Studies in the chemistry of benzo-bicyclic systems

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S U M M A R Y

The work described in this thesis is concerned with the major factors controlling the acid-catalysed rearrangements of methyl-substituted 1-methoxybenzobarrelenes.

A short summary is presented in chapter one on the cycloaddition reactions of arynes with arenes, discussing the principle reactions and factors influencing the orientation of the 1,4-cycloaddition. Some of the recent advances in the chemistry of carbocations involved in the secondary rearrangements of highly substituted benzobarrelenes have been discussed.

Chapter two discusses the reactions of tetrahalogeno-benzyne with mono- and polysubstituted anisoles (e.g. 2-methyl, 2,3-dimethyl, and 2,3,5,6-tetramethyl etc.) which results in the formation of substituted tetrahalogenobenzobarrelenones and 1-methoxytetrahalogenobenzobarrelenes. A method for the preparation of 2,3-dimethoxytoluene in high yield has been presented.

Chapter three is introduced by a detailed survey on dechlorination methods. The dechlorination of tetrachloro-benzobicyclo[2.2.n] systems using sodium wire and t-butanol in tetrahydrofuran proceeds in high yield and without reduction in the tetrachlorobenzobicyclo[2.2.2]octatriene series. The structural features in the tetrachlorobenzobicyclo[2.2.1]hept-adiene series which result in dechlorination and reduction of an olefinic residue using the sodium, t-butanol, T.H.F. system

have also been studied.   The effect of neighbouring groups have been examined carefully, particularly when the hetero-atom was present in the ring system.

The acid-catalysed rearrangements of the methyl-substituted 1-methoxybenzobarrelenes are summarized in Chapter four.   The rearrangements are governed by the regioselective protonation of the olefinic double bonds.   With certain 1-methoxybenzobarrelene derivatives, having methyl groups on the bicyclic residue, reactions carried out in concentrated sulphuric acid have been shown to result in the formation of sultones.   This unexpected feature of the rearrangement reactions has been studied in detail.   The work in this area has been extended to include a study of the reactions of certain bicyclic ketones with the sulphur trioxide-dioxan complex which also affords sultones.   The structures of these sultones have been established by their X-ray crystallography.   The structures of diastereomeric mixture of diketones, obtained from the rearrangement reaction of 2,6-dimethyl-1-methoxybenzobarrelene was investigated.   An alternative method for the preparation of these diketones have been discussed.   Rearrangement of 2,3,5,6-tetramethyl-1-methoxytetrachlorobenzobarrelene shows that the presence of extra methyl groups promotes further rearrangements by stabilising additional carbocations formed by secondary rearrangements.

Finally, in Chapter five, the substituent shift effects in the ^{13}C nuclear magnetic resonance spectra on a number of benzobicyclooctane derivatives have been reported.

ACKNOWLEDGEMENTS

DEDICATED

TO

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CHAPTER ONE

i)   Cycloaddition Reactions of Arenes and Arynes.

ii)   Benzobicyclo[2.2.2]octen-2-yl and Octadien-2-yl

        cations.

Cycloaddition Reactions of Arenes and Arynes:-

The chemistry of the reactive molecules having two non-bonding electrons on carbon which may or may not be spin-paired (carbenes) or two electrons and two weakly bonding orbitals on neighbouring atoms (arynes, cycloalkynes) has been recently transformed into independent fields of research. The development of these has been reflected in a number of monographs[1-6] and reviews.[7-9] Organometallic compounds, which are sometimes the only precursors of many of the unstable species, play an extremely important role in the chemistry of arynes and carbenes.

The term ortho-dehydrobenzene (DHB), usually known as benzyne, or more generally as an aryne, was first introduced by Wittig in 1942,[10] as an unstable intermediate presumed to be involved in the reaction of fluorobenzene with phenyllithium. It is the simplest aromatic hydrocarbon in which one of the C-C linkages is formally a triple bond.

[A']   [B']   [C']
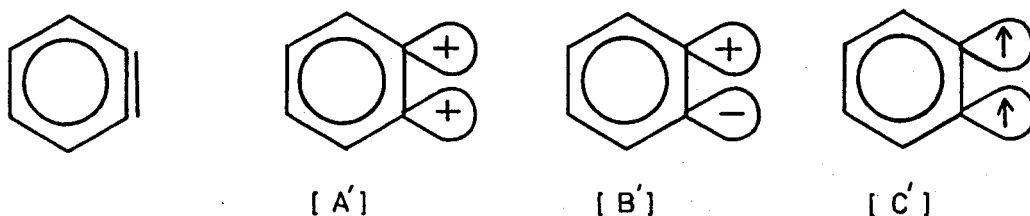
The steric strain arising following the introduction of a triple bond into the rigid aromatic system of benzene is responsible for its high reactivity. Like other arynes, it is a short-lived intermediate species under normal chemical reaction conditions. Models of the electronic structure show that the ring strain is not excessively high and can be compared with that in the cyclopropene ring.[11]

A: Symmetric, B: Antisymmetric, C: a triplet and two singlets (A) & (B).

1.

According to quantum-chemical calculations, the ortho-dehydrobenzene molecule, which is in the singlet ground state, is characterized by a high energy of the highest occupied molecular orbital (HOMO), which is unique for hydrocarbons, and a low energy for the lowest vacant molecular orbitals (LVMO), the boundary orbitals being centred between the C-1 and C-2 atoms and being formed from weakly over-lapping σ orbitals of the two atoms. As a consequence of this, the molecule should exhibit a high electrophilic reactivity in relation to unsaturated systems and also an ability to enter into reactions characteristic of both singlet biradicals and unsaturated compounds.

The available data on the reactivity of the ortho-dehydrobenzene (benzyne) can be summarized as follows: It readily reacts as a dienophile in the Diels-Alder reaction, enters into many other cycloaddition reactions, and is capable of being inserted into single C-H, C-metal, and C-C bonds.[2,3] Arynes do not persist in solution and the reactions observed will depend on the reactivity and availability of the other potential reaction partners. In many reactions, dimerization occurs if the aryne generated is in sufficiently high concentration.[2] In many aryne reactions the product is accompanied by substantial amounts of the unidentifiable tar.

The mechanism of the interaction of benzynes with planar conjugated cisoid-dienes is consistent with   concerted $(2 + 4)\pi$ cycloaddition reactions.[12,13]

[1-1]   [1-2]
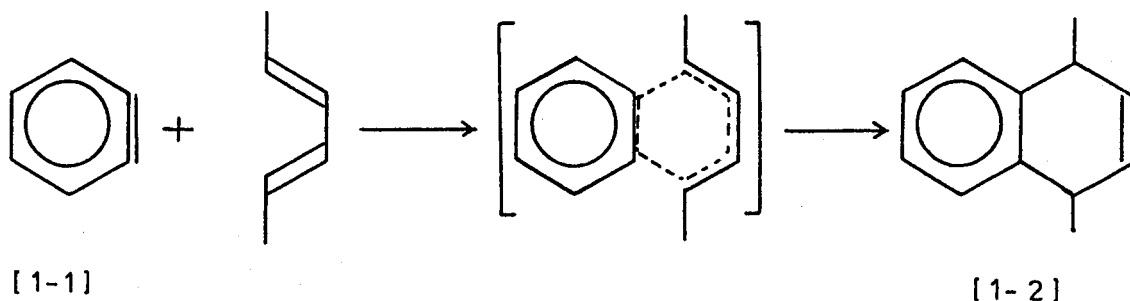
The reaction involving the 1,4-cycloaddition of benzyne to aromatic

systems probably proceeds via the same mechanism as explained by Heaney and his co-workers.[14] When benzyne is generated from a suspension of benzene-diazonium-2-carboxylate in the presence of benzene as a solvent at high dilution, benzobarrelene (1-3) is found in up to 14% yield.[15]

[1-1]   [1-3]
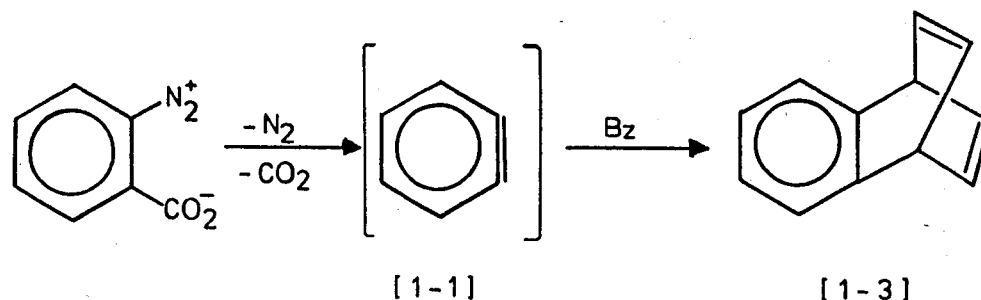
When potential co-reactants other than the arene are excluded from the reaction medium, $(4 + 2)\pi$ cycloaddition does not always take place; there may be other electrocyclic reactions which compete for the available aryne. A consequence of this reactivity is that the substituent which may be tolerated in Diels-Alder reactions of arynes will depend on the reactivity of the arene as a diene.

In reactions of arynes with olefins $(2 + 2)\pi$ cycloaddition reactions are observed. Judging from the dependence of its stereoselectivity on the nature of the olefin, it appears that these reactions may also proceed in a concerted manner. Extended Hückel calculations[16] suggest that when the energy of the singlet-triplet splitting is low, the extremely rapid conversion of the triplet DHB molecule into the singlet molecule occurs. Evidently this mechanism may also operate in the dimerization of DHB to biphenylene and other products in the gas-phase generation of DHB.[2]
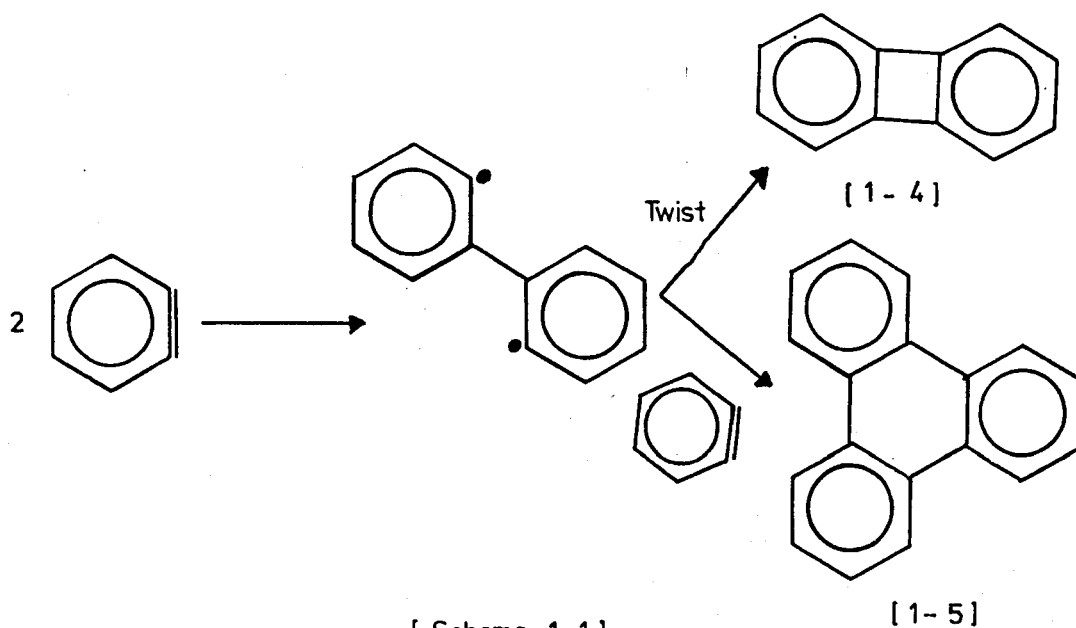
[Scheme 1-1]

The formation of triphenylene, proceeds either via the concerted

(2 + 2 + 2)π cycloaddition or, more probably, via a stepwise biradical

process due to the transoid approach of the reactants as shown above

[Scheme 1-1]. The cycloaddition of benzyne to (E)-deuterio-3,3-but-1-ene

proceeds with predominant retention of configuration,[17] which also

argues for a rotationally non-equilibrated biradical intermediate.

Most nucleophiles will attack arynes[2] to produce substituted aryl

anions. The attack of the conjugate acids of strong bases on arynes to

produce the substituted arenes is one of the classical examples of the

reaction.[2]

Hetero-atoms with lone pairs also attack arynes to some extent.[2]

Ethers, sulphides, and tertiary amines are all capable of attacking

arynes to give aryl heteronium species. The low reactivity of arenes

as dienes results in the incompatability of many of the above mentioned

groups with successful Diels-Alder reactions of arenes.

Halogeno-substituents do not interfere with the reaction,[18] although

their survival sometimes depends upon the methods used for the generation

of arynes.[2] Similarly, trialkylsilyl- and trialkylstannyl-substients

are normally unaffected by aryne reactions.[19] Dialkylamino-substituents

4.

are equally good reactants, if the nucleophilicity of the lone pair is reduced by co-ordination.[20] Sterically hindered amides can also add to the aryne without much difficulty.[21] Enamines react similarly, but in these cases the probable mechanism is the nucleophilic attack by the olefin on the benzyne followed by ring closure (Scheme 1-2).

[Scheme 1-2]
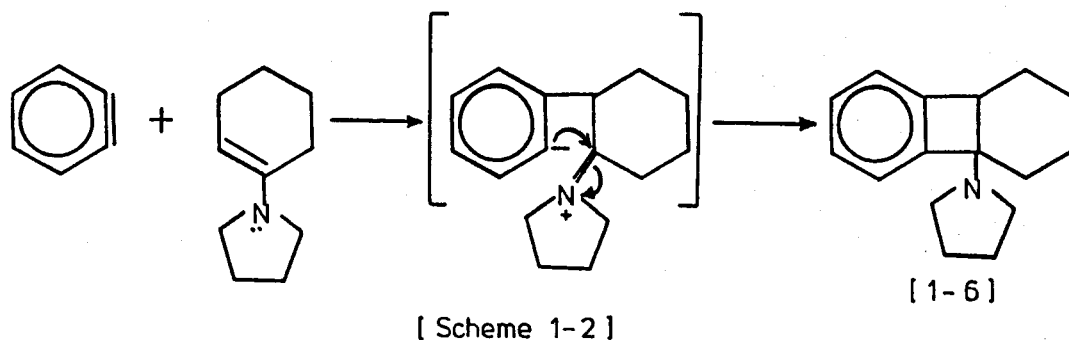
Olefins with an allylic hydrogen can react with activated olefins and acetylenes by a concerted 'ene' reaction which is analogous to the Diels-Alder reaction. Styrenes also undergo $(4 + 2)\pi$ cycloaddition, but the olefinic bond acts as a part of the diene component and gives dihydrophenanthrenes as the major product (Scheme 1-3).[22]

[Scheme 1-3]
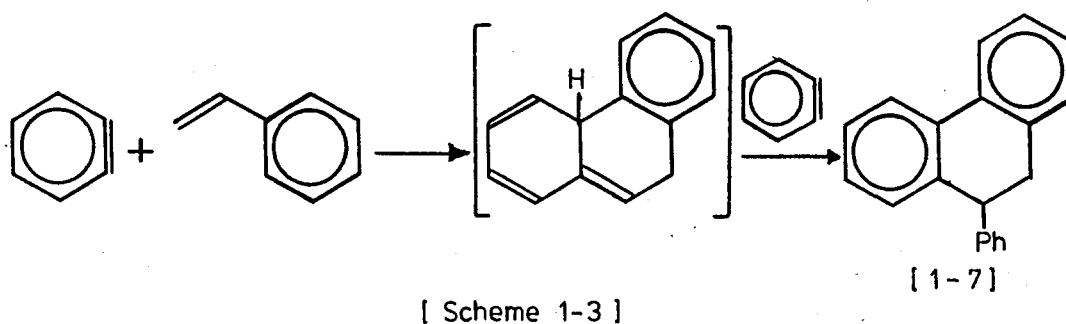
Overall the aryl group seems to exert greater activating effect on conjugating substituents than do the substituents on the aryl group. For instance azides and diazo-compounds can add as 1,3-dipoles to benzyne giving good to excellent yields, of benzotriazole (1-8)[23] and of imidazole (1-9).[24] Similarly there are a number of other studies in which benzyne reacts with the C=N bond of 2,3-diphenyl-1-aziridine to give 2,3-diphenylindole

5.

in a (2 + 2) cycloaddition,[25] and also of the formation of benzo-fused
N- and S-heterocycles by addition of benzyne to mesoionic compounds,[26]
to 1,2-dithiole-3-thiones,[27] and to 1,2,4-dithiazole-3-thiones.[27]

[1-8]

[1-9]
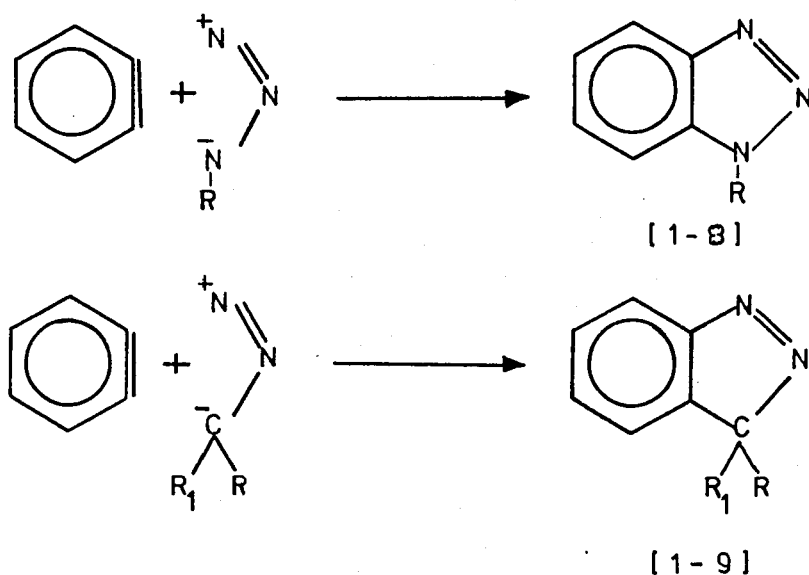
With polar olefins, benzyne forms cyclobutane derivatives, though
these reactions may not be concerted cycloadditions.

When an aryne reacts with substituted arenes, a mixture of isomeric
products [Scheme 1-4] is usually formed. The number of products and
their ratio depends upon the directing effect of the substituent on the
molecule. When more than one substituent is present, the product ratio
will depend upon the directing effect exerted by each substituent upon
the other. The role of this directing effect of the substituents is not
fully understood, although an attempt has been made to understand some
of the factors involved.

[1-10]   [1-11]

[Scheme 1-4]

6.
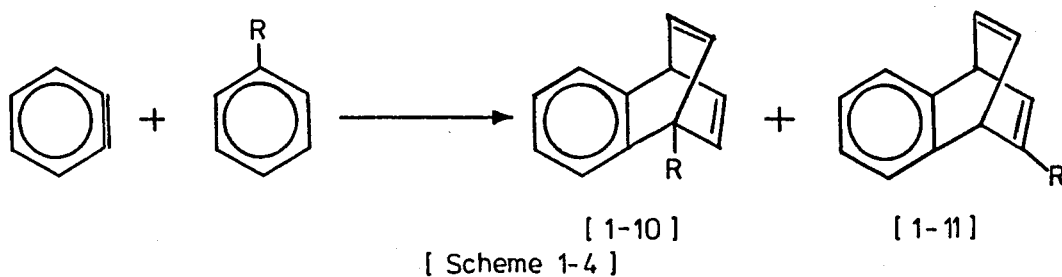
The tetrahalogenobenzynes are more electrophilic than benzyne and as such react with weak nucleophiles more efficiently than is the case of reactions involving benzyne. Thus, tetrachlorobenzyne (1-12) reacts with substituted arenes, giving chlorinated adducts, which on dechlorination give the same products as those obtained from reactions involving benzyne. The reaction of tetrachlorobenzyne with benzene gives a 68% yield of tetrachlorobenzobarrelene (2-47), which on dechlorination gave 92% yield of benzobarrelene (3-30)[28] (Scheme 1-5). This alternative method has been found to be much more efficient giving good yields of products which are virtually inaccessible by other means.

[1 - 12′]　　　　　[2 - 47]　　　　　[3 - 30]
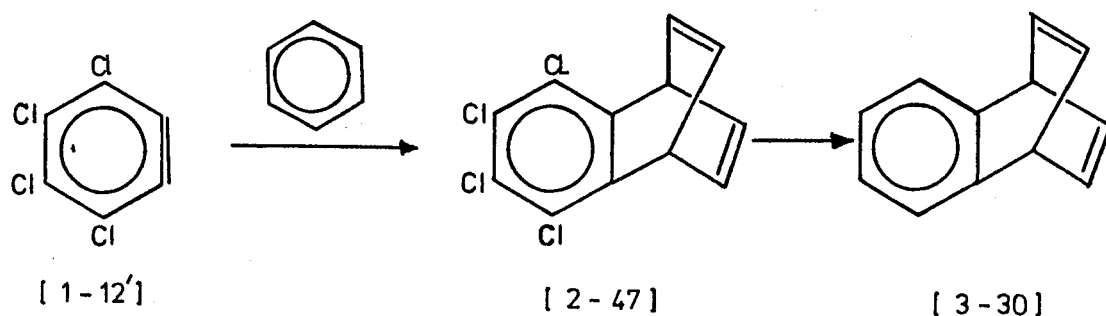
[Scheme 1-5]

The monoalkyl-benzenes undergo Diels-Alder cycloaddition, giving rise to both the possible adducts. Di- and poly-substituted arenes, similarly produce a mixture of products, depending upon the number and position of the substituents in the arene, with one reservation that when two alkyl groups stand para- to each other, the adduct with two bridgehead substituents is completely avoided, if possible.[6] Aryl ethers[29] and dimethylamino-substituted arenes[20] undergo 1,4-cycloaddition reactions, but again a para-substituent directs the addition towards the 2,5(≡3,6)-positions whether the para-substituent is an alkyl group or an additional ether group (Scheme 1-6).

