2-*l*]phenanthrene (172) (8 mg, 7%), m.p. and m.m.p. (toluene/hexanes) 185-186° with prior sublimation.

The less mobile fraction from flash chromatography was also subjected to plc (5:1 hexanes:ethyl acetate), the bands being located as described above. Band C, R_f 0.4-0.5, coloured orange-brown after spraying, afforded a white solid identified as *(1α,4α,4aβ,12bβ)-1,4,4a,12b-tetrahydro-1,4-epoxy-4a,12b-methanotriphenylene* (181) (16 mg, 13%). Recrystallisation (ethyl acetate) provided white prisms, m.p. 183-190° (decomp.) (Found: m/z 258.1037. $C_{19}H_{14}O$ requires 258.1045). H-1 δ 0.78, d, *J*=5.2 Hz, 1H, H-13 *anti*; 1.98, d, *J*=5.2 Hz, 1H, H-13 *syn*; 5.36, br s, 2H, H-1,4; 6.45, br s, 2H, H-2,3; 7.2-7.4, m, 4H; 7.5-7.6, m, 2H; 7.9-8.1, m, 2H. C-13 δ 32.1, 35.3, C-4a,12b,13; 84.9, C-1,4; 123.6, 126.7, 128.0, 129.1, all C-H; 130.7, quaternary; 133.2, C-H; 135.1, quaternary.

In a separate experiment, performed in the same way as that outlined above, but in the absence of furan, no discrete products were obtained.

Attempted Reaction of the Selenonium Tetrafluoroborate (179) with Potassium t-Butoxide in the Presence of α-Pyrone.

Five solutions of the selenonium tetrafluoroborate (179) (0.2-0.4 mmol) in tetrahydrofuran (0.5-1.0 cm^3) were prepared as described previously (p. 108). They were treated with potassium t-butoxide and α-pyrone† under the following conditions: (2 equiv. base followed by an excess of α-pyrone, -50°); (1 equiv. base followed by an excess of α-pyrone, -50°); (2 equiv. base at 20° followed by an excess of α-pyrone); (1 equiv. base at 20° followed by an excess of α-pyrone); (an excess of α-pyrone at 20° followed by 2 equiv. of base). All reaction mixtures were then stirred at 20° for 20 h. Tlc and proton nmr analysis of the severely discoloured product mixtures showed no evidence for the formation of the norcaradiene† (186).

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† Samples of α-pyrone and the norcaradiene (186) were kindly given by Professor E. Vogel, University of Köln.

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