7.

The enol ethers and enamines are usually obtained as their hydrolysis products, the benzobarrelenones (e.g. 1-14).

It has been observed that the cycloaddition of tetrachlorobenzyne to anisole predominantly involves the 1,4-positions, whereas cycloaddition of 4-methylanisole involves predominantly 2,5($\equiv$3,6)-position (Scheme 1-6).
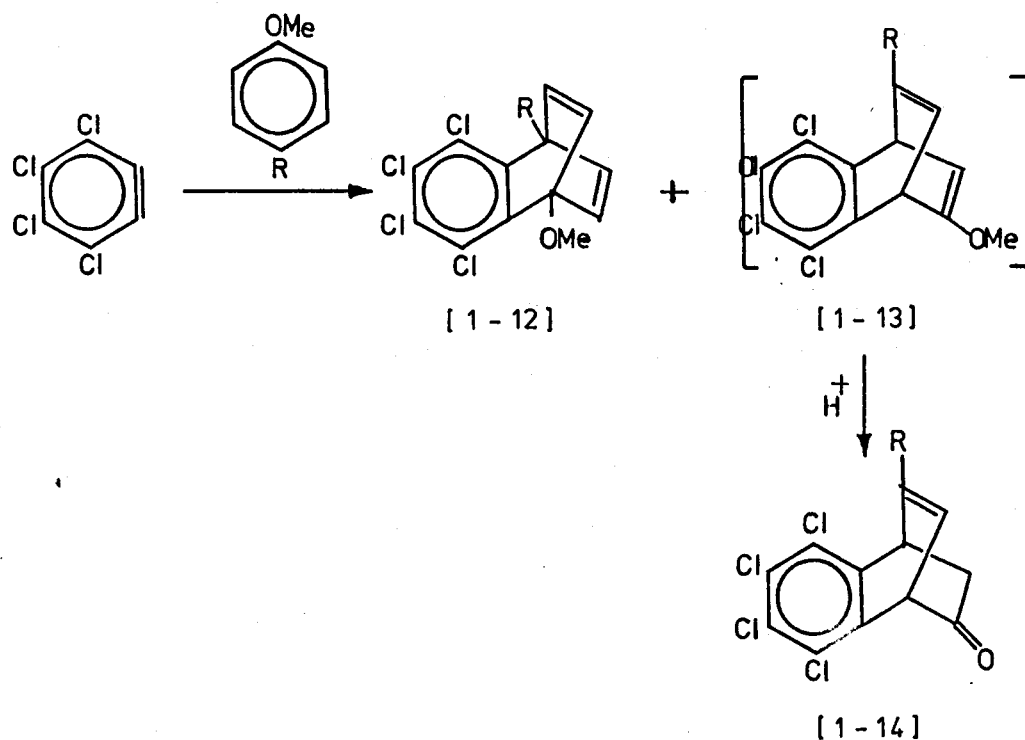
[Scheme 1-6]

N.J.Hales[30] in this laboratory, has successfully demonstrated the use of the derivatives of tin for the cycloaddition reactions. Since the carbon-tin bond can be easily cleaved, one could design and utilize such systems for the preparation of various compounds which are difficult to achieve by other methods. For example, tetrachlorobenzobarrelenone (1-17) was obtained by the Diels-Alder cycloaddition of tetrachlorobenzyne to tri-n-butyl-(4-methoxyphenyl) tin (1-15). The initial product (1-16) gave, on hydrolysis with sulphuric acid in aqueous dioxan, the desired product (1-17)[30] (Scheme 1-7).
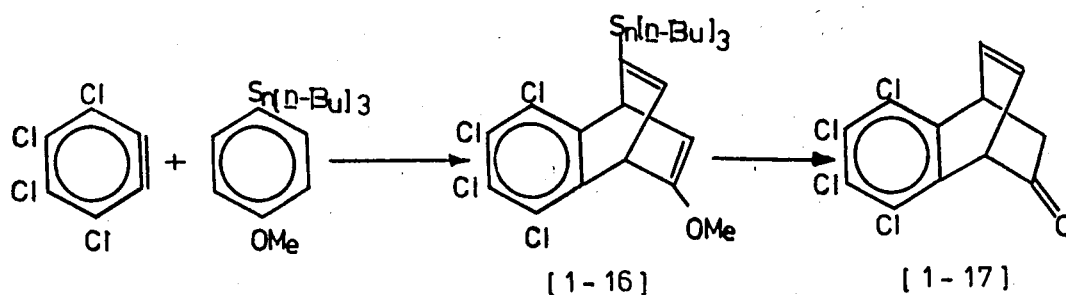
[Scheme 1-7]

In summary the majority of the reactions of arynes with arenes give benzobarrelenes. A choice of the reactants can be made to give either 1-methoxytetrahalogenobenzobarrelene (1-12) with some tetrahalogenobenzobarrelenone (1-14) or exclusively tetrahalogenobenzobarrelenone (1-14). The reactions between tetrafluoro- and tetrachlorobenzynes and substituted anisoles are particularly successful and can lead to the formation of potentially useful enol ethers.

Earlier studies of carbonium ions involved a study of the products produced during the solvolysis reactions at an asymmetric carbon atom. In various other solvolytic studies where organic cations have no carbonium ion character, the positive charge is localized largely on the oxygen (oxonium ion). Since the last chapter of the thesis involves similar studies, the following discussion involves some of the recent developments on solvolytic studies.

Benzobicyclo[2.2.2]octen-2-yl and octadien-2-yl cations:

Barkhash and co-workers[31] have investigated the solvolyses of exo- and endo-benzobicyclo[2.2.2]octadien-2-yl tosylates and have studied the effect on reaction rates and product compositions by reducing the double bond and by varying the aromatic substitution pattern. It was shown that the solvolyses, in a mixture of trifluoroacetic and sulphuric acids, take place with the assistance of the σ and π bonds and reaction mixtures with different compositions are formed under kinetically controlled conditions.

9.

Under thermodynamically controlled conditions identical results are obtained from each substrate. The most stable species derived from the benzotricyclo[3.2.1.0^{2,7}] octene system is formed. The reactions investigated made it possible to reveal the relative importance of σ and π participations of the aromatic ring and also the relative transformations of the respective carbonium ions in strongly acidic media. These data indicate conversion of the homobenzylic ion (A) to the homoallylic ion (B) under the solvolysis conditions, however, these changes are not observed in a more nucleophilic medium.

[A]   [B]
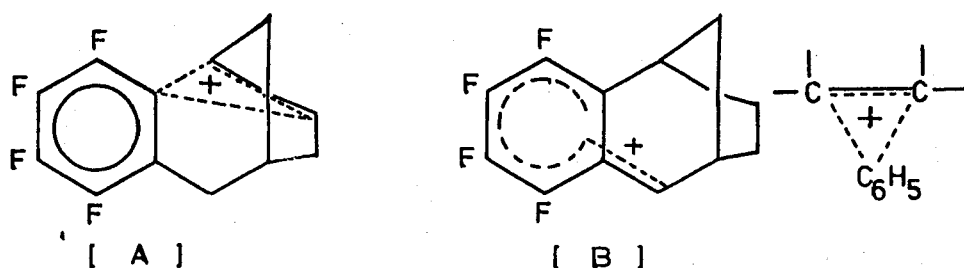
Within the framework of this conversion the initial S_N1 reaction product can be described by the term ion pair. This ion pair can be pictured as subsequently separating further to form a solvent-separated ion pair and finally a set of completely separated ions (eqn. 1.1). This process has been supported in extensive studies of solyolysis reactions by Winstein and his co-workers.[32]

$$ R\ X \rightleftharpoons R^+X^- \rightleftharpoons R^+\ II\ X^- \rightleftharpoons R^+ + X^- \qquad [\ 1.1\ ] $$

tight ion   solvent separated   separated
   pair   ion pair   ions
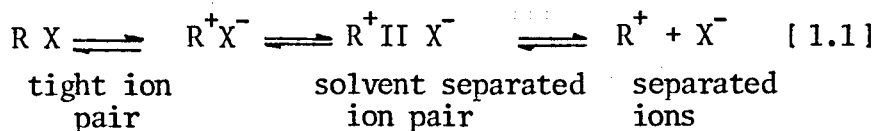
In any S_N1 reaction, great difficulties exist in elucidating the exact degree of association of the carbonium ion with the counterion or solvent and the interrelation of this solvation with rearrangement, racemization, ion-pair recombination and finally with the observed rate law for the given reaction.

It was shown during the investigations of trifluoroacetolysis of isomeric 2-exo-(1-18) and 2-endo-tosyloxy-7,8-tetrafluorobenzobicyclo - [2.2.2]octadiene (1-19) that different compositions of reaction products can be explained on the basis of the assumptions of the primary intermediate formation of isomeric nonclassical ions (C) and (D) rather than classical ion (E).[33]

[C]   [D]   [E]

[F]
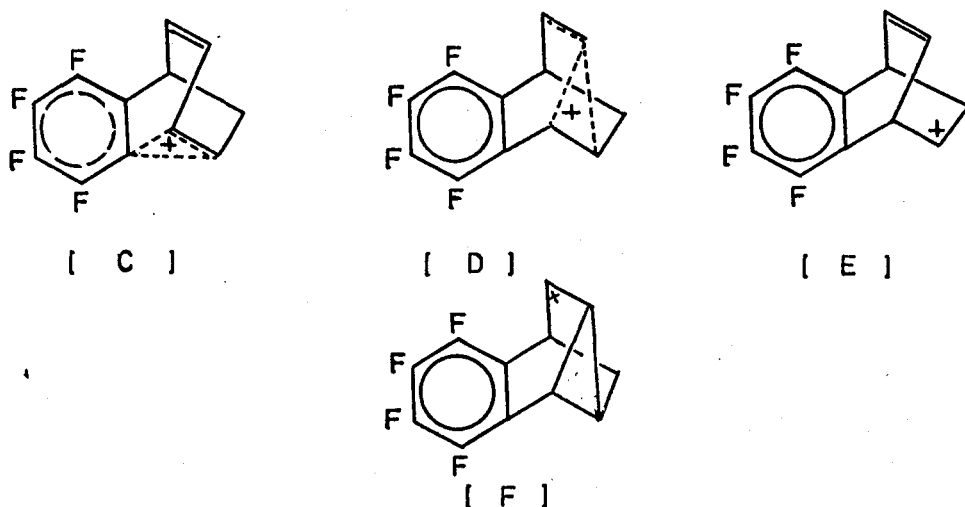
On the basis of earlier reports[33] it was assumed that the formation of classical ion (E) is more likely. To verify this assumption, the solvolytic studies of 2-exo-(1-18) and 2-endo-tosyloxy-7,8-tetrafluoro-benzobicyclo[2.2.2]octadienes (1-19) in a mixture of trifluoroacetic and sulphuric acids were carried out to obtain practically the same mixture of products. When the individual samples of the trifluoroacetates (1-20) and (1-21) were held under the solvolysis conditions, the reaction seems to proceed through a common intermediate (D) giving rise to a mixture of products (1-25) (40%), (1-26) (43%), and (1-23) (12%) after only 12 minutes (Scheme 1-8).

Ionization of compound (1-19) proceeds with the intermediate formation of a homoallylic ion (D), attack on which by the nucleophile leads to the trifluoroacetates (1-24), (1-25), and (1-26). The homobenzylic ion (C),

from which the trifluoroacetates (1-20) and (1-22) are obtained, is formed as the initial intermediate during the ionization of (1-18). Compound (1-18) is extremely unstable under the reaction conditions and during ionization gives the allylic ion (G) which in turn results in the formation of an equilibrium mixture of the acetates (1-20) and (1-21). The allylic ion (G) is evidently in equilibrium with the homobenzylic ion (C).Under the suggested conditions, where the nucleophilicity of the medium is extremely low, conversion of ion (C) to ion (D) clearly occurs, depending upon the lifetime of the ions.[31] Unlike the earlier investigations[33] of solvolysis reactions of compound (1-18) in more nucleophilic media, the energy barrier which separates the isomeric ions (C) and (D) is comparable with the energy barrier in the reaction of ion (C) with the nucleophile. Under thermodynamically controlled conditions, the most stable compounds of the isomeric 2,3-benzobicyclo[2.2.2]octadienes, 3,4-benzobicyclo[3.2.1]octadienes, 6,7-benzobicyclo[3.2.1]octadienes, and 3,4-benzotricyclo[3.2.1.0^{2,7}]octenes were found to be the latter.

Within the framework of an asynchronous mechanism one might assume that compounds (1-22) and (1-23) are products of the nonstereospecific capture classical ion (E) by the nucleophile. The anion is apparently still bonded to the proton in the initially formed protonium ion; opening of the protonium ion to give an ion pair, proceeds more rapidly than reorientation of gegenion or than attack by a relatively weak nucleophile on the protonium ion to give trans products. The work has been further verified by deuterium labelling.[34] Cristol and his co-workers[35] have suggested that the formation of such ion-pairs during their study of the addition of CD_3COOD to benzonorbornadiene, however, the stereochemical peculiarities of the latter compound do not make it possible to distinguish this process from a truly synchronous cis addition.

10M H$_2$SO$_4$ in CF$_3$COOH

[1-18]

[C]

[1-22]

[1-20]

10M H$_2$SO$_4$ in CF$_3$COOH

[1-19]

[D]

[G]

[1-21]

[1-23]

[1-24]

[1-25]

[1-26]
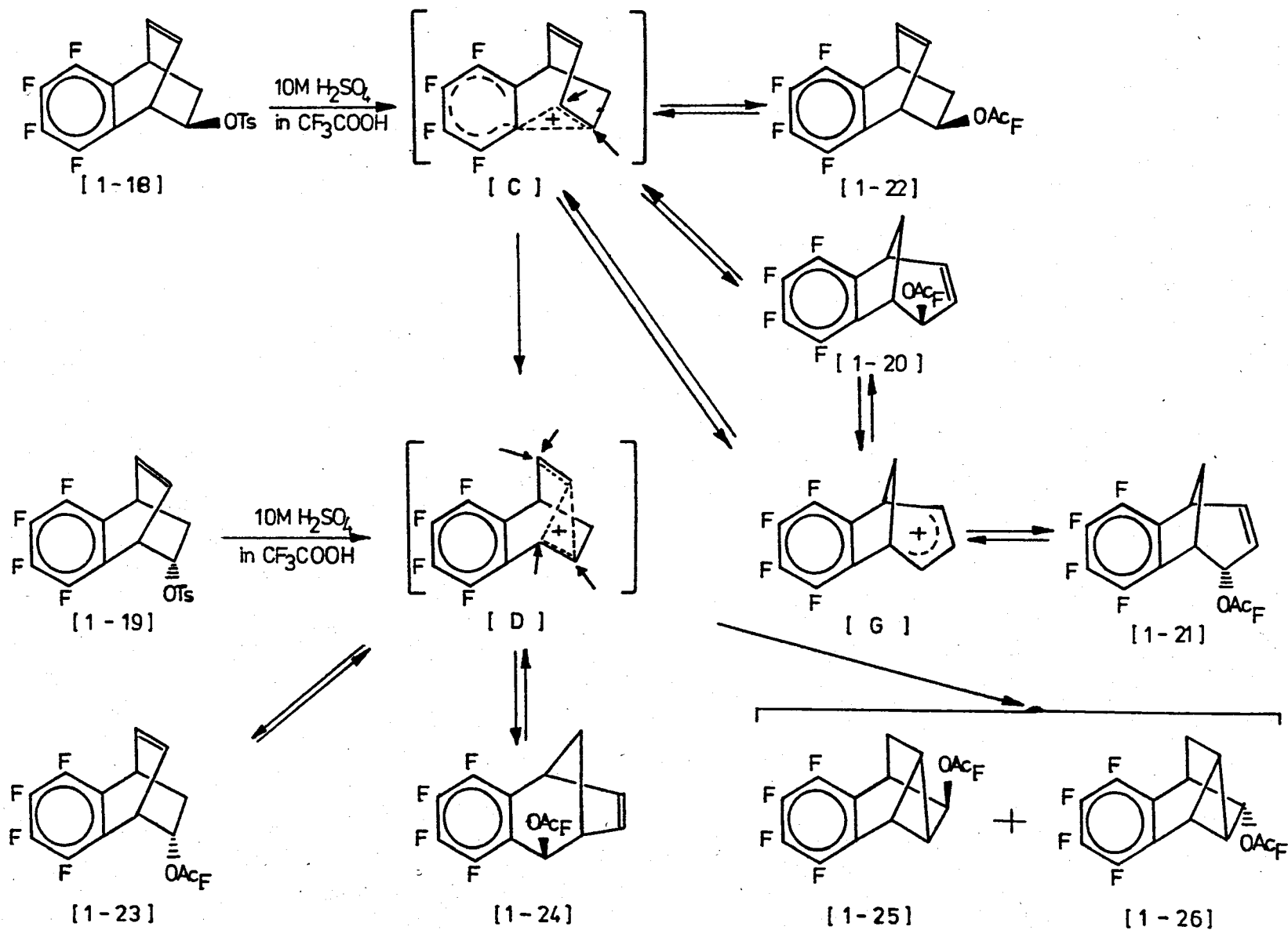
[Scheme 1-8]

The fact that different reaction mixtures are formed in the trifluoroacetolysis of epimeric pairs of the tosylates (1-18) and (1-19) excludes the possibility of the initial formation of common classical cations with the same skeletal structure as the starting compounds and also excludes extra rapid equilibration of the classical ions that imitate the equilibration of the non-classical ions. Thus, while conversion of the initially formed nonclassical ions to classical ions by a 1,2-shift of the C-C bonds is observed in the acetolysis of the tosylates (1-18) and (1-19), almost no such shift is observed in the trifluoroacetolysis of the same substrates.[36]

It is known that the degree of anchimeric assistance of the σ and π bonds is a function required for developing the cationic centre; thus anchimeric assistance increases sharply when electron-acceptor groups are introduced in the α or β position relative to the developing cation centre. Specific solvation of the carbonium ions is insignificant in trifluoroacetic acid, and this should lead to the substantial reinforcement of the anchimeric assistance of the σ and π bonds in the solvolysis transition state and to the formation of delocalized nonclassical carbonium ions. This effect may partially compensate for the decrease in solvation. In so far as the classical cations are concerned, the conditions for their solvation deteriorate sharply on passing from acetic to trifluoroacetic acid, and their relative stabilities consequently decrease substantially. This effect plays a significant role for classical ions, which have relatively localized charges, rather than for nonclassical ions. Thus the stabilities of the nonclassical ions relative to the isomeric classical ion increase on passing from acetolysis to trifluoroacetolysis. The result of all of this is that the energy barrier to reaction of nonclassical ions (C) and (D) with a nucleophile is lower in trifluoroacetic acid than the energy barrier to rearrangement to classical ions (E) and (F).

The peculiarities of the reactivities of the nonclassical ions formed from the same substrates in different media may be due to the difference not only in the electronic structures and energy barriers but also in their corresponding ion pairs and in their solvation processes. One can assume that in the reaction of trifluoroacetic acid, the initially formed R^+OTs^-, the tight ion pairs are more 'discrete' than in acetic acid and this increases the 'need' for anchimeric assistance.

It should be noted that an increase in the regioselectivity in nucleophilic attack on the delocalized nonclassical ion is observed as the nucleophilicity of the medium decreases. However, the ratio of the products depends upon the nature of the nucleophile and the site of the attack.

Thus, the aryl group undergoes 1,2 shift to a lesser extent during trifluoroacetolysis than during acetolysis. The attacking nucleophile in trifluoroacetolysis should be more selective than in acetolysis. The regioselectivity in the case of trifluoroacetolysis of the tosylate (1-19) [attack only at C-1 in ion D] is evidently due to the higher positive charge on C-1 than on C-6. The latter circumstance proved to be more important than the relative stabilities of the bicyclo[2.2.2]-octene and bicyclo[3.2.1]octene systems.

The reaction of the tosylates (1-18) and (1-19) with sodium azide in D.M.S.O. [i.e. with the participation of a strong nucleophile in a medium that has good solvating capacity with respect to carbonium ions] proceeds completely differently, in this case only the solvent effect is realized, and retention of the skeleton and inversion of the configuration are observed.[37] This stereochemical result excludes the intermediate formation of a symmetrically solvated classical ion as well as an ion pair separated by the solvent. Tight ion pairs are evidently the most probable intermediates [Scheme 1-9].

[1 - 18]   [1- 27]   [1- 28]

[1 - 19]   [1 - 29]   [1 - 30]

[Scheme 1-9]

RX $\rightleftharpoons$ R$^+$X$^-$ $\rightleftharpoons$ R$^+$||X$^-$ $\rightleftharpoons$ R$^+$ X$^-$

Tight ion   Solvent separated   Separated
pair   ion pair   ions
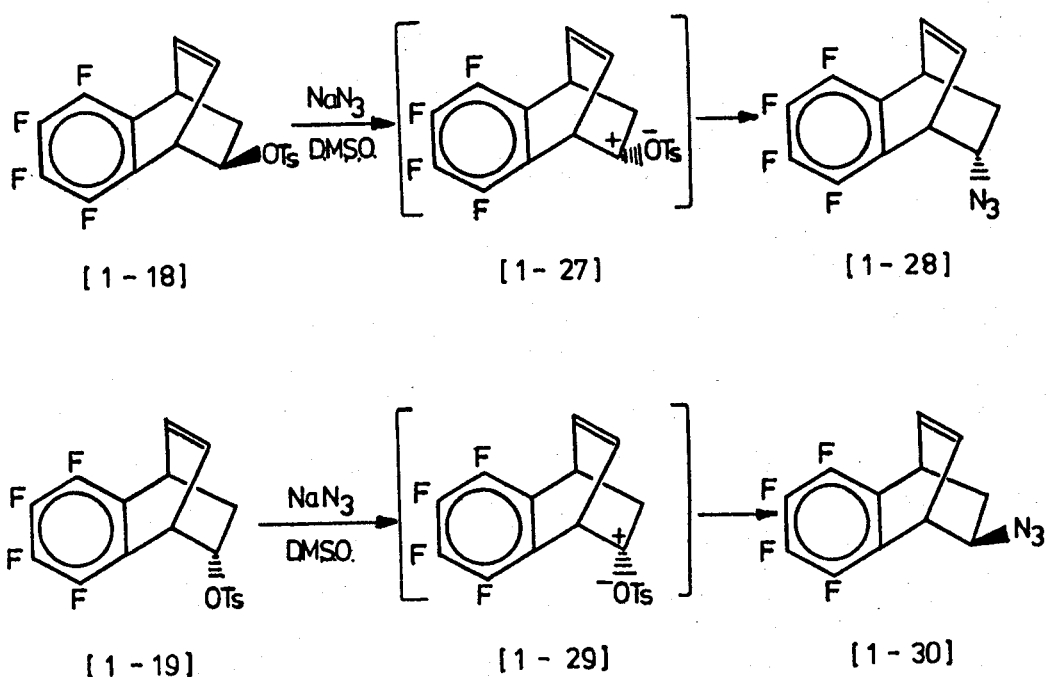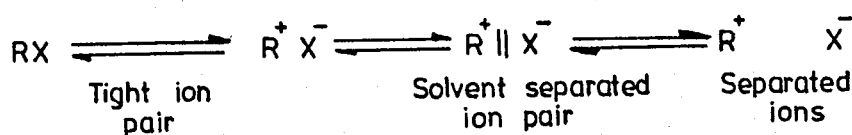
Similar results were obtained in the solvolytic studies of benzo-
bicyclo[2.2.2]octadien-2-yl tosylates by Tanida and his co-workers.[38]
The reactions were carried out under kinetically controlled conditions
and the first order rate constants were calculated. The greater rate
of acetolyses as compared to those ethanolyses in these systems was
interpreted on the basis of solvent assisted ionization and cationic
intermediates.

The acetolysis of 2-exo-benzobicyclo[2.2.2]octadien-2-yl brosylate
(1-31) proceeded with complete rearrangement to benzobicyclo[3.2.1]-
octadien-2-yl derivatives (1-32) and (1-33). The allyl cation was
captured stereoselectively from the exo-face to give the quasi-axial

16.

acetate (1-32) as the major product (Scheme 1-10).
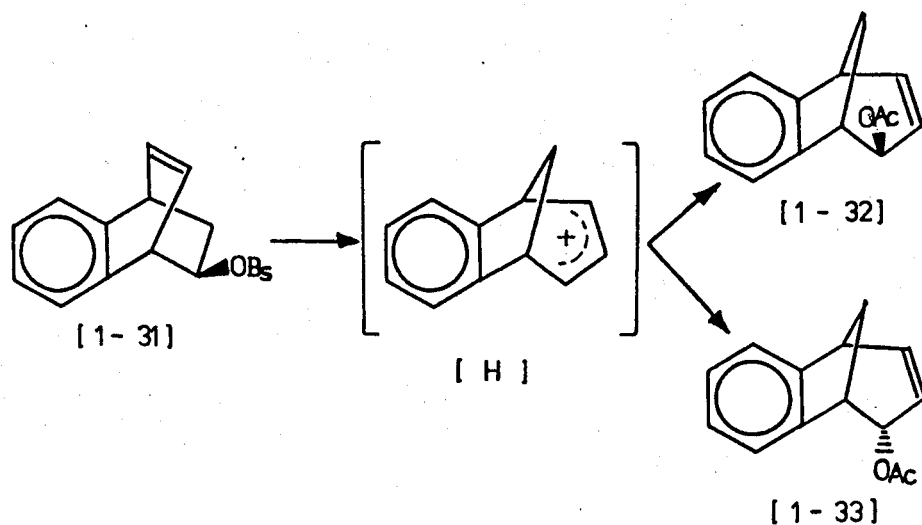
[Scheme 1-10]

The greater stability of the allyl cation (H) is probably the important factor in determining the product distribution. The true extent of the rearrangement may be masked by the symmetry of the intermediate allyl cation; it would be interesting to know whether scrambling of the termini of the allyl system occurs, and if so, whether the extent of scrambling is the same in the two products (1-32) and (1-33).[39]

Tanida and his co-workers[38] have measured solvolysis rates of several substituted benzobicyclo[2.2.2]octen-2-yl derivatives. Thus, the presence of homo-para-methoxy-group at position-6 of the 2-exo-benzobicyclo[2.2.2]octen-2-yl brosylate (1-34) showed a strikingly large rate accelerating effect in the rearrangement reactions whereas the presence of homo-meta-7-methoxy-substituent (1-35) depresses the rate slightly. Similar products[(1-36) to (1-38), (1-39) and (1-40)] were obtained during the acetolysis reaction from either of the sub-strates (Scheme 1-11). The steric course of the solvolysis is entirely controlled by the neighbouring aryl groups; it does not differ

significantly from that as shown in Scheme 1-11.
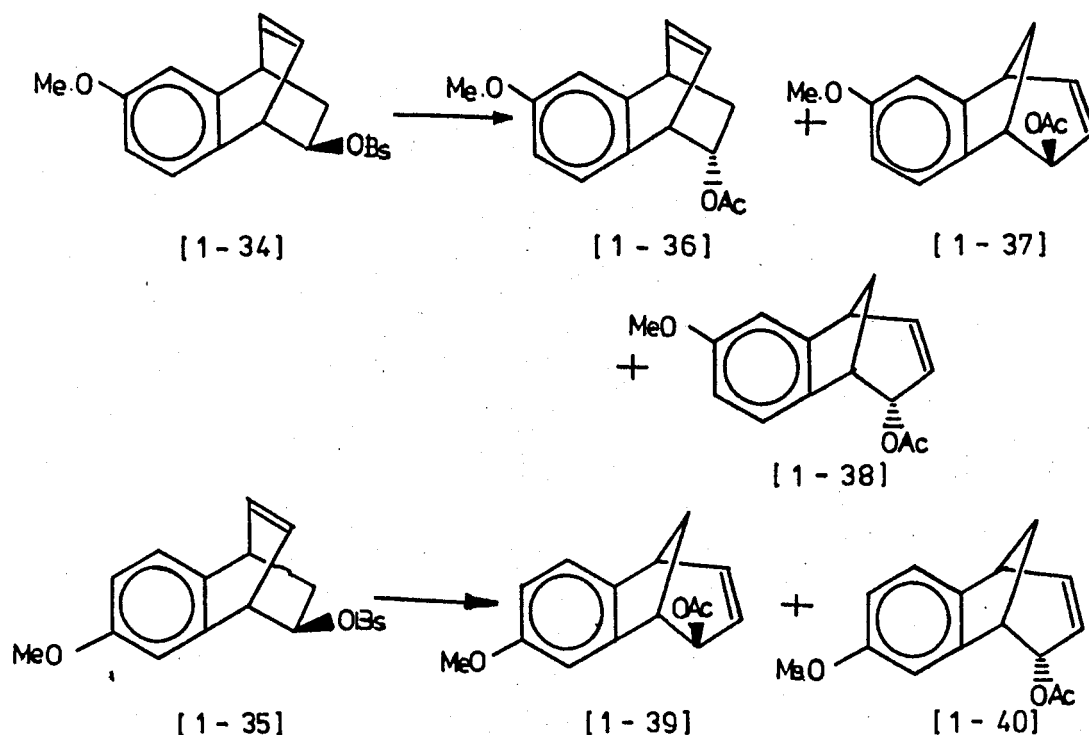
[Scheme 1- 11]

As the substituents become more electronegative, the products from exo-brosylates become more complex. The steric course of the solvolysis of the homo-meta-2-exo-7-nitrobenzobicyclo[2.2.2]octen-2-yl brosylate (1-41) is shown in Scheme 1-12. A linear correlation for the rate of solvolysis was established and it was suggested that the $\rho - \sigma^+$ treatment of acetolysis of the compound (1-41) was much higher (observed rate 47%) relative to the aromatic-unsubstituted exo-brosylate (1-31). On the basis of observations, it was also suggested that the solvolysis of this deactivated brosylate (1-31) gives neither of the products associated with the aryl participation (Scheme 1-12).
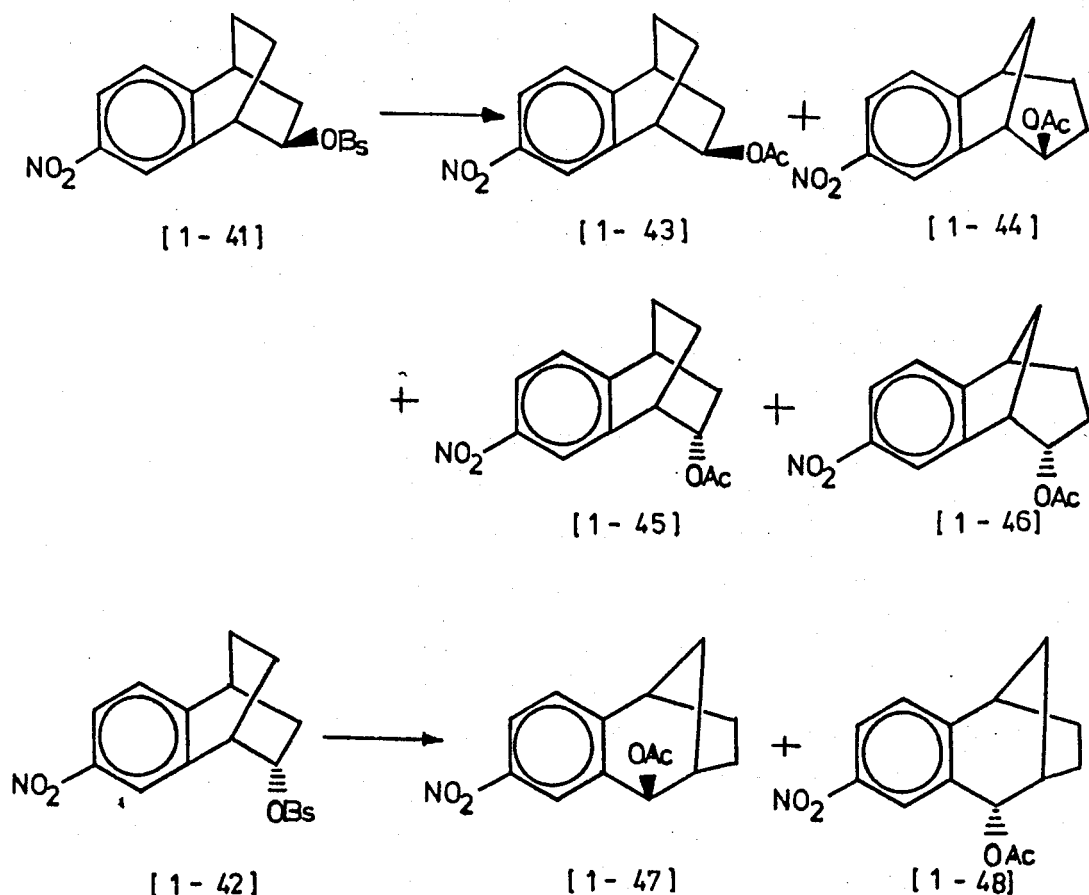
[Scheme 1-12]

However, the presence of an additional nitro group in the exo-
derivative (1-49) did not alter the acid-catalysed rearrangement pattern
significantly. It was suggested that in these solvolyses, the aryl group
controls the stereospecificity and composition of the products. The
various acetolysis products of 6,7-dinitro-2-exo-benzobicyclo[2.2.2]octen-
2-yl brosylate (1-49) are represented in Scheme 1-13.

[1- 54]   [1 - 55]   [1- 56]
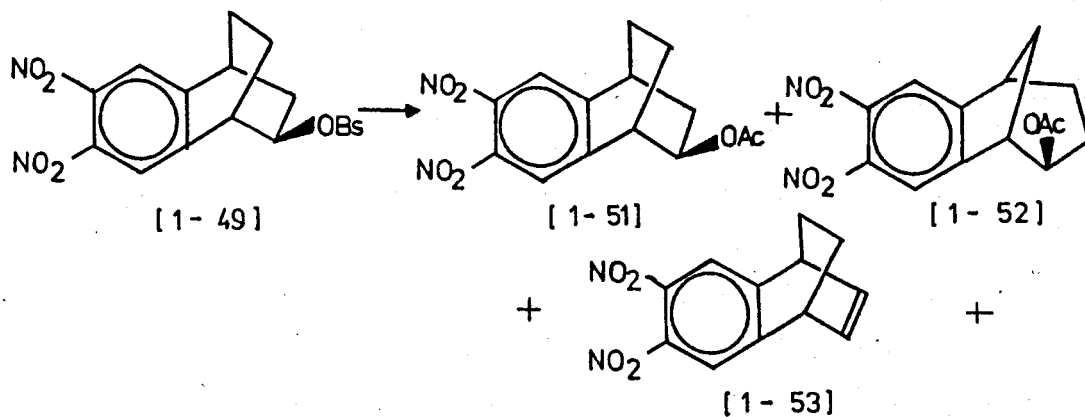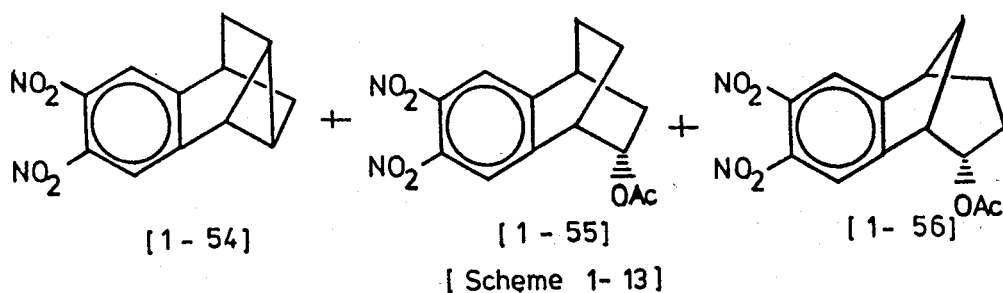
[Scheme 1- 13]

In case of endo-series (Scheme 1-14), the effects of nuclear

substitution on the relative rates correlated with σ rather than σ^+,

indicating that inductive effects are predominant. The etheno-bridge

migration to produce a benzyl cation, which is then captured by the

solvent, predominantly proceeds via the exo-face. The course of the

reaction closely follows that of the solvolysis of 2-exo series (Scheme

1-13). The acetolysis of 6,7-dinitro-2-endo- benzobicyclo[2.2.2]octen-

2-yl brosylate (1-50) gave the following products (Scheme 1-14).

[1- 50]   [1- 55]   [1- 57]

+

[1- 58]   [1- 53]   [1- 54]

[Scheme 1- 14]
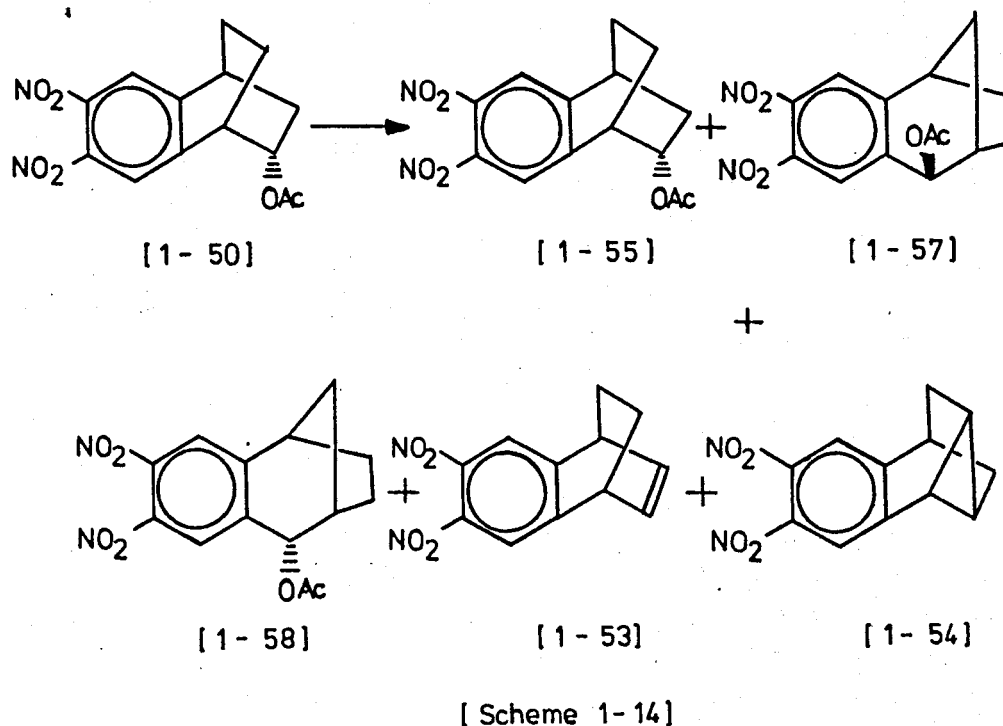
It was observed that the gradual change in the substitution pattern

from the unsubstituted brosylate (1-31) to the homo-meta-nitro- (1-49)

and then the homo-meta-homo-para-dinitro-substituted derivatives (1-50),

resulted in a significant decrease in exo:endo-ratio of the benzobicyclo-

20.

[3.2.1]oct-3-en-2-yl derivatives [e.g. (1-60)(1-61)] and was rationalized

on the basis of their reaction conditions.[40] The products which retain

the benzobicyclo[2.2.2]octane skeleton result from the decreasing

stability of the benzyl cation (formed by rearrangement) as the electron

withdrawing substituents accumulated on the arene residue. The decreasing

stability of the benzyl cation is also reflected in the decreasing stereo-

selectivity of solvent attack. From the product ratio in the rearrangement

of exo- and endo-dinitro-brosylate derivatives (1-49) and (1-50) it is

clearly indicative that aryl participation becomes less important in the

exo-series, and the etheno-bridge migration becomes less favourable in

the endo-series than the intermediate cationic species and the reaction

seems to proceed from the common intermediate. The other two products

are the cyclopropyl carbinyl derivatives (1-54) and (1-54[1]) and they

significantly represent the influence of the double bond on the course

of the solvolysis (Scheme 1-14).

Further evidence for the formation of cyclopropyl carbinyl derivatives

was obtained from the much simpler systems carrying no benzyl cations.

Thus, 2-exo-bicyclo[2.2.2]octen-2-yl brosylate (1-59) on acetolysis gave

four products [(1-60), (1-61), (1-62), and (1-63)] and the reaction seems

to proceed via cyclopropyl carbinyl cation (I) intermediate (Scheme 1-15).

Similar results were obtained in the case of endo- precursor; however, the

product's endo:exo ratio depended upon the reaction conditions.

[1- 59] [I] [1- 60]
(90%)

[1 - 61]   [1 - 62]   [1 - 63] OAc
(3%)   (3%)   (7%)
          [Scheme 1- 15]
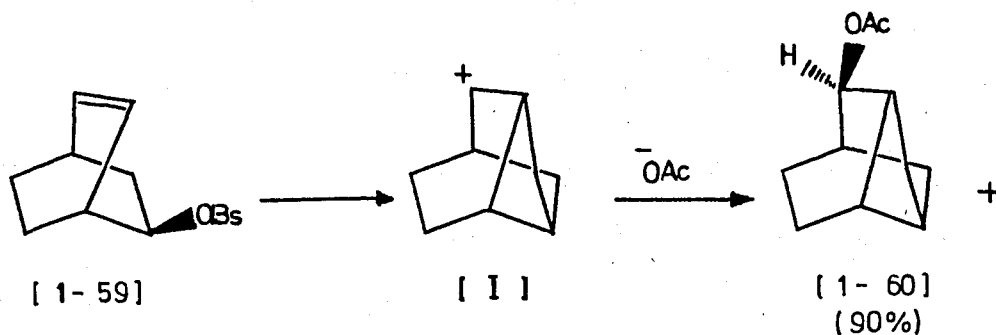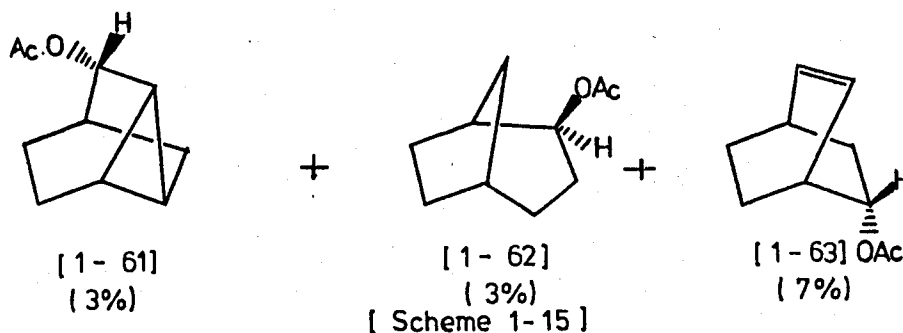
From the above discussion it is clear that in the exo-series, the
aryl bridging in the ionization transition state in the case of benzo-
bicyclo[2.2.2]octen-2-yl derivatives convincingly suggests that the
phenonium ion is the most stable cationic intermediate which governs the
reaction pathway. Whereas the aryl bridging in the ionization transition
state of benzobicyclo[2.2.2]octadien-2-yl-derivatives seems probable, the
phenonium ion is unlikely to be stable as the allyl cation (B), and
presumably the product formation in this case is being directed by the
latter species.

The stereochemistry of attack by nucleophiles on the various benzo-
bicyclo[3.2.1]octadien-2-yl cations is dominated by the exo-face to
form axial- or quasi-axial products. So far we have not said anything
about the stable bicyclo octenyl cations. Olah and his co-workers[41]
showed that the ionization of 2-substituted bicyclo[2.2.2]octanes and
bicyclo[3.2.1]octanes in superacidic media lead to the formation of the
bicyclo[3.3.0]octyl cation with a very rapid 1,2-shift of hydrogen
between the bridgehead positions. Although individual reactions evidently
differ considerably in the stereoselectivities they exhibit, the results
reveal a consistent pattern. In all cases, the cis-bicyclo[3.3.0]octane
system exhibits the least preference for exo-attack, presumably because
of its higher flexibility and relatively less inaccessible endo-face.
In all cases, the stereoselectivity indicated by the norbornane system
is intermediate.[42]   The substituted benzobicyclo[2.2.2]octenyl and
benzobicyclo[3.2.1]octenyl compounds investigated by Barkhash and his

22.

co-workers,[43] ionize to form cations with different structures, e.g.

6,7-benzobicyclo[3.2.1]octenyl cation, 10-syn- and 10-anti-chloro-6,7-

tetrafluorobenzobicyclo[3.2.1]octenes (1-64) and (1-65), however, formed

an ion (K) with a completely different structure. [Scheme 1-16].

[Scheme 1-16]
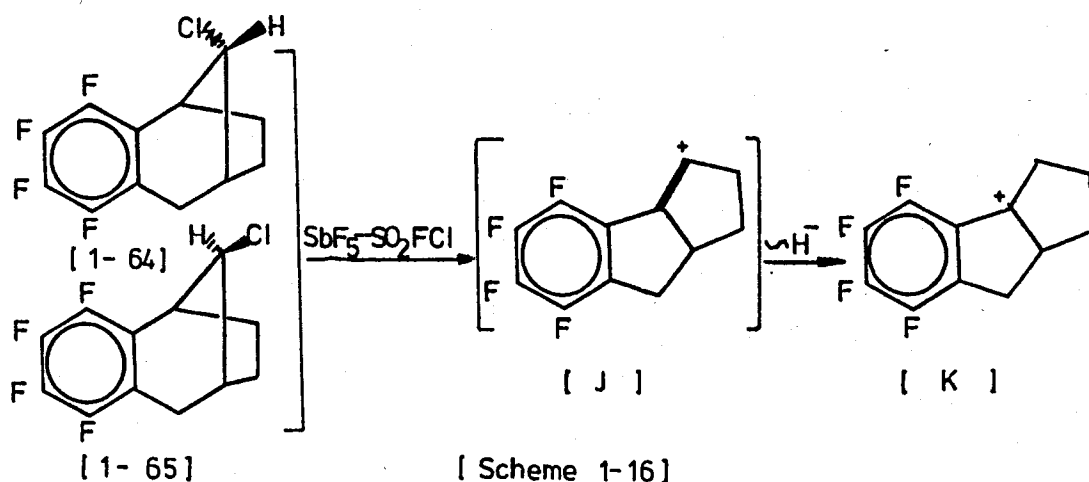
In similar studies,[44] addition of bromine to tetrafluorobenzo-

bicyclo[2.2.2]octadiene (1-66), skeletal isomerization took place through

homoallyl conjugation and also through Wagner-Meerwein rearrangements

[1,2]. The retention of the structure gave trans-5,6-dibromotetrafluoro-

benzobicyclo[2.2.2]octene (1-67). However, at higher temperature

skeletal changes were observed[(1-68), (1-69), and (1-70)] [Scheme 1-17].

In contrast,the addition of acetyl hypochlorite [t-butylhypochlorite in

glacial acetic acid] at -10° proceeded with complete rearrangement to

give 2-exo-acetoxy-10-syn-chlorotetrafluorobenzobicyclo[3.2.1]octene

(1-71) [Scheme 1-17].

[1- 66]　　　　　　　　　　　[1- 67]

[Scheme 1-17]
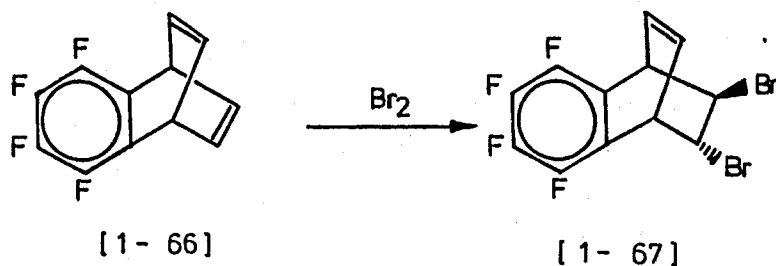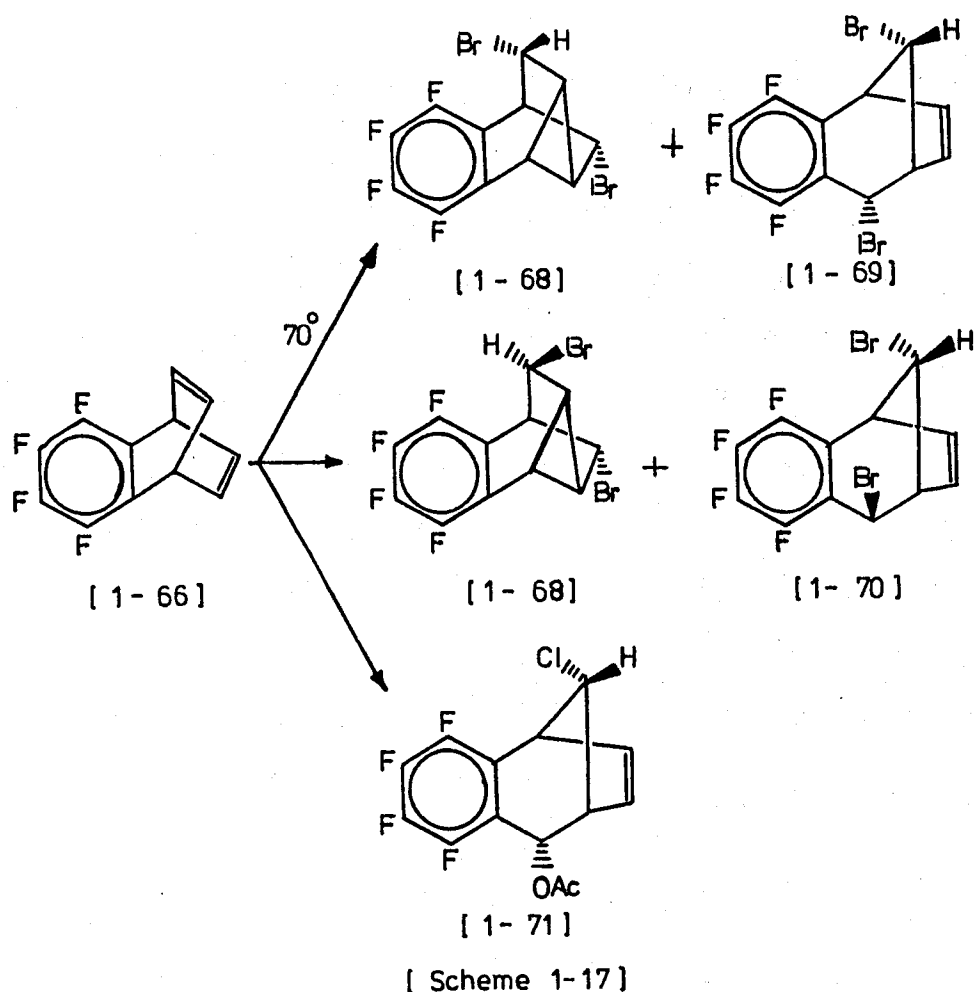
The various published discussions[45] suggest that the homobenzylic ion (A) with a bicyclic framework and, in particular, 2-, and 9-benzonorbornenyl ions have frequently been postulated as intermediate compounds in solvolysis and electrophilic addition reactions.

Olah and Liang[46] in their solvolytic studies of 2-substituted benzonorbornenes suggested the ions of the type (L) in preference to the ions of the type (M). This statement was further justified on the grounds that the initial π-participation of the benzene ring in the transition state of the ionization of the (C-2)-X bond to form the homobenzylic ion (O), which was then converted into the symmetrical ion (N) [Scheme 1-18].

24.

[L]   [M]   [N]

[1- 72]   [O]   ⟶ [N]
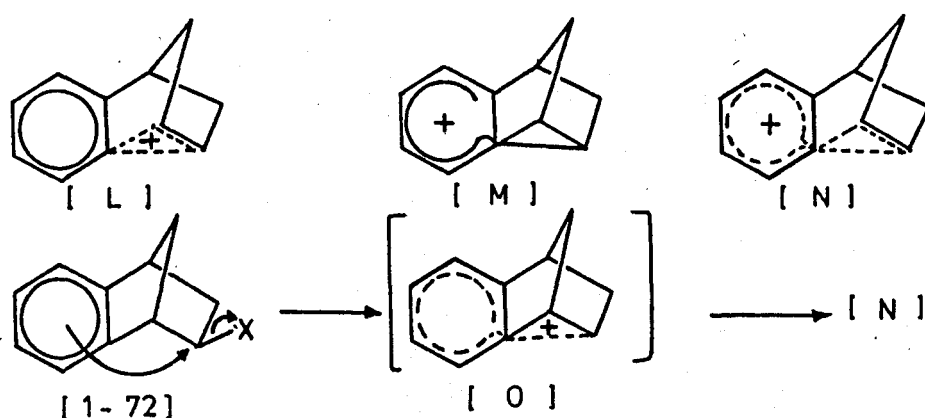
[Scheme 1- 18]

The key to these observations is the behaviour of the molecule under
the different environments. The significance of these investigations goes
beyond the study of the chemical properties of bicyclic olefins and is
directly related to the problem of the possibility of the formation of
nonclassical carbonium ions in chemical reactions. As a rule, an electro-
phile attacks the benzonorbornadiene molecule only from the exo- side;
this can be explained by the very high steric accessibility of the Sp^2
hybridized atom in the benzonorbornene skeleton and by the fact that σ
participation of (C-1)-(C-6) bond is possible only in the case of exo-
attack. In the case of endo-attack the participation of the (C-1)-(C-7)
bond would be hindered because of an increase in the angular strain.[47]
The classical 2-norbornyl cation is attacked by the nucleophile from the
exo-side for steric reasons and the nonclassical 2-norbornyl also reacts
only from the exo-side, but for stereoelectronic reasons. Therefore, it
is difficult to make a choice between classical or nonclassical
carbonium ions from the stereochemical results of the addition of
various nucleophiles to the reactive intermediates. Finally, attack by
an electrophilic reagent on norbornene occurs only from the exo-side,
which does not make it possible to conclude whether there is a dependence
between the configuration of the intermediately formed 'onium' ion, and
the direction of the skeletal shift. The above conclusions make it

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impossible to make a choice, for short-lived ions, between the nonclassical ion and fast equilibration of isomeric 'localized' classical ions; both explanations can justify the stereospecificity in the attack of the nucleophile.

The classical 2-norbornyl ion as a rule is converted into a nonclassical intermediate cation, which may be directly formed from the 'onium' ion; the present situation hinders the establishment of the role of these particles in electrophilic addition reactions.

The literature contains a number of reviews devoted to the classification of the mechanism of the addition of acetic and trifluoroacetic acid (as well as their deuteriated analogues) to bicyclic systems.[48] It seems quite obvious that benzobicyclo-octadiene and benzobicyclo-octene derivatives are more systematic models for the study of the role of the various carbonium ions - classical and nonclassical - in solvolytic rearrangements and electrophilic addition reactions.

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CHAPTER TWO

Cycloaddition Reactions of Tetrahalogenobenzynes with Aromatic Systems.

Cycloaddition Reactions of Tetrahalogenobenzynes with Aromatic Systems:-

Introduction:

Many polynuclear aromatic compounds theoretically should undergo a Diels-Alder cycloaddition reaction with maleic anhydride or other simple dienophiles, to give two or more isomeric adducts differing in their exo-endo or Syn-anti-stereochemistry. A large number of such cases have now been reported and in general only one adduct has been found. Examples are the condensation of 2-equivalents of maleic anhydride with pentaphene[1] and with dibenzo[b,i]-phenazine.[2] In each case six adducts may conceivably form; yet only one product has been reported, in the latter case in a yield of over 80%.

Two adducts of maleic anhydride and 2-naphthol have been obtained.[3] Their structures were assigned on the basis of dipole moments. The major adduct had the anhydride ring Syn to the benzene ring. Similarly the adducts of maleic anhydride and naphthalene have been obtained, again the position of anhydride ring in the major product was as before.[4]

A number of papers have appeared in which benzyne has been used as a reactive precursor for the generation of bicyclic systems.[5] It was observed that benzyne [because of its short lifetime] usually gives low yields of cycloadducts,[6] and shows a high propensity towards dimerization, yielding biphenylene.[7] The tetrahalogenobenzynes are more electrophilic than benzyne and because of their high electrophilicity undergo cycloaddition reactions with a variety of aromatic hydrocarbons.[8] Earlier work in this laboratory has shown that tetrafluorobenzyne and tetrachlorobenzyne both form 1,4-adducts[3] in high yield (~75%) with a large number of dienes.[9]

It had been noted previously that the reactions of the tetrahalogeno-benzynes with anisoles result in (2 + 4)π cycloaddition in which there was

a marked preference in favour of the formation of the cyclo-adduct bearing the methoxy group at a bridgehead position.[10] In similar reactions with alkyl benzenes the essential orientation was the reverse, so that the reactions with p-xylene or durene resulted in the formation of only one product.[10] For example, the ratio of bridgehead substituted benzobarrelenes to the ethenyl substituted isomers produced in the reactions of tetrahalogenobenzyne with mono-alkylbenzenes did not reflect any steric strain in the transition state leading to the bridgehead substituted product,[11] even though severe hindrance to rotation was observed in an adduct formed between tetrafluorobenzyne with t-butylbenzene.[12]

Results and Discussion:

In the present work well-established methods[1] of generating tetra-halogenobenzynes were used and need very little comment. The best results were frequently obtained from the reactions in which organometallic precursors were used for the arynes. It was observed that the large amounts of highly coloured impurities were obtained in many reactions when tetra-chlorobenzyne was generated either by the aprotic diazotization of tetra-chloroanthranilic acid or by the decomposition of 2-carboxytetrachlorobenzene-diazonium salts. The increase in electrophilicity of these diazonium salts as compared to benzenediazonium salts suggests that they could lead to the ready formation of azo-compounds with methoxy arenes.[14]

The main objective of this particular study was to obtain the highest yield possible of benzobarrelene and various other derivatives in a quick and straightforward procedure. It was decided that the dechlor-ination of tetrachlorobenzobarrelenes (see Chapter 3) was the key to this objective. It was not possible to increase the yield in the dechlorination step but it was possible to increase the yield of tetrachlorobenzobarrelene (2-47) by varying the reaction conditions. The major difficulty in the reaction leading to the tetrachlorobenzobarrelene (2-47) was that, since benzene is not a particularly good diene, its reaction with tetrachloro-benzyne results in Diels-Alder 1,4-cycloaddition in a relatively low yield.[15] It was necessary to devise a procedure in which tetrachlorobenzyne was formed from its precursor slowly and in the presence of a large volume of benzene to facilitate a maximum yield of the required adduct.

Three different methods for the generation of tetrahalogenobenzynes were used: tetrachlorobenzyne was prepared either from pentachlorophenyl-lithium[10] or 2-carboxytetrachlorobenzenediazonium tetrafluoroborate[10] or from tetrachloroanthranilic acid-pentyl nitrite[10] by decomposing them

in the presence of large excess of the reactants. The tetrafluorobenzyne was prepared by decomposing pentafluorophenyl magnesium chloride[10] in the presence of the equimolar amount of the reactants. The structure of various products (Table I) was established by elemental analysis and from spectroscopic data. These results are collected in Table I.

[I]   [II]

Reactions of tetrahalogenobenzynes with substituted anisoles.

Anisole Substituents	No.	Type	R_1	R_2	R_3	R_4	R_5	R_6	X	Yield %
–	(2-1)	I	OMe	H	H	H	H	H	Cl	73
2-Methyl-	(2-2)	I	OMe	Me	H	H	H	H	Cl	72
2,3-Dimethyl-	(2-3)	I	OMe	Me	Me	H	H	H	Cl	73
2,5-Dimethyl-	(2-4)	I	OMe	Me	H	H	Me	H	Cl	85
2,6-Dimethyl-	(2-5)	I	OMe	Me	H	H	H	Me	F	42
	(2-6)	II	Me	Me	H	H	H	H	F	9
	(2-7)	II	Me	H	Me	H	H	H	F	14
2,6-Dimethyl-	(2-8)	I	OMe	Me	H	H	H	Me	Cl	44
	(2-9)	II	Me	H	Me	H	H	H	Cl	40
3,5-Dimethyl-	(2-10)	I	OMe	H	Me	H	Me	H	Cl	46
	(2-11)	II	H	H	H	Me	H	Me	Cl	16
2,3,5-Trimethyl-	(2-12)	I	OMe	Me	Me	H	Me	H	Cl	80
	(2-13)	II	H	H	Me	Me	H	Me	Cl	12
2,3,5,6-Tetramethyl-	(2-14)	I	OMe	Me	Me	H	Me	Me	Cl	90

(Table continued)
Reactions of tetrahalogenobenzynes with substituted anisoles

Anisole Substituents	No.	Type	R$_1$	R$_2$	R$_3$	R$_4$	R$_5$	R$_6$	X	%
2,6-Dimethyl-1-trimethylsilyloxy-	(2-15)	I	-OSiMe$_3$	Me	H	H	H	Me	Cl	34
	(2-16)	II	Me	H	Me	H	H	H	Cl	34
2-Methoxy-	(2-17)	II	-OMe	H	H	H	H	H	Cl	52
3-Methoxy-	(2-18)	II	H	H	H	-OMe	H	H	Cl	76
3-Methyl-5-methoxy-	(2-19)	II	H	H	H	-OMe	H	Me	Cl	72
2-Methoxy-6-methyl-	(2-20)	II	-OMe	H	Me	-H	H	H	Cl	37
	(2-21)	II	-OMe	H	H	H	H	Me	Cl	16
	(2-22)	II	-H	H	H	H	H	H	Cl	15

The various substituted anisoles were prepared by methylating the phenols by conventional methods using sodium hydroxide and dimethyl sulphate in the aqueous phase.[16] However, the methylation of tetramethyl phenol gave only 40% yield of the substituted anisole, so in order to improve upon the yield, the modified method of Heaney and co-workers[17] was employed. Thus, when 2,3,5,6-tetramethylphenol was stirred with powdered potassium hydroxide and acid free dimethyl-sulphate in dry dimethylsulphoxide at room temperature for three hours, 92% yield of the tetramethylanisole was obtained (Scheme 2-1). The method was found
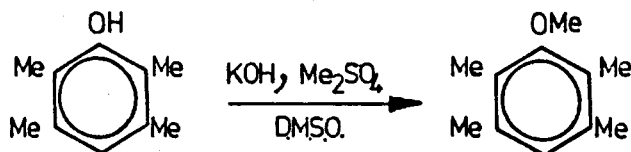
[Scheme 2-1]

to be easy in handling and either dimethylsulphate or methyl iodide can be conveniently used as the methylating agent. The various methylation

35.

results are collected in Table II.
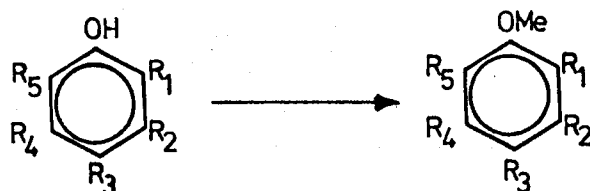
Anisole Products

Phenol Substituents	R_1	R_2	R_3	R_4	R_5	C.M.[*]	M.M.[*]
-	H	H	H	H	H	90	97[**]
2-Methyl-	Me	H	H	H	H	82	95[**]
2,3-Dimethyl-	Me	Me	H	H	H	80	94[**]
2,5-Dimethyl-	Me	H	H	Me	H	87	95[***]
2,6-Dimethyl-	Me	H	H	H	Me	86	94[**]
2,3,5-Trimethyl-	Me	Me	H	Me	H	76	89[**]
2,3,5,6-Tetramethyl-	Me	Me	H	Me	Me	40	92[**]
2-Hydroxy-	OMe	H	H	H	H	90	97[***]
3-Hydroxy-	H	-OMe	H	H	H	86	97[***]
3-Hydroxy-5-methyl-	H	-OMe	H	Me	H	78	92[**]

The use of 2,3-dimethoxytoluene is in a subsequent chapter of this thesis. Since 2,3-dimethoxytoluene is not commercially available we decided to prepare this compound. There are a few published routes, which involve a number of complicated steps, ending up with low yields.[18] In the present route a number of modifications have been made to the existing procedures, which resulted in reasonably good yields of the

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[*] C.M. = conventional method; M.M. = modified method;

[**] method 1(B); [***] method 1(C).

36.

desired product. One of the routes used is schematically represented in Scheme 2-2.

According to the present scheme, the first step was the nitration of o-cresol. In earlier studies[19] it was shown that the nitration of a variety of highly reactive/compounds, such as phenols, readily undergo nitration even under very mild conditions (dilute nitric acid), and at a far more rapid rate than can be explained on the basis of concentration of NO_2^+ that is present in the mixture. This was shown to be due to the presence of nitrous acid in the system which nitrosates the reactive nucleus via the nitrosonium ion NO^+ or its equivalent. The nitroso-phenols so obtained are known to be oxidized very readily by nitric acid to yield the nitrophenols (2-22) and nitrous acid; thereby the process is progressively speeded up as the amount of nitrous acid increases in the reaction mixture. Some direct nitration by NO_2^+ also takes place simultaneously, depending upon the reaction conditions.

aromatic

$$HNO_2 + 2HNO_3 \rightleftharpoons H_3O^+ + NO^+ + 2NO_3^-$$
[2-23]
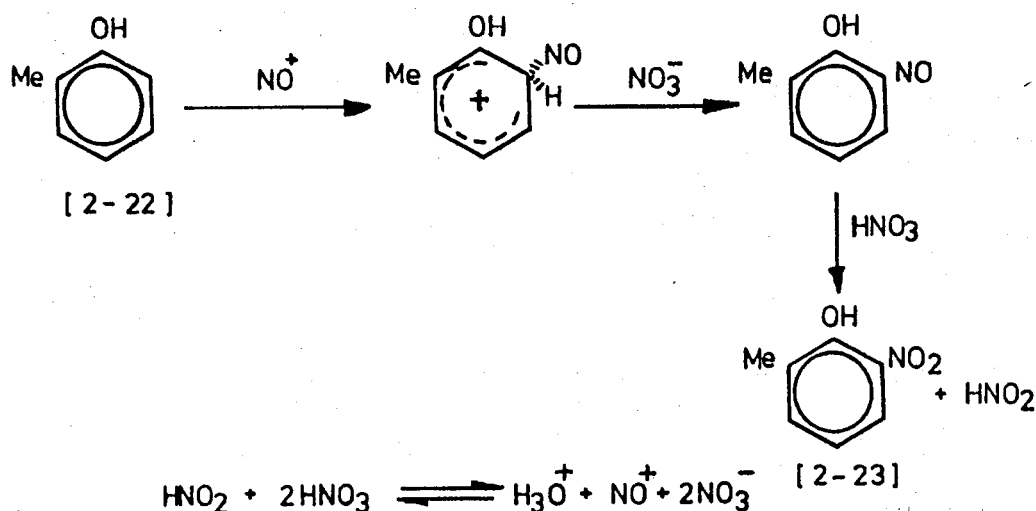
The nitration process is temperature-dependent; the formation of dinitro-derivatives can be controlled using the appropriate reaction

37.
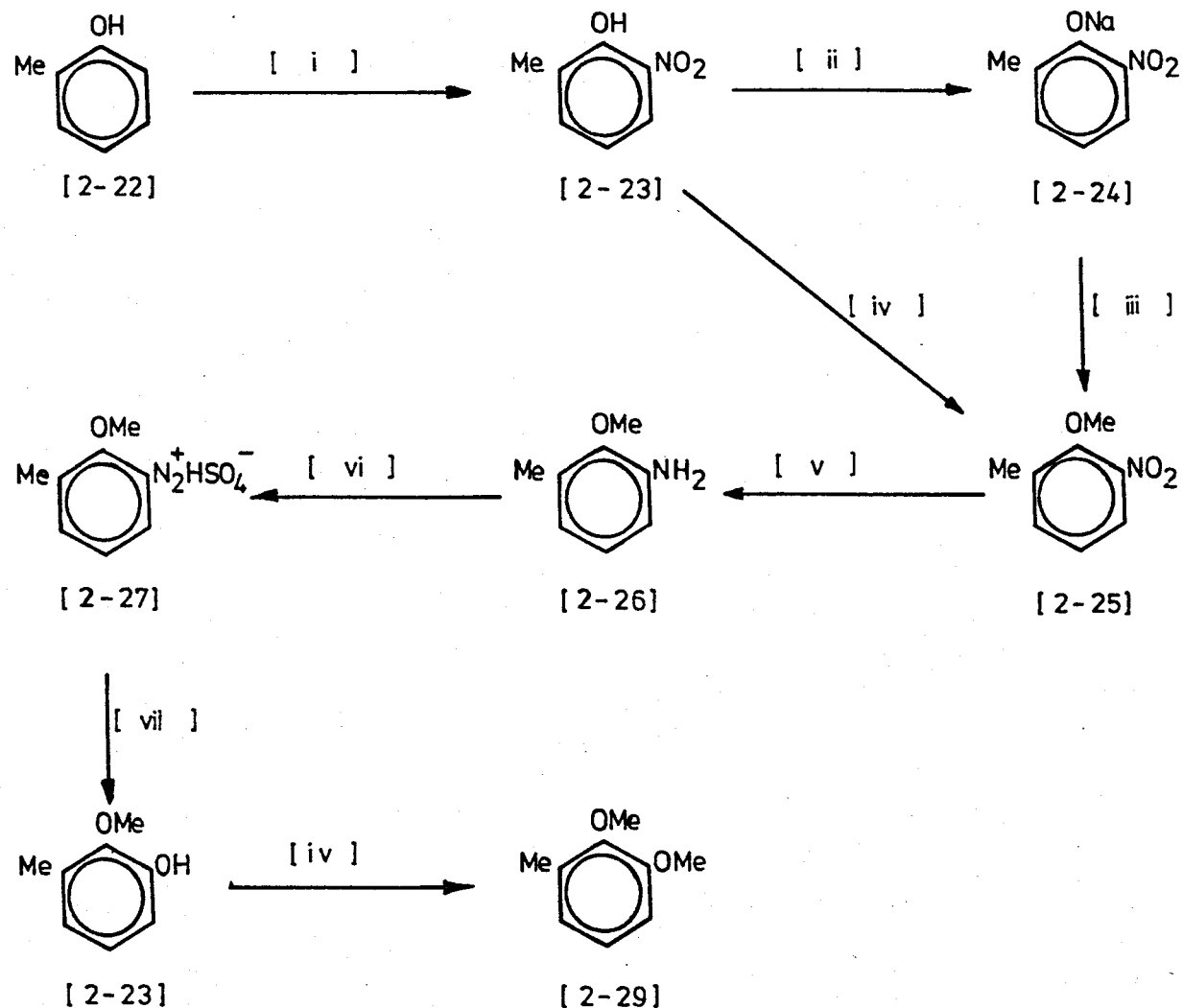
Solvents: [i] $HNO_3 - CH_3COOH$;[ii] $C_2H_5ONa - Bz$;

[iii] $(CH_3O)_2SO_2$;[iv] $KOH - DMSO - Me_2SO_4$;

[v] $Pd/C - C_2H_5OH - H_2NNH_2H_2O$;[vi] $NaNO_2 - H_2SO_4$; [vii] $Aq.H_2SO_4$.

[Scheme   2-2]

conditions. Gibson[20] reported the direct nitration of o-cresol using nitric acid in glacial acetic acid at -5° over a period of four hours, in 35% yield. In addition 3,5-dinitro-o-cresol (10%) and 5-nitro-o-cresol (15%) were obtained as by-products. We repeated the same reaction under similar conditions except that the reaction temperature was maintained at -25° during the mixing period and was then allowed to stir at ±2° for 4-5 hours, before pouring onto crushed ice-water mixture. An improved yield of 3-nitro-o-cresol (42%) was obtained, and only a 13% mixture of the 3,5-dinitro- and 5-nitro-derivatives of o-cresol were recovered.

The sodium salt of 3-nitro-o-cresol (2-23), as an intermediate for the alkylation, was conveniently prepared by reacting sodium ethoxide in dry benzene with 3-nitro-o-cresol at refluxing temperature. This step can be easily avoided in the case where the alkylation was carried out in D.M.S.O. by the procedure explained above. The yields of the alkylated products are equally good in both the reactions but the direct alkylation saves one step and avoids complication, since the sodium salt is hygroscopic.[21]

The other steps are simple. The reduction of 2-methoxy-3-nitro-toluene with 5% palladium on charcoal and hydrazine hydrate in ethanol proceeds smoothly without any complication giving a quantitative yield of the amine (2-26), which on treatment with sodium nitrite and sulphuric acid affords a solution of the diazonium salt (2-27) which quickly hydrolyses to give 2-methoxy-3-hydroxytoluene (2-28) in 51% yield. The phenol was then readily methylated using the standard procedure to give the desired 2,3-dimethoxytoluene (2-29) in 97% yield. All the intermediate products had sharp melting and boiling points comparable to those reported earlier (Scheme 2-2).

In an alternative method[22] o-vanillin (2-30) was methylated by
using potassium hydroxide and methyl iodide in D.M.S.O. The alkylated
product (2-31) was then subjected to Clemmensen reduction using zinc-
mercury amalgam in aqueous hydrochloric acid to give 2,3-dimethoxytoluene
(2-29) in 78% yield. The reaction can be summarized as in Scheme 2-3.
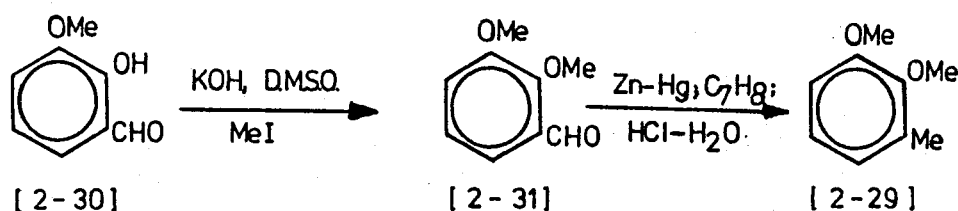
[Scheme 2-3]

The reaction of tetrachlorobenzyne with 2,3-dimethoxytoluene (2-29)
gave a mixture of benzobarrelenones (2-20) and (2-21) in total yield of
53%. The compound (2-20) was a mixture of exo- and endo-isomers in the
ratio of 0.5:9.5 (Scheme 2-4).

[Scheme 2-4]

40.
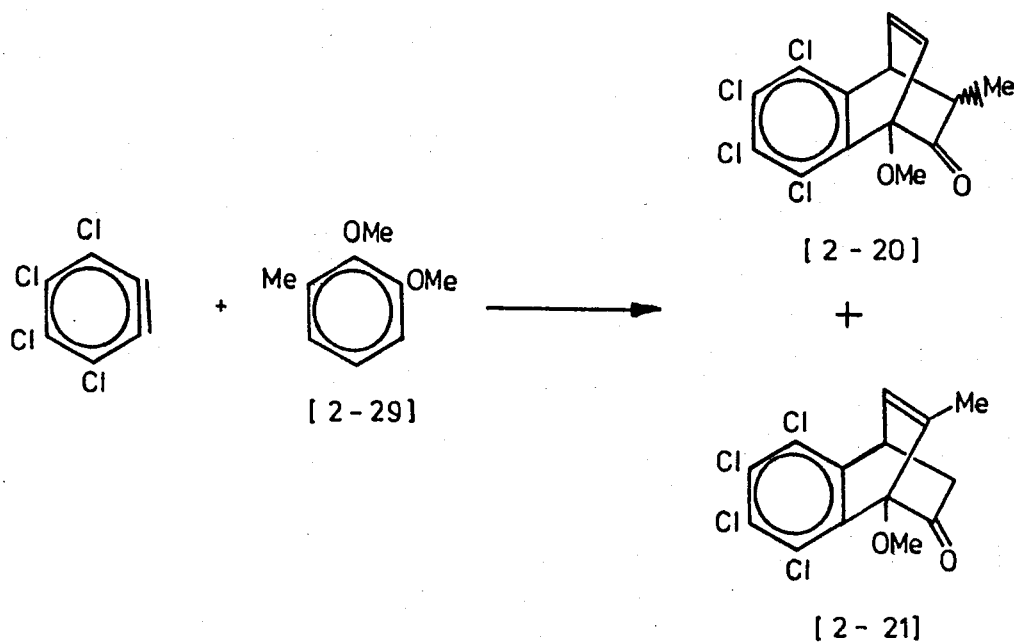
The structures of these compounds were established on the basis of their proton n.m.r. spectrum and other spectral evidence. The infrared spectra of the benzobarrelenones showed carbonyl stretching frequencies at ν_{max} (KBr)1740 and 1735 cm.$^{-1}$ However, their 90 MHz ^{1}H n.m.r. spectra differed significantly. The presence of methyl group in compound (2-20) was shown by the usual pattern as a doublet at τ(CDCl$_3$) 9.10 ($\underline{J}$ = 7 Hz) along with two olefinic protons shown by the multiplet at τ(CDCl$_3$) 3.08-3.28, whereas in the case of compound (2-21) the methyl also appeared as a doublet at τ(CDCl$_3$) 8.07 ($\underline{J}$ = 2.2 Hz). The proton on the olefinic double bond appeared as a doublet of quartets at τ(CDCl$_3$) 3.65 ($\underline{J}$ = 2.2 Hz and 7.0 Hz). The various other positions were assigned on the basis of spin-spin decoupling experiments.

Similarly the reactions of tetrachlorobenzyne with veratrole, m-dimethoxybenzene, and 3,5-dimethoxytoluene gave only one major product, the benzobarrelenone, in reasonably good yield. The various reactions are as summarized in Table I. The major product of tetrachlorobenzyne reaction with 3,5-dimethoxytoluene was 5-methyl-1-methoxy-tetrachloro-benzobarrelen-3(H)-one (2-19) in 71% yield (Scheme 2-5).

[2 - 19]

[Scheme 2-5]

41.
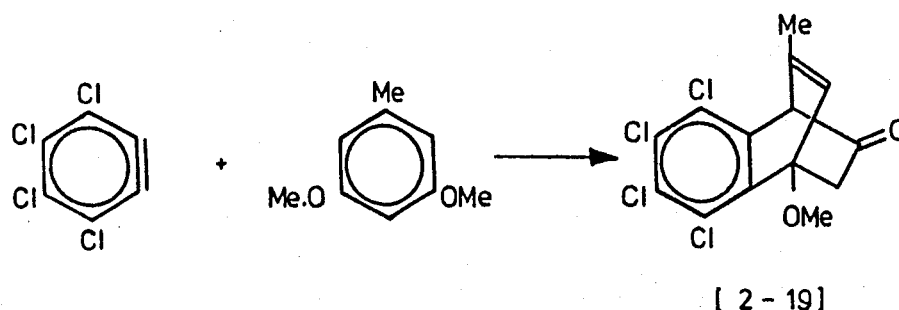
The structure of the adduct (2-19) was established on the basis of its spectral data. Thus, the infrared spectrum showed the carbonyl stretching frequency at ν_{max} (KBr) 1730 cm.$^{-1}$ The 90 M Hz ^{1}H n.m.r. spectrum showed the following resonances: the methyl appeared as a doublet at τ(CDCl$_3$) 7.98 ($\underline{J}$ = 2.2 Hz) indicating the methyl group on the double bond, whereas the other proton on the olefinic double bond appeared as a multiplet at τ(CDCl$_3$) 3.52. Similarly other positions were assigned on the basis of spectral measurements. However, mass spectrometry showed the highest m/e value at 310. This is in accord with earlier measurements which have shown that most of the benzobarrelenones readily lose ketene (H$_2$C=C=O; m/e 42) on the probe, giving rise to a stable naphthalene ion (2-32).[23]
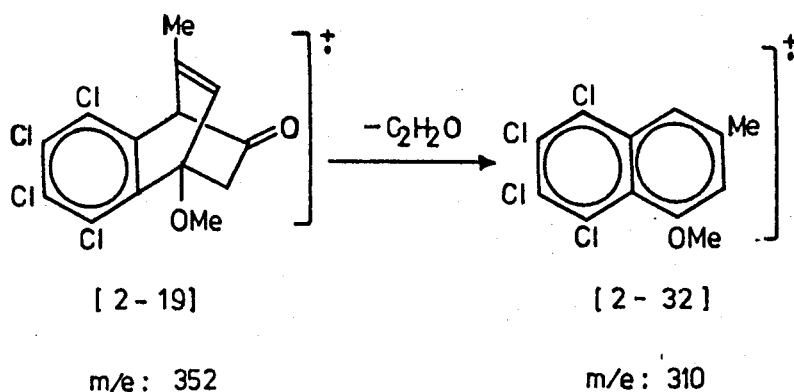
In the majority of the reactions, the initially formed enol-ethers were so unstable that we were unable to obtain any evidence for their presence in the reaction mixtures. However, one such stable enol ether has been reported from the reaction of tetrafluorobenzyne with 2,6-dimethoxy-toluene.[10]

Having established the structures of these benzobarrelenones, the ketone (2-19) was hydrolysed by base to the hydroxy acid (4-32). The ring opening reactions of benzobarrelenone by means of base have been studied

previously.[24] The other details of base-catalysed reaction are discussed in the last chapter of this thesis.

While these studies were in progress, we decided to investigate some of the cycloaddition reactions between tetrachlorobenzyne and suitably protected phenols, in order to obtain products with hydroxyl groups at bridgehead positions. The phenolic hydroxyl groups were protected as the trimethylsilyl ethers. The reaction between tetrachlorobenzyne and 2,6-dimethyl-1-trimethylsilyl phenyl ether (2-33)[25] gave the product (2-34) in which the trimethylsilyloxy-group was present at the bridgehead position. It was observed that the silyl ethers can be conveniently used for the aryne reactions, without damaging the -O-Si bond under the reaction conditions and that this can be purified by column chromatography. The compound (2-15) on acid hydrolysis gave the desired adduct (2-34) with hydroxyl group at the bridgehead position. The reaction can be summarized as in Scheme 2-6.
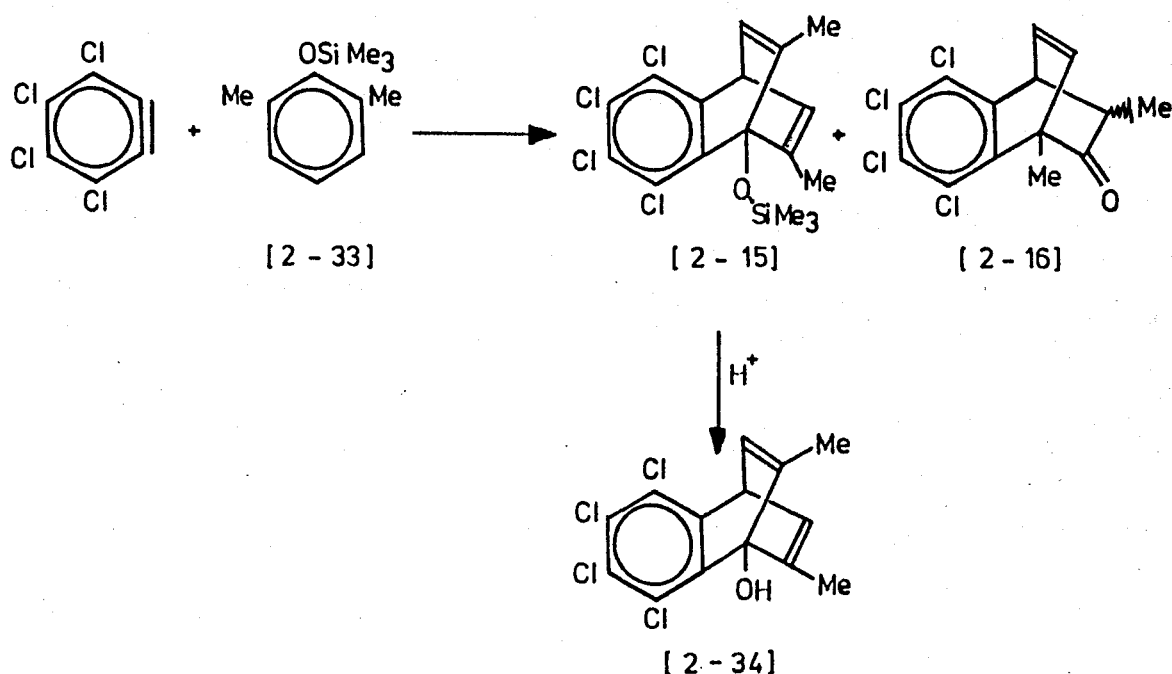
[Scheme 2-6]

A number of similar other cycloaddition reactions were conducted in which aryltrimethylsilyl ethers were used as the coreactant and the cycloadducts obtained were found to carry the trimethylsilyl group intact. The utility of these silyl ethers increases the range of reactants which can be used in obtaining a large number of compounds which cannot be achieved by other means.

In the reactions of arynes with tertiary amines a number of products are usually formed. S.V.Ley in this laboratory investigated the reaction of tetrafluorobenzyne with N,N-dimethylaniline in detail in an attempt to characterize the products formed and to establish the various mechanistic pathways.[26] In the present study we decided to repeat the reaction using tetrachlorobenzyne. Thus, when pentachlorophenyl lithium was decomposed at room temperature in ether containing an excess of N,N-dimethylaniline, the two expected products were obtained, compound (2-35) in 48% yield and the benzobarrelenone (2-22) in 1.5% yield.
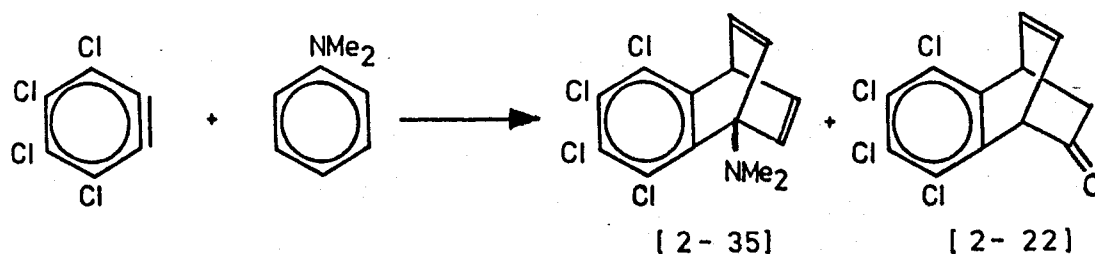
[Scheme 2-7]

Since we required the adduct (2-35) for dechlorination studies no further reactions were undertaken.

In view of our intention to study the details of the dechlorination process, a large number of other benzobicyclic derivatives were also obtained by reacting tetrachlorobenzyne with other appropriate co-reactants. Thus, when tetrachlorobenzyne was generated either by the

44.

aprotic diazotization of tetrachloroanthranilic acid (which was
prepared by the improved method of N.J.Hales) or by the decomposition
of 2-carboxytetrachlorobenzenediazonium tetrafluoroborate in the presence
of three equivalents of cyclopentadiene (freshly distilled), tetrachloro-
benzonorbornadiene (2-36) was obtained in 40% yield along with a large
amount of highly coloured impurities. The reaction is summarized in
Scheme 2-8.
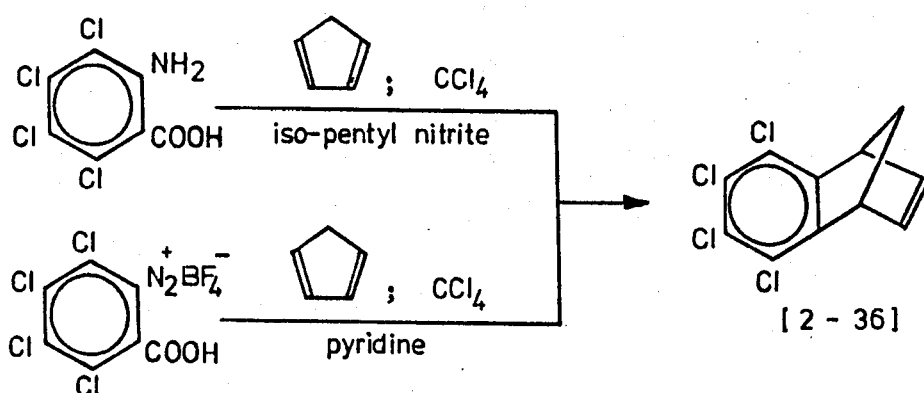
[Scheme 2-8]

The structure of the benzonorbornadiene (2-36) was established by
comparison with the earlier published spectroscopic data.[27] The catalytic
hydrogenation using 10% palladium on charcoal in ethanol under a positive
pressure of hydrogen gave tetrachlorobenzonorbornene in 100% yield. The
decomposition of pentachlorophenyl lithium in ether containing 6,6-di-
methylfulvene (2-37) at room temperature gave 80% yield of the cyclo-
adduct (2-38). The structure of the compound (2-38) was in accord with
the literature values.[28] The adduct (2-38) was also reduced catalytically
using 5% palladium on charcoal under a positive pressure of hydrogen.
The reaction is summarized in Scheme 2-9.
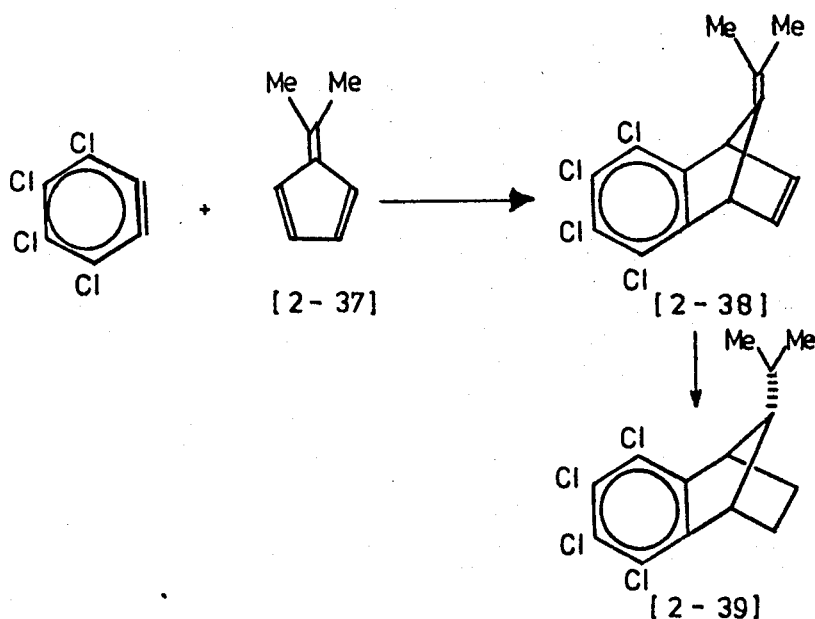
[Scheme 2-9]

Good yields of Diels-Alder cyclo-adducts were obtained when tetra-chlorobenzyne was added to furan and pyrroles. Thus, when pentachloro-phenyl lithium was decomposed at room temperature in ether containing a large excess of furan[5] or substituted N-methylpyrroles[29] the expected 1,4-dihydro-1,4-epoxynaphthalene (2-40) or the substituted 1,4-dihydro-1,4-iminonaphthalene derivatives were obtained, depending upon the reactant, in reasonably good yield. The various reactions are summarized in Table III.

(TABLE III)

46.
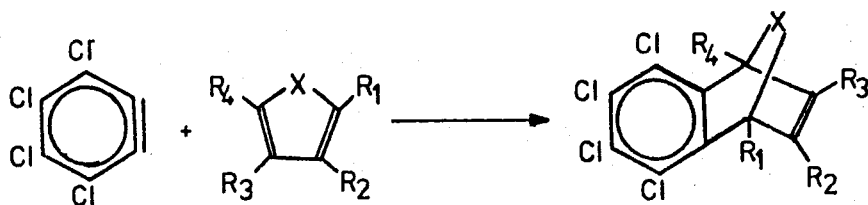
Substituent	No.	R$_1$	R$_2$	R$_3$	R$_4$	X	Yield %
		Product					
Furan	(2-40)	H	H	H	H	O	66
N-Methylpyrrole	(2-41)	H	H	H	H	NMe	86
1,2,5-Trimethyl-pyrrole	(2-42)	Me	H	H	Me	NMe	68

The structures of various compounds were established on the basis of spectroscopic measurements. Vernon and his co-workers[29] have reported the preparation and acid-catalysed reactions of various 1,4-dihydro-1,4- iminonaphthalene derivatives with bridgehead substituents. Our results were in accord with the previously published data.

Similarly the cycloaddition of tetrachlorobenzyne to 5,5-dimethoxy-tetrachlorocyclopentadiene (2-43) at room temperature in ether gave the stable octachlorobenzonorbornadiene (2-44) adduct. Deketalization of this adduct by acidic hydrolysis using sulphuric acid in o-dichloro-benzene led to the formation of octachloronaphthalene (2-46). As expected no ketone (2-45) was obtained. This is in agreement with the results obtained by Wilt and co-workers[30] in their studies of 7,7-dimethoxytetrachlorobenzonorbornadiene. The octachloronaphthalene (2-46) was characterized by comparison with an authentic sample. The results are summarized in Scheme 2-10.

[2 - 43]   [2 - 44]
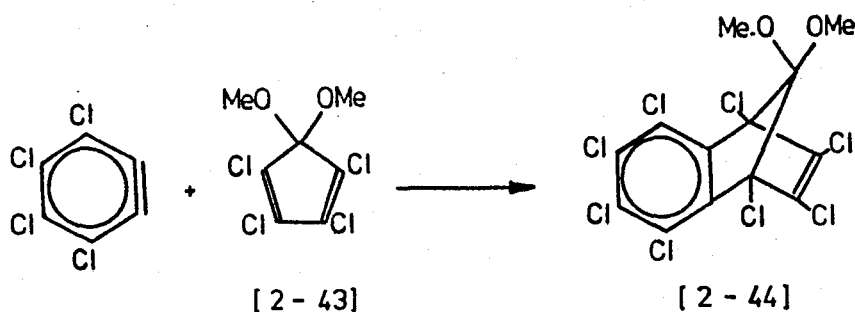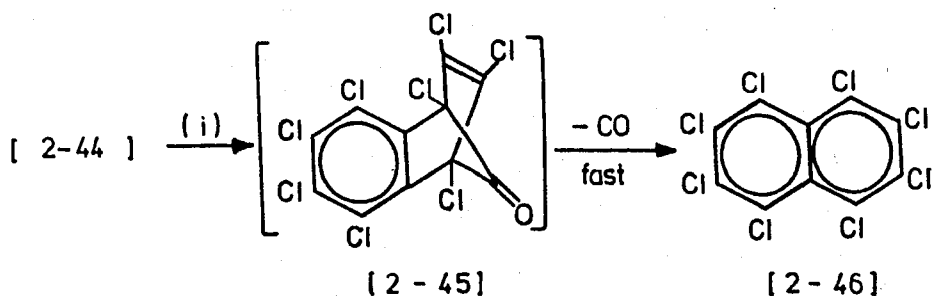
Solvents : (i) $O-C_6H_4Cl_2 - H_2SO_4$

[Scheme 2-10]

The reactions of tetrachlorobenzyne with benzene,[5] mesitylene[5,31] t-butylbenzene[5] and tri-t-butylbenzene gave reasonably good yields of the cycloadducts. The reaction between tetrachlorobenzyne and t-butylbenzene gave a mixture of two products in the ratio 8.1:1.9, non-bridgehead to bridgehead substitution of the t-butyl group. The mixture was successfully separated by column chromatography on alumina. The two products were identified by the proton n.m.r. analysis of the olefinic region and the bridgehead protons (on the basis of their integration measurements). The structure of these compounds was established on the basis of comparison with previously published data. The various results are summarized in Table IV.

Table IV.
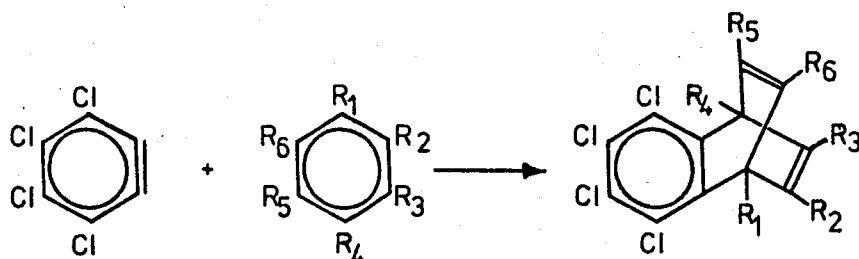
Reactant	No.	R	R	R	R	R	R	Yield %
Benzene	(2-47)	H	H	H	H	H	H	66
Mesitylene	(2-48)	Me	H	Me	H	Me	H	82
t-Butylbenzene	(2-49)	H	^{t}Bu	H	H	H	H	50
	(2-50)	^{t}Bu	H	H	H	H	H	12
Tri-t-butylbenzene	(2-51)	^{t}Bu	H	^{t}Bu	H	^{t}Bu	H	69

Finally, the reactions of tetrachlorobenzyne with substituted naphthalene derivatives resulted in good yields of 9,10-dihydro-9,10-ethenoanthracene derivatives. Thus, 1-methoxynaphthalene and tetrachlorobenzyne gave a 70% yield of the 9-methoxytetrachloroetheno-anthracene (2-52), which was catalytically reduced by palladium on charcoal to give the dihydro-derivative in 100% yield (Scheme 2-11). Similarly a reaction of N,N-dimethylaminonaphthalene with tetrachloro-benzyne resulted in the 9-N,N-dimethylaminotetrachloroethenoanthracene (2-53) in 77% yield, which on catalytic reduction gave 100% yield of the reduced product (2-54) (Scheme 2-11).
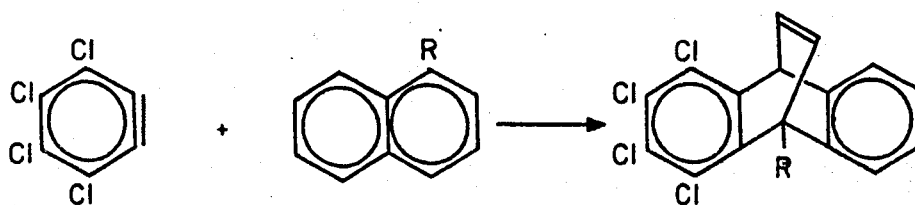
[Scheme 2-11]

Substituent	No.	Product R	Yield (%)
1-Methoxynaphthalene	(2-52)	-OMe	70
1-N,N-Dimethylamino-naphthalene	(2-53)	-NMe$_2$	77

The structures of all these compounds were established from elemental analyses and spectroscopic data.

The ^{1}H and ^{13}C n.m.r. spectra of 1,2,3,4-tetrachloro-9-N,N-dimethyl-amino-9,10-dihydro-9,10-ethenoanthracene showed the presence of diastereotopic methyl groups.

Since we required most of these compounds for the dechlorination study in order to facilitate the dechlorination work of benzobarrelenones, the carbonyl group of the benzobarrelenones were protected as their ethylene dioxy ethers (ketals). The ethylenedioxy derivatives of various benzobarrelenes were prepared using ethane-1,2-diol and boron trifluoride etherate in dichloromethane in the ratio 1:5:5:30 by stirring the mixture at room temperature for 50-60 h. Various ketals prepared are as reported in Table V.

Table V
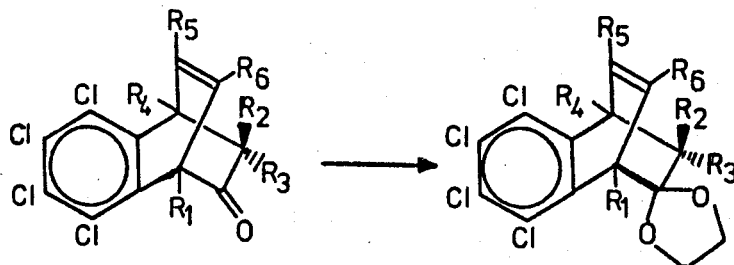
Reagents : (CH$_2$OH)$_2$, BF$_3$(C$_2$H$_5$)$_2$O in Dichloromethane

Anisole Ketals	No.	R$_1$	R$_2$	R$_3$	R$_4$	R$_5$	R$_6$	Yield %
2,2-Ethylenedioxy-	(2-55)	-OMe	H	H	H	H	H	85
2,2-Ethylenedioxy-6-methyl-	(2-56)	-OMe	H	H	H	H	Me	95
3,3-Ethylenedioxy-	(2-57)	-H	H	H	-OMe	H	H	88
3,3-Ethylenedioxy-5-methyl-	(2-58)	-H	H	H	-OMe	H	Me	89

50.

Most of these compounds have been used for dechlorination purposes and acid-catalysed rearrangement reactions. The various results are discussed in the next two chapters.

EXPERIMENTAL

General Procedures:

All reactions involving organometallic reagents were carried out in glassware oven-dried at 120°, under an atmosphere of dry, oxygen-free nitrogen. All solvents were distilled and dried to the appropriate degree by conventional methods before use.

Analytical t.l.c. was carried out using 0.50 mm thick layers of silica-gel (GF_{254}: according to Stahl); or aluminium (60 PF_{254} Type E, according to Merck); preparative t.l.c. was carried out using 0.75 mm thick layers of silica-gel (PF_{254}: according to Stahl); or alumina (60 PF_{254} Type E: according to Merck).

Analytical g.l.c. was carried out using a Pye 104 series gas chromatograph fitted with a flame ionization detector. The 5 ft. columns used were:

A. 8% SE 30 on chromosorb W.

B 10% SE 30 on firebrick.

C. 10% carbowax on chromosorb W.

D. 10% Apiezon on chromosorb W.

E. OV-17.

Infrared spectra were determined for potassium bromide discs, or thin films, on a Perkin-Elmer 457 spectrophotometer. Ultra-violet spectra were determined on a Pye-Unicam SP 8000 spectrophotometer.

^{1}H n.m.r. spectra were determined for approximately 20% w/v solutions containing tetramethyl silane as internal standard at 60 M Hz Varian EM 360A or 90 M Hz on Perkin-Elmer R32 spectrometers.

Mass spectra were determined on an A.E.I. MS 12 mass spectrometer.

Melting points were determined on a Koffler hot stage and are uncorrected.

Light petroleum refers to the fraction boiling between $40-60^\circ$ unless otherwise stated.

1. Preparation of Substituted Anisoles:

Method A: A mixture of substituted phenol (1000.0 mmole), sodium hydroxide (1100.0 mmole) and water (500 ml) was stirred at room temperature for 15 minutes. Dimethyl sulphate (1000.0 mmole) was then added dropwise over 1 h and the mixture was heated under reflux for 3 h. The two layers were separated and the aqueous phase was extracted with ether (3 x 100 ml). The combined extracts were washed with sodium hydroxide (2$\underline{N}$, 4 x 100 ml) and dried (KOH pallets). The solvent was evaporated under reduced pressure and the residual oily mass was fractionally distilled to give the desired substituted anisole.

The alkaline washings on acidification (N̄HCl) gave unchanged phenol.

Method B: A mixture of substituted phenol (1000.0 mmole), powdered potassium hydroxide (1000.0 mmole) and dimethylsulphoxide (600 ml) was stirred at room temperature for 1.5 h. Acid-free dimethyl sulphate (1000.0 mmole) was then added dropwise over a period of 3 h., and the mixture was diluted with water (600 ml). The mixture was then extracted with ether (4 x 150 ml) and the combined extracts were dried (NaOH pallets). The solvent was removed under reduced pressure and the residual oil was fractionally distilled to give the desired substituted anisole.

The unchanged phenol was recovered as explained earlier.

Method C: A mixture of substituted phenol (1000.0 mmole), powdered potassium hydroxide (1000.0 mmole) and dimethylsulphoxide (600 ml) was stirred at room temperature for 2.0 h. Freshly distilled methyl iodide (1100.0 mmole) was then added dropwise over a period of 1 h and the mixture was allowed to stir at room temperature overnight. The mixture was then diluted (600 ml of water) and the reaction was worked up as explained in method B to get the desired anisole.

2. Reaction of Tetrachlorobenzyne with Anisole:

A stirred solution of pentachlorophenyl lithium [prepared from a suspension of hexachlorobenzene (28.5 g, 100 mmole) in dry ether (ca. 400 ml) and n-butyl-lithium in hexane (2.3 molar, 62.5 ml, 138 mmole) and maintained at -78°] was treated with anisole (100 ml). The reaction mixture was allowed to warm to $24-25^O$ and the mixture was allowed to stir at this temperature for 58 h. The reaction mixture was diluted with ether (200 ml) and treated with hydrochloric acid (2N, 100 ml). The organic phase was washed with water (2 x 100 ml), and dried (MgSO₄). The solvents and excess of anisole were evaporated under reduced pressure and the residual mass (ca. 35 g) was purified by column chromatography (silica gel) to give: i) 1-methoxytetrachlorobenzobarrelene[5,6,7,8-tetrachloro-1,4-dihydro-1-methoxy-1,4-ethenonaphthalene] (2-1): (23.66 g, 73%) m.p. $122-23^O$ (from ethanol) (lit.[5] m.p. 122°). Spectral data agreed with those previously reported; and ii) tetrachlorobenzobarrelen-2-one[-5,6,7,8-tetrachloro-3,4-dihydro-1,4-ethenonaphthalen-2(H)-one] (2-22) (1.7 g, 5%) m.p. $160-61^O$ (from ethanol) (lit.[5] m.p. 162°). Spectral data agreed with those previously reported.

3. Reaction of Tetrachlorobenzyne with 2-Methylanisole:

A stirred solution of pentachlorophenyl lithium was treated with 2-methylanisole (70.0 g) as explained in experiment 2. The reaction on working up gave: 2-methyl-1-methoxytetrachlorobenzobarrelene[5,6,7,8-tetrachloro-1,4-dihydro-1-methoxy-2-methyl-1,4-ethenonaphthalene] (2-2): (24.80 g, 72%) m.p. $129-30^O$ (from ethanol) (lit.[10] m.p. $129-31^O$). Spectral data agreed with those previously reported.

4. Reaction of Tetrachlorobenzyne with 2,3-Dimethylanisole:

A stirred solution of pentachlorophenyl lithium was treated with 2,3-dimethylanisole (80.0 g) as explained in experiment 2. The reaction

mixture on purification by column chromatography (silica gel, 10% ether in light petroleum) gave: 2,3-dimethyl-1-methoxytetrachlorobenzobarrelene [5,6,7,8-tetrachloro-1,4-dihydro-1-methoxy-2,3-dimethyl-1,4-etheno-naphthalene] (2-3) (25.70 g, 73% m.p. 155-56° (from ethanol) (lit.[10] m.p. 155-56°). Spectral data agreed with those previously reported.

5. Reaction of Tetrachlorobenzyne with 2,5-Dimethylanisole:

A stirred solution of pentachlorophenyl lithium was treated with 2,5-dimethylanisole (80.0 g) as explained earlier in experiment 2. The reaction mixture on purification by column chromatography (silica gel, 20% ether in light petroleum) gave: 2,5-dimethyl-1-methoxytetrachloro-benzobarrelene[5,6,7,8-tetrachloro-1,4-dihydro-1-methoxy-2,9-dimethyl-1,4-ethenonaphthalene] (2-4): (30.2 g, 85%) m.p. 160-61° (from ethanol) (lit.[10] m.p. 150-53°).

M^{+} (Mass spectrometry): 350.

^{1}H n.m.r. τ(CDCl$_3$): 3.34 (m, 1H); 3.65 (m, 1H); 5.10 (dd, 1H, J = 6 Hz, J = 2.2 Hz); 6.28 (s, 3H); 8.04 (d, 3H, J = 2.2 Hz); and 8.14 (d, 3H, J = 2.2 Hz).

ν_{max}^{KBr}: 3010, 2975, 2945, 2915, 2835, 1445, 1365, 1340, 1295, 1240, 1175, 1110, 1060, 1025, 990, 930, 840, 800, 755, 745, 685, and 645 cm.$^{-1}$

6. Reaction of Tetrafluorobenzyne with 2,6-Dimethylanisole:

A stirred solution of pentafluorophenyl magnesium chloride [prepared from chloropentafluorobenzene (10.12 g, 50 mmole) and magnesium (1.7 g, 70 mg-atoms) in ether (100 ml) in the presence of 1,2-dibromoethane (0.5 ml), maintaining the temperature at ca. 35°] was treated with 2,6-di-methylanisole (72 ml) in cyclohexane (80 ml). The reaction temperature was raised to 82°, by the removal of ether and heated under reflux for 3 h. The reaction mixture was cooled and diluted with ether (100 ml). The ethereal layer was extracted with hydrochloric acid (2N, 100 ml),

washed and dried (MgSO₄). Removal of the solvents and excess of 2,6-dimethylanisole under reduced pressure gave an oil which was separated by column chromatography [silica gel, 20% ether in light petroleum] to afford i) 2,6-dimethyl-1-methoxytetrafluorobenzobarrelene [5,6,7,8-tetrafluoro-1,4-dihydro-1-methoxy-2,10-dimethyl-1,4-ethenonaphthalene] (2.5): (5.95 g, 42%), b.p. 110° at 4 mm (lit.[26] b.p. 110° at 4 mm). Spectral data agreed with those previously reported. ii) A mixture of ketones was obtained which was further separated by preparative t.l.c. to give:

a) 1,3-exo-dimethyltetrafluorobenzobarrelen-2-one [5,6,7,8-tetrafluoro-1,4-dihydro-1,3-exo-dimethyl-1,4-ethenonaphthalen-2(H)-one] (2-6): (1.20 g, 9%) m.p. 85-87° (from ethanol) (lit.[26] m.p. 86-87°). Spectral data agreed with those previously reported.

b) 1,3-endo-dimethyltetrafluorobenzobarrelen-2-one [5,6,7,8-tetrafluoro-1,4-dihydro-1,3-endo-dimethyl-1,4-ethenonaphthalen-2(H)-one] (2-7): (2.0 g, 14%) m.p. 58-60° (from ethanol (lit.[26] m.p. 58-59°). Spectral data agreed with those previously reported.

7.   Reaction of Tetrachlorobenzyne with 2,6-Dimethylanisole:

A stirred solution of pentachlorophenyl lithium was treated with 2,6-dimethylanisole (120.0 g) as explained earlier in experiment 2. The crude mixture obtained was separated by column chromatography (silica gel, 10% ether in light petroleum) to give:

i) 2,6-dimethyl-1-methoxytetrachlorobenzobarrelene [5,6,7,8-tetrachloro-1,4-dihydro-1-methoxy-2,10-dimethyl-1,4-ethenonaphthalene] (2-8). (15.50 g, 44%) m.p. 148-50° (from ethanol) (lit.[10] m.p. 148-50°). Spectral data agreed with those previously reported.

ii) 1,3-dimethyltetrachlorobenzobarrelen-2-one [5,6,7,8-tetrachloro-1,4-dihydro-1,3-dimethyl-1,4-ethenonaphthalen-2(H)-one] (2-9). (13.5 g, 40%) m.p. 139-40° (from ethanol) (lit.[10] m.p. 138-140°). Spectral data agreed with those previously reported.

8. <u>Catalytic Hydrogenation of 1,3-Dimethyltetrachlorobenzobarrelen-2-one (2-9)</u>.

A suspension of palladised charcoal [10% Pd/C] in a solution of 1,3-dimethyltetrachlorobenzobarrelen-2-one (2-9) [0.50 g, 0.150 mmole] in absolute ethanol [25 ml] and ethyl acetate [5 ml] was stirred under positive pressure of hydrogen for 8 h. The catalyst was filtered and the filtrate was concentrated under reduced pressure. The residual pale yellow solid was purified by preparative t.l.c. [silica, 20% ether in light petroleum] to give: <u>1,3-exo-dimethyltetrachlorobenzobicyclo[2.2.2]oct-7-ene-2-one (2-9')</u>:

(470 mg, 92%) m.p. 130-31° (from ethanol).

M$^{+}_{\cdot}$ (Mass Spectrometry): 282.

^{1}H n.m.r. τ(CDCl$_3$): 5.95-6.12 (m, 1H); 7.4-7.81 (m, 1H), 7.81-8.35 (m, 4H); 8.10 (s, 3H); 8.9-9.2 (d, 3H, $\underline{J}$ = 7.2 Hz)

ν^{KBr}_{max}: 3000, 3990, 2940, 2900, 1735, 1450, 1375, 1355, 1305, 1260, 1190, 1140, 1090, 1060, 965, 922, 895, 860, 785, 745, 700, 685, and 640 cm.$^{-1}$

9. <u>Reaction of Tetrachlorobenzyne with 3,5-Dimethylanisole</u>:

A stirred solution of pentachlorophenyl lithium was treated with 3,5-dimethylanisole (80.0 g) as explained earlier in experiment 2. The reaction mixture was purified by column chromatography [silica gel, 10% ether in light petroleum] to give :

<u>i</u>)' <u>3,5-dimethyl-1-methoxytetrachlorobenzobarrelene[5,6,7,8-tetrachloro-1,4-dihydro-1-methoxy-3,9-dimethyl-1,4-ethenonaphthalene</u>] (2-10) :

(6.5 g, 46%) m.p. 125-26° (from ethanol).

(Found: C, 51.3; H, 3.4%; C$_{15}$H$_{12}$Cl$_4$O requires, C, 51.45; H, 3.4%).

M$^{+}_{\cdot}$ (Mass spectrometry): 350.

^{1}H n.m.r. τ(CDCl$_3$): 3.38-3.57 (m, 2H); 5.17-5.34 (m, 1H); 6.3 (s, 3H); 7.88-8.17 (d, 6H, $\underline{J}$ = 2.2 Hz).

ν_{max}^{KBr}: 3060, 2975, 2935, 2910, 2850, 2840, 1442, 1365, 1345, 1290, 1278, 1248, 1175, 1125, 1100, 1040, 1015, 990, 920, 855, 820, 780, 745, 725, and 645 cm.$^{-1}$

ii) 1,5-dimethyltetrachlorobenzobarrelen-3-one[5,6,7,8-tetrachloro-1,4-dihydro-1,9-dimethyl-1,4-ethenonaphthalen-3(1$\underline{H}$)-one] (2-11):

(5.2 g, 16%) m.p. 170-71° (from ethanol).

(Found: C, 49.8; H, 3.0%; $C_{14}H_{10}Cl_4O$ requires C, 50.0; H, 3.00%).

$M^{+}_{\cdot}$ (Mass spectrometry): 294

^1H n.m.r. $\tau(CDCl_3)$: 3.9-4.1 (m, 1H); 5.05-5.24 (d, 1H, $\underline{J}$ = 2.2 Hz); 7.77-7.96 (m, 2H); 7.94 (s, 3H); 7.96-8.16 (d, 3H, J = 2.2 Hz).

ν_{max}^{KBr} : 3020, 3000, 2975, 2935, 2910, 2880, 2850, 1730, 1460, 1440, 1375, 1355, 1285, 1240, 1214, 1170, 1125, 1080, 895, 825, 788, 750, 695, and 645 cm.$^{-1}$

10. Reaction of Tetrachlorobenzyne with 2,3,5-Trimethylanisole:

A stirred solution of pentachlorophenyl-lithium was treated with 2,3,5-trimethylanisole (50.0 g) in dry ether (400 ml) as explained earlier in experiment 2. The reaction mixture was purified by column chromatography [silica gel, 1 0% ether in light petroleum] to give :

i) 2,3,5-trimethyl-1-methoxytetrachlorobenzobarrelene[5,6,7,8-tetra-chloro-1,4-dihydro-1-methoxy-2,3,9-trimethyl-1,4-ethenonaphthalene] (2-12)

(29.20g, 80%) m.p. 139-40° (from ethanol)

(Found: C, 52.4; H, 4.3%; $C_{16}H_{14}Cl_4O$ requires, C, 52.45; H, 4.37%).

$M^{+}_{\cdot}$ (mass spectrometry): 366.

^1H n.m.r. $\tau(CDCl_3)$: 3.28-3.45 (m, 1H); 5.2-5.38 (d, 1H, $\underline{J}$ = 2.2 Hz); 6.29 (s, 3H) 7.98 (d, 3H, $\underline{J}$ = 2.2 Hz); 8.1 (q, 3H, $|\underline{J}|$ = 1.5 Hz); and 8.24 (q, 3H, $|\underline{J}|$ = 1.5 Hz)

ν_{max}^{KBr} : 2990, 2975, 2955, 2915, 2835, 1655, 1437, 1370, 1358, 1342, 1285, 1250, 1215, 1195, 1115, 1098, 990, 965, 935, 850, 825, 785, 747, 695, 660, 640, and 630 cm.$^{-1}$

ii) 3,4,6-trimethyltetrachlorobenzobarrelen-2-one [5,6,7,8-tetrachloro-1,4-dihydro-3,4,10-trimethyl-1,4-etheno-naphthalen-2(1H)-one] (2-13):

(4.5 g, 12%) m.p. 145-46° (from ethanol).

(Found: C, 51.3; H, 3.4%; $C_{15}H_{12}Cl_4O$ requires C, 51.4; H, 3.4%).

m/e (Mass spectrometry): 284.

^{1}H n.m.r. τ(CDCl$_3$): 3.9-4.1 (m, 1H); 5.1-5.3 (d, 1H, $\underline{J}$ = 2.2 Hz); 7.8-8.15 (m, 1H); 8.0 (s, 3H); 8.05-8.15 (d, 3H, $\underline{J}$ = 2.2 Hz); and 9.02-9.24 (d, 3H, $\underline{J}$ = 7.2 Hz).

ν_{max}^{KBr} : 3025, 2985, 2950, 2930, 2890, 1728, 1458, 1445, 1378, 1360, 1290, 1255, 1245, 1190, 1092, 905, 855, 820, 790, 760, and 690 cm.$^{-1}$

11.   Catalytic Hydrogenation of 3,4,6-trimethyltetrachlorobenzobarrelen-2-one (2-13):

A suspension of palladium on charcoal (10% Pd/C, 40 mg) in a solution of 3,4,6-trimethyltetrachlorobenzobarrelen-2-one (2-13) (0.50 g, 1.150 mmole) in ethyl alcohol (25 ml) and ethyl acetate (10 ml) was stirred under positive pressure of hydrogen for 3 h. The catalyst was filtered and the filtrate was concentrated under reduced pressure. The residue was purified by preparative t.l.c. to give: 3,4,6-trimethyl-tetrachlorobenzobicyclo[2.2.2]oct-7-ene-2-one (2-13')

(500 mg, 98%) m.p. 142-43° (from ethanol)

(Found: C, 51.3; H, 3.8%; $C_{15}H_{14}Cl_4O$ requires, C, 51.15; H, 4.00%).

m/e(Mass spectrometry): 285.

ν_{max}^{KBr}: 3020, 2990, 2955, 2940, 2880, 1727, 1458, 1450, 1380, 1365, 1260, 1195, 1130, 1090, 960, 875, 830, 790, 765, and 692 cm.$^{-1}$

12.   Reaction of tetrachlorobenzyne with 2,3,5,6-tetramethylanisole.

A stirred solution of pentachlorophenyl lithium was treated with 2,3,5,6-tetramethylanisole (38.0 g) in ether (400 ml) as explained earlier in experiment 2. The crude product obtained was purified by column

chromatography [silica gel, 10% ether in light petroleum] to give

2,3,5,6-tetramethyl-1-methoxytetrachlorobenzobarrelene [5,6,7,8-tetra-chloro-1,4-dihydro-1-methoxy-2,3,9,10-tetramethyl-1,4-ethenonaphthalene] (2.14):

(34.20 g, 90%) m.p. 166-67° (from ethanol)

(Found: C, 53.5; H, 4.2%; $C_{17}H_{16}Cl_4O$ requires, C, 53.95; H, 4.25%).

M.$^+$ (Mass spectrometry): 378

^{1}H n.m.r. τ(CDCl$_3$): 5.38 (s, 1H); 6.29 (s, 3H); 8.16 (s, 12H)

ν_{max}^{KBr}: 2990, 2970, 2930, 2860, 1450, 1375, 1365, 1350, 1300, 1285, 1240, 1190, 1121, 1095, 1012, 955, 832, 795, and 648 cm.$^{-1}$

13.   Reaction of tetrachlorobenzyne with 2,6-Dimethylphenyl-1-trimethylsilyl ether.

A stirred solution of pentachlorophenyl lithium was treated with 2,6-dimethylphenyl-1-trimethylsilyl ether (42.0 g) as explained earlier in experiment 2. The residual mass was purified by column chromatography [silica gel, 10% ether in light petroleum] to give:

i)   2,6-dimethyl-1-trimethylsilyloxytetrachlorobenzobarrelene[5,6,7,8-tetrachloro-1,4-dihydro-1-trimethylsilyloxy-2,10-dimethyl-1,4-etheno-naphthalene] (2-15).

(6.5 g, 34%) m.p. 132-33° (from ethanol)

(Found: C, 49.6; H, 4.3%; $C_{17}H_{18}Cl_4SiO$ requires C, 50.0; H, 4.4%).

M.$^+$ (mass spectrometry): 408.

^{1}H n.m.r. τ(CDCl$_3$): 3.45-3.72 (m, 2H); 4.85-5.12 (t, 1H, $\underline{J}$ = 7.0 Hz); 7.92-8.16 (d, 6H, $\underline{J}$ = 2.2 Hz); and 9.58 (s, 9H).

ν_{max}^{KBr}: 3065, 3015, 2965, 2925, 2850, 1448, 1430, 1365, 1345, 1290, 1265, 1250, 1190, 1113, 1018, 968, 938, 921, 885, 840, 825, 790, 755, and 710 cm.$^{-1}$

ii) 1,3-dimethyltetrachlorobenzobarrelen-2-one [5,6,7,8-tetrachloro-1,4-dihydro-1,3-dimethyl-1,4-etheno-naphthalen-2(1H)-one] (2-16):

(5.6 g, 34%) m.p. 139-40° (from ethanol) (lit.[10] m.p. 138-39°).
Spectral data agreed with those previously reported.

14. Reaction of Tetrachlorobenzyne with 1,2-Dimethoxybenzene:

A stirred solution of pentachlorophenyl lithium was treated with 1,2-dimethoxybenzene (60.0 g) in dry ether (400 ml) as explained earlier in experiment 2. The reaction mixture on work up and purification by column chromatography [silica gel, 10% ether in light petroleum] gave: 1-methoxytetrachlorobenzobarrelen-2-one [5,6,7,8-tetrachloro-1,4-dihydro-1-methoxy-1,4-ethenonaphthalen-2(1H)-one] (2-17):

(17.60 g, 52%) m.p. 149-51° (from ethanol).

(Found: C, 45.7; H,2.35%; $C_{13}H_8Cl_4O_2$ requires, C, 46.15; H, 2.35%).

m/e (Mass spectrometry): 296.

^{1}H n.m.r. τ(CDCl$_3$): 3.01-3.31 (m, 2H); 5.01-5.33 (m, 1H); 6.24 (s, 3H); 7.5-8.14 (dq, 2H, $\underline{J}$ = 15 Hz).

v_{max}^{KBr}: 3085, 3010, 2950, 2855, 1745, 1620, 1458, 1412, 1373, 1360, 1338, 1310, 1285, 1260, 1238, 1198, 1125, 1085, 1025, 953, 895, 850, 830, 772, 715, 700, and 648 cm.$^{-1}$

15. Reaction of Tetrachlorobenzyne with 1,3-Dimethoxybenzene:

A stirred solution of pentachlorophenyl lithium was treated with 1,3-dimethoxybenzene (70.0g) as explained earlier in experiment 2. The reaction mixture on purification by column chromatography [silica gel, 20% ether in light petroleum] gave: 1-methoxytetrachlorobenzobarrelen-3-one [5,6,7,8-tetrachloro-1,4-dihydro-1-methoxy-1,4-etheno-naphthalen-3(1H)-one] (2-18):

(25.70 g, 76%) m.p. 151-53° (from ethanol)

(Found: C, 46.2; H, 2.35%; $C_{13}H_8Cl_4O_2$ requires, C, 46.15; H, 2.35%).

m/e (Mass spectrometry): 296.

^{1}H n.m.r. τ(CDCl$_3$): 2.9-3.15 (m, 1H); 3.15-3.45 (m, 1H); 4.96 (m, 1H); 6.31 (s, 3H); 7.29-7.82 (q, 2H, $\underline{J}$ = 15 Hz).

ν_{max}^{KBr}: 3080, 3035, 3000, 2975, 2950, 2933, 2842, 1740, 1615, 1472, 1455, 1387, 1370, 1355, 1270, 1242, 1218, 1165, 1130, 1110, 1065, 1015, 935, 915, 885, 815, 712, 685, and 635 cm.$^{-1}$

16. <u>Reaction of Tetrachlorobenzyne with 3,5-Dimethoxytoluene:</u>

A stirred solution of pentachlorophenyl lithium was treated with 3,5-dimethoxytoluene (60.0 g) as explained earlier in experiment 2. The reaction mixture on purification by column chromatography [silica gel, 20% ether in light petroleum] gave :

<u>5-methyl-1-methoxytetrachlorobenzobarrelen-3-one[5,6,7,8-tetrachloro-1,4-dihydro-1-methoxy-9-methyl-1,4-ethenonaphthalen-3(1<u>H</u>)-one]</u> (2-19): (25.20 g, 71%) m.p. 160-62° (from ethanol).

(Found: C, 47.3; H, 2.8%; $C_{14}H_{10}Cl_4O_2$ requires, C, 47.7; H, 2.85%).

m/e (Mass spectrometry): 310.

^{1}H n.m.r. τ(CDCl$_3$): 3.52 (m, 1H); 5.23 (d, 1H, $\underline{J}$ = 2.2 Hz); 6.34 (s, 3H); 7.54 (d, 2H, $\underline{J}$ = 6.5 Hz); 7.98 (d, 3H, $\underline{J}$ = 2.2 Hz).

ν_{max}^{KBr}: 3005, 2960, 2935, 2910, 2838, 1730, 1660, 1465, 1440, 1370, 1350, 1268, 1233, 1200, 1137, 1100, 1016, 895, 803, 780, 748, and 685 cm.$^{-1}$

17. <u>Preparation of 2-Nitro-o-cresol[2-Hydroxy-3-nitrotoluene] (2-23):</u>

A solution of o-cresol[100.0g, 926.0 mmole] in glacial acetic acid (100 ml) was added carefully to a vigorously stirred mixture of nitric acid [Sp. gr. 1.42, 107 ml] and glacial acetic acid (300 ml), while maintaining the temperature <u>ca</u>. -25°, over a period of 4 h. The reaction mixture was allowed to stir for further 2 h at ±2° and then the mass was

poured onto crushed ice-water mixture (2 1.); the crystals separated were steam distilled. The crude 3-nitro-o-cresol, containing traces of 3,5-dinitro-o-cresol, was fractionally distilled in steam, to give pure 3-nitro-o-cresol (2-23). (60.20 g, 42%) m.p. 70° (b.p. 70-72°/ 0.5 mm) [lit.[20] m.p. 70°].

18. Preparation of Sodium Salt of 3-Nitro-o-cresol (2-24):

Freshly distilled ethanol (300 ml) was added dropwise to a suspension of sodium metal [in small cubes, 23.0 g, 100.0 mmole] in dry benzene [300 ml]. The mixture was heated under reflux until no sodium metal was left behind. A solution of 3-nitro-o-cresol [160.0 g, 1045.0 mmole] in dry benzene (300 ml) was then added dropwise, whereupon brick red coloured precipitates started separating out. The mixture was heated under reflux for 3 h, cooled, and filtered. The solid was washed with dry benzene (2 x 50 ml) and dried in vacuum to give the sodium salt of 3-nitro-o-cresol (2-24):

(170.0 g, 93%) (lit.[20]).

19. Preparation of 2-Methoxy-3-nitrotoluene [3-Nitro-o-cresol methyl ether] (2-25).

A mixture of sodium salt of the 3-nitro-o-cresol (2-24) (100.0 g, 571 mmole) and freshly distilled dimethyl sulphate (190.0 g, 1525 mole) was heated at 120° for 3 h. The reaction mixture was then subjected to steam distillation to get a mixture of 2-methoxy-3-nitrotoluene (2-25) and 3-nitro-o-cresol (2-23). The aqueous phase was extracted with ether (4 x 200 ml), washed with sodium hydroxide (2N, 4 x 100 ml) and dried over KOH pellets (100 g). The solvent was evaporated under reduced pressure and the residual oil was fractionally distilled. The oil solidified on keeping to give: 2-methoxy-3-nitrotoluene (2-25):

(83.5g, 87%) m.p. 30-31° (b.p. 102-103°/10 m.m. Hg) (lit.[20] m.p. 30-31°).

^{1}H n.m.r. τ(CDCl$_3$): 2.25-2.72 (m, 2H), 2.78-3.05 (m, 1H); 6.11 (s, 3H); and 7.73 (s, 3H).

ν_{max}^{oil}: 3090, 3010; 2950, 2870, 2830, 1607, 1580, 1535, 1480, 1460, 1355, 1262, 1238, 1160, 1090, 1000, 918, 820, 800, 780, 762, and 720 cm.$^{-1}$

The combined alkali washings were diluted and acidified with hydrochloric acid (2$\underline{N}$). Yellow crystalline solid separated out and was filtered to give 3-nitro-o-cresol (2-23): (5.0 g, 5%) m.p. 68-69° (lit.[20] m.p. 70°).

20.   Preparation of 2-Methoxy-3-aminotoluene[3-Amino-o-cresol methyl ether] (2-26):

A suspension of palladium on charcoal (5%,1.2 g) in a solution of 3-nitro-o-cresol methyl ether (2-25) (66.80 g, 400 mmole) and ethanol (1200 ml) was warmed to 50°. Hydrazine hydrate [32 %, 120 ml] was then added slowly over 30 min., followed by a further addition of palladium on charcoal (5%, 200 mg). The mixture was then heated under reflux for 3 h, cooled and filtered through a pad of Florasil. The filtrate was evaporated under reduced pressure and the residual oil was fractionally distilled to give: 2-methoxy-3-aminotoluene (2-26): (49.30 g, 90%) b.p. 232-34° (lit.[33] b.p. 235°).

^{1}H n.m.r. τ(CDCl$_3$): 2.6-3.02 (m, 3H); 6.18 (s, 3H); 6.32 (s, 2H); and 7.81 (s, 3H).

ν_{max}^{oil}: 3450, 3370, 3030, 2990, 2940, 2830, 1615, 1485, 1475, 1318, 1300, 1220, 1170, 1080, 1003, 810, 775, and 750 cm.$^{-1}$

21.   Preparation of 2-Methoxy-3-hydroxytoluene[2-Methoxy-3-methyl phenol] (2-28):

A solution of 3-amino-o-cresol methyl ether (35.0 g, 255 mmole) was added to a vigorously stirring mixture of sulphuric acid (Sp. gr. 1.84,

64.

101.0 g, 55 ml) and water (75 ml). Crushed ice (<u>ca</u>. 200 g) was then added, followed by the addition of ice cooled solution of sodium nitrite (18.0 g) in water (40 ml) dropwise over a period of 15 min. The stirring was continued for a further 20 minutes and finally it was allowed to stand for 20 minutes.

While the diazotization was in progress, concentrated sulphuric acid (sp. gr. 1.84, 165.0 ml) was cautiously added to water (150 ml). The mixture was heated just to boiling, the supernatant liquid (diazonium salt) was then added to the hot mixture at such a rate that the mixture boiled vigorously [about 15-20 min.] and then the whole mass was subjected to steam distillation. The steam distillate was extracted with ether (4 x 150 ml), washed and dried (Na$_2$SO$_4$). The solvent was evaporated under reduced pressure and the residual oil was fractionally distilled to give 2-methoxy-3-hydroxytoluene (2-28):

(18.0 g, 51%) b.p. 120-21/0.4 mm (lit.[20] b.p. 120-21°/0.4 mm)

^{1}H n.m.r. τ(CDCl$_3$): 2.54-2.95 (m, 3H), 4.21-4.45 (broad hump, 1H); 6.12 (s, 3H); and 7.78 (s, 3H).

ν_{max}^{oil}: 3410, 3040, 3005, 2945, 2840, 1610, 1595, 1475, 1430, 1342, 1282, 1270, 1225, 1155, 1080, 1025, 998, 945, 810, 775, 745, and 670 cm.$^{-1}$

22. Preparation of 2,3-Dimethoxytoluene (2-29):

A solution of 2-methoxy-3-hydroxytoluene (2-28) (18.0 g, 131 mmole) was methylated using dimethsulphate in D.M.S.O. as explained earlier in experiment I(b). The crude oil was purified by fractional distillation to give: 2,3-dimethoxytoluene (2-29):

(18.5 g, 97%) b.p. 104-105° at 25 m.m. Hg (lit.[21] b.p. 104° at 25 mm)

^{1}H n.m.r. τ(CDCl$_3$): 2.51-2.92 (m, 3H); 6.14 (s, 6H); and 7.81 (s, 3H).

ν_{max}^{oil}: 3040, 3000, 2940, 2920, 2840, 1587, 1475, 1380, 1305, 1260, 1193, 1167, 1110, 1090, 1018, 875, 810, 765, 710, and 680 cm.$^{-1}$

23. **Preparation of 2,3-Dimethoxybenzaldehyde (2-31):**

A solution of o-vanillin (2-30) [50.66 g, 330.0 mmole] was
methylated using methyl iodide in D.M.S.O. as explained earlier in
experiment 1(c). The crude product obtained was purified by column
chromatography [silica gel, light petroleum] to give:
2,3-dimethoxybenzaldehyde (2-31):
(50.5 g, 90% m.p. 54-55° (from ligroin) lit.[19] m.p. 54°).

24. **Reduction of 2,3-Dimethoxybenzaldehyde (2-31):**

A solution of 2,3-dimethoxybenzaldehyde (3-31) (83.0 g, 500 mmole)
in toluene (400 ml) was added to granulated zinc-mercury amalgam
(240 g: 24 g) followed by the addition of hydrochloric acid (sp. gr.
1.16; 350 ml) and water (150 ml). The mixture was heated under reflux
for 30 h., during which an additional amount of concentrated hydro-
chloric acid (600 ml) was added. The mixture was cooled and the two
layers were separated. The aqueous phase was extracted with ether (3 x
100 ml) and the combined extracts were washed and dried (CaCl$_2$). The
solvents were removed under reduced pressure and the residual oil was
fractionally distilled to give: 2,3-dimethoxytoluene (2-29):
(61.0 g, 78%), b.p. 104-105° at 25 m.m. Hg (lit.[22] b.p. 90-91° at
5 m.m.).

Spectral data agreed with those previously reported.

25. **Reaction of Tetrachlorobenzyne with 2,3-Dimethoxytoluene:**

A stirred solution of pentachlorophenyl lithium was treated with
2,3-dimethoxytoluene (60 g) as explained earlier in experiment 2. The
reaction mixture was purified by column chromatography [silica gel,
10% ether in light petroleum] to give:

i) 3-methyl-1-methoxytetrachlorobenzobarrelen-2-one[5,6,7,8-
tetrachloro-1,4-dihydro-1-methoxy-3-methyl-1,4-ethenonaphthalen-2-
(1H)-one] (2.20);

(12.95 g, 37%) m.p. 155-56° (from ethanol)

(Found: C, 48.1; H, 2.9%; $C_{14}H_{10}Cl_4O_2$ requires, C, 47.75; H, 2.85%).

m/e (Mass spectrometry): 296.

^{1}H n.m.r. τ(CDCl$_3$): 3.08-3.28 (m, 2H); 5.24-5.46 (m, 1H); 6.26 (s, 3H); 7.51-7.82 (m, 1H); 9.10 (d, 3H, J = 7 Hz).

ν_{max}^{KBr}: 3090, 3005, 2975, 2940, 2880, 2845, 1740, 1624, 1480, 1465, 1450, 1370, 1355, 1310, 1300, 1250, 1235, 1190, 1130, 1120, 1070, 1035, 990, 950, 930, 870, 830, 795, 745, 695, and 670 cm.$^{-1}$

ii) 6-methyl-1-methoxytetrachlorobenzobarrelen-2-one[5,6,7,8-tetra-chloro-1,4-dihydro-1-methoxy-10-methyl-1,4-ethenonaphthalen-2(1H)-one] (2.21):

(5.80 g, 16%) m.p. 164-65° (from ethanol).

(Found: C, 47.6; H, 2.90%; $C_{14}H_{10}Cl_4O_2$ requires, C, 47.75; H, 2.85%).

m/e (Mass spectrometry): 310.

^{1}H n.m.r. τ(CDCl$_3$): 3.65 (dd, 1H, J = 2.2 Hz, J = 7.0 Hz): 5.26-5.53 (m, 1H); 6.09 (s, 3H); 7.48-7.98 (m, 2H); 8.07 (d, 3H, J = 2.2 Hz).

ν_{max}^{KBr}: 3060, 3005, 2990, 2950, 2920, 2840, 1735, 1465, 1415, 1375, 1365, 1355, 1320, 1280, 1235, 1165, 1120, 1080, 1020, 990, 940, 905, 885, 840, 820, 800, 755, 705, and 650 cm.$^{-1}$

26. Preparation of 2,6-Dimethyl-1-hydroxytetrachlorobenzobarrelene (2-34)

A solution of 2,6-dimethyl-1-trimethylsilyloxytetrachlorobenzo-barrelene (2-15) (1.0 g, 2.45 mmole) in T.H.F. (5 ml) was stirred vigorously with aqueous hydrochloric acid (3$\underline{N}$, 25 ml) for 24 h. The reaction mixture was then diluted with water (10 ml) and extracted with ether (4 x 25 ml). The combined extracts were dried (MgSO$_4$) and evaporated under reduced pressure to give: 2,6-dimethyl-1-hydroxytetra-chlorobenzobarrelene (2-34):

(820 mg, 100%) m.p. 152-54° (from ethanol).

M.$^+$ (Mass spectrometry): 346.

^{1}H n.m.r. τ(CDCl$_3$): 3.32 (dq, 2H, $\underline{J}$ = 6.2 Hz, $|\underline{J}|$ = 1.6 Hz); 4.92

(t, 1H, $\underline{J}$ = 6.0 Hz); 7.92 (s, 6H); and 8.02 (broad hump, 1H).

ν_{max}^{KBr}: 3460, 3070, 3035, 2964, 2928, 2850, 1610, 1480, 1435, 1405, 1388,

1350, 1325, 1305, 1228, 1170, 1070, 945, 890, 810, 760, 745, and 690 cm.$^{-1}$

27. Reaction of Tetrachlorobenzyne with N,N-Dimethylaniline:

A stirred solution of pentachlorophenyl lithium was treated with

N,N-dimethylaniline (70.0 g) in dry ether (400 ml) as explained in

experiment 2. The crude reaction mixture was purified by column chroma-

tography [alumina, 20% ether in light petroleum] to give:

i) 1-N,N-dimethylaminotetrachlorobenzobarrelene[5,6,7,8-tetrachloro-

1,4-dihydro-1-N,N-dimethylamino-1,4-ethenonaphthalene] (2-35):

(16.2 g, 48%) m.p. 109-110° (from ethanol (lit.[26] m.p. 110°).

Spectral data agreed with those previously reported.

ii) Tetrachlorobenzobarrelen-2-one[5,6,7,8-tetrachloro-1,4-dihydro-

1,4-ethenonaphthalen-2(1H)-ene](2-22):

(4.30 g, 1.5%) m.p. 160-62° (from ethanol) (lit.[5,26] m.p. 150°).

Spectral data agreed with those previously reported.

28. Preparation of 2-carboxytetrachlorobenzenediazonium tetrafluoroborate:

The tetrachloroanthranilic acid and the 2-carboxytetrachlorobenzene-

diazonium tetrafluoroborate salts were prepared according to the modified

methods of Heaney and his co-workers.[10]

29. Reaction of Tetrachlorobenzyne with Cyclopentadiene:

A stirred solution of freshly prepared 2-carboxytetrachlorobenzene-

diazonium tetrafluoroborate [3.4 g, 9.09 mmole] in cyclopentadiene [4 ml]

and carbon tetrachloride [30 ml] was treated with a solution of pyridine

[1.7 g, 20 mmole] in CCl$_4$ [5 ml] at room temperature during 5 min.

The reaction mixture was stirred at room temperature for 1 h, and then

filtered through a short column of alumina (60.0 g) [20% ether in light petroleum]. The solvent was evaporated under reduced pressure to give: tetrachlorobenzonorbornadiene[5,6,7,8-tetrachloro-1,4-dihydro-1,4-methenonaphthalene] (2-36): (1.80 g, 70%) m.p. 118-19° (from ethanol) (lit.[27] m.p. 119-20°). Spectral data agreed with those previously reported.

30. <u>Reaction of Tetrachlorobenzyne with 6,6-Dimethylfulvene:</u>

A stirred solution of pentachlorophenyl-lithium was treated with 6,6-dimethylfulvene (2-37) (15.0 g) as explained earlier in experiment 2. The crude product on purification gave: 7-isopropylidenetetrachlorobenzonorbornadiene[5,6,7,8-tetrachloro-1,4-dihydro-7-isopropylidino-1,4-methenonaphthalene] (2-38):

(12.8 g, 80%) m.p. 129-30° (from ethanol) (lit.[28] m.p. 129-31°). Spectral data agreed with those previously reported.

31. <u>Catalytic Hydrogenation of 7-isopropylidenetetrachlorobenzonorbornadiene (2-28):</u>

A stirred solution of 7-isopropylidenetetrachlorobenzonorbornadiene (2-38) (1.0 g, 3.12 mmole) was catalytically reduced using palladium on charcoal (5%, 40 mg) as explained earlier in experiment 8. The crude product on purification gave: 5,6,7,8-tetrachloro-1,2,3,4-tetrahydro-9-isopropyl-1,4-methanonaphthalene (2-38'):

(1.0 g, 99%) m.p. 159-60° (from ethanol) (lit.[28] m.p. 160-61°). Spectral data agreed with those previously reported.

32. <u>Reaction of Tetrachlorobenzyne with Furan:</u>

A stirred solution of pentachlorophenyl-lithium was treated with furan (100.0 g) in dry ether (200 ml) as explained earlier in experiment 2. The residual mass on purification by column chromatography [alumina, 10% ether in light petroleum] gave: tetrachloronaphthalene endoxide-

69.

[5,6,7,8-tetrachloro-1,4-dihydro-1,4-epoxynaphthalene] (2-40):
(9.3 g, 66%) m.p. 117-18° (from ethanol) [lit.[5] m.p. 118°].
Spectral data agreed with those previously reported.

33.　Reaction of Tetrachlorobenzyne with N-methylpyrrole:

A stirred solution of pentachlorophenyl lithium was treated with
n-methylpyrrole (16.5 g) in dry ether (200 ml) as explained earlier in
experiment 2. The crude product on purification by column chromatography
[alumina, 20% ether in light petroleum] gave: N-methyliminotetrachloro-
naphthalene [5,6,7,8-tetrachloro-1,4-dihydro-N-methyliminonaphthalene] (2-41):
[12.78 g, 86%] m.p. 162-63° (from ethanol) (lit.[29] m.p. 157-58°).
Spectral data agreed with those previously reported.

34.　Reaction of Tetrachlorobenzyne with 1,2,5-trimethylpyrrole:

A stirred solution of pentachlorophenyl lithium was treated with
1,2,5-trimethylpyrrole (30.0 g) as explained earlier in experiment 2.
The reaction mixture on purification by column chromatography [alumina,
10% ether in light petroleum] gave: trimethyl tetrachloronaphthalene-
imine[5,6,7,8-tetrachloro-1,4-dihydro-1,4-dimethyl-N-methyliminonaphthalene]
(2-42):
(11.12 g, 68%) m.p. 180-81° (from ethanol) (lit.[29] m.p. 180-82°).
Spectral data agreed with those previously reported.

35.　Reaction of Tetrachlorobenzyne with 5,5-dimethoxytetrachlorocyclo-
pentadiene:

A stirred solution of pentachlorophenyl lithium was treated with
5,5-dimethoxytetrachlorocyclopentadiene (35.0 g) as explained earlier
in experiment 2. The crude reaction mixture was purified by column
chromatography [alumina, 15% ether in light petroleum] to give:
5,5-dimethoxyoctachlorobenzonorbornadiene[1,2,3,4,5,6,7,8-octachloro-
1,4-dihydro-9,9-dimethyl-1,4-methenonaphthalene] (2.44).

(10.2 g, 42%) m.p. 152-53° (from ethanol)

m/e(Mass spectrometry): 478.

^{1}H n.m.r. τ(CDCl$_3$): 6.42 (s, 6H).

ν_{max}^{KBr}: 3050, 2987, 2938, 2880, 1612, 1445, 1390, 1345, 1295, 1212, 1103, 1065, 985, 935, 860, 780, 760, 712, 695, and 665 cm.$^{-1}$

36.   Acid Hydrolysis of 9,9-Dimethoxy-octachlorobenzonorbornadiene (2-44):

A mixture of 9,9-dimethoxyoctachlorobenzonorbornadiene (2-44) (1.0 g, 2.092 mmole) and sulphuric acid (70%, 10 ml) in o-dichlorobenzene (20 ml) was vigorously stirred overnight at 60°C. The solid separated out on cooling, was filtered, washed with water and dried in vacuum, gave octachloronaphthalene (2-46):

(0.60 g, 70%) m.p. 197-98° (lit.[32] m.p. 197-98°).

Spectral data agreed with those of the authentic sample.

37.   Reaction of Tetrachlorobenzyne with Benzene:

A stirred solution of pentachlorophenyl lithium was treated with benzene (4 l.) in ether (400 ml) as explained earlier in experiment 2. The reaction mixture on purification by column chromatography [alumina, 5% ether in light petroleum] gave: tetrachlorobenzobarrelene[5,6,7,8-tetrachloro-1,4-dihydro-1,4-ethenonaphthalene] (2-47):

(19.50 g, 66%) m.p. 130-31° (from ethanol) (lit.[5] m.p. 125-27°).

Spectral data agreed with those previously reported.

38.   Reaction of Tetrachlorobenzyne with Mesitylene:

A stirred solution of pentachlorophenyl lithium was treated with mesitylene (40.0 g) in dry ether (400 ml) as explained earlier in experiment 2. The reaction mixture on work up and purification by column chromatography [alumina, 5% ether in light petroleum] gave: trimethyltetrachlorobenzobarrelene[5,6,7,8-tetrachloro-1,4-dihydro-1,3,9-trimethyl-1,4-ethenonaphthalene] (2-48).

(27.30 g, 82%) m.p. 130-31° (from ethanol) (lit.[5] m.p. 110°).

Spectral data agreed with those previously reported.

39.   Reaction of Tetrachlorobenzyne with t-Butylbenzene:

A stirred solution of pentachlorophenyl lithium was treated with t-butylbenzene (100.0 g) as explained in experiment 2. The reaction mixture was separated by column chromatography [alumina,5% ether in light petroleum] to give:

i)   2-t-butyltetrachlorobenzobarrelene[5,6,7,8-tetrachloro-1,4-dihydro-2-t-butyl-1,4-etheno-naphthalene] (2-49):

(17.1 g, 50%) m.p. 106-107° (from ethanol) (lit.[31] m.p. 108°).

Spectral data agreed with those previously reported.

ii)   1-t-butyl tetrachlorobenzobarrelene[5,6,7,8-tetrachloro-1,4-dihydro-1-t-butyl-ethenonaphthalene] (2-50):

(4.2 g, 12%) m.p. 169-70° (from ethanol) (lit.[31] m.p. 159°).

Spectral data agreed with those previously reported.

40.   Reaction of Tetrachlorobenzyne with 1,3,5-Tri-t-butylbenzene:

A stirred solution of pentachlorophenyl lithium was treated with 1,3,5-tri-t-butylbenzene (42.0 g) as explained earlier in experiment 2. The reaction mixture on work up and purification by column chromatography [alumina, 10% ether in light petroleum] gave 1,3,5-tri-t-butyl-tetra-chlorobenzobarrelene[5,6,7,8-tetrachloro-1,4-dihydro-1,3,9-tri-t-butyl-1,4-ethenonaphthalene] (2-51):

(15.8 g, 69%) m.p. 162-63° (from ethanol).

(Found: C, 62.3; H, 6.5%; $C_{24}H_{30}Cl_4$ requires C, 62.6; H, 6.5%).

M$^+$ (Mass spectrometry): 460.

^{1}H n.m.r. τ(CDCl$_3$): 3.71 (d, 2H, J = 2.2 Hz); 4.66 (t, 1H, J = 1.5 Hz); 8.31 (s, 6H); 8.79 (s, 3H); and 8.93 (s, 18H).

ν_{max}^{KBr}: 3100, 3040, 2985, 2975, 2915, 2875, 1480, 1462, 1403, 1390, 1380, 1365, 1335, 1235, 1170, 1120, 1090, 940, 845, 828, 765, 710, and 668 cm.$^{-1}$

41. Reaction of Tetrachlorobenzyne with 1-Methoxynaphthalene:

A stirred solution of pentachlorophenyl lithium was treated with 1-methoxynaphthalene (60.0 g) as explained earlier in experiment 2. The reaction mixture on purification by column chromatography [silica gel, 10% ether in light petroleum] gave: 1-methoxytetrachloroethenoanthracene[5,6,7,8-tetrachloro-9,10-dihydro-9-methoxy-9,10-ethenoanthracene] (2-52):

(26.20 g, 70%) m.p. 191-93° (from ethanol).

(Found: C, 54.7; H, 2.8%; $C_{17}H_{10}Cl_4O$ requires C, 54.85; H, 2.70%).

M$^+$ (Mass spectrometry): 372.

^{1}H n.m.r. τ(CDCl$_3$): 2.3-2.52 (m, 1H); 2.56-3.18 (m, 5H): 4.39 (dd, 1H, J = 2.2 Hz); 6.12 (s, 3H).

ν_{max}^{KBr}: 3080, 2990, 2950, 2850, 1603, 1470, 1455, 1330, 1298, 1230, 1180, 1108, 1085, 1022, 945, 915, 880, 810, 740, 685, and 650 cm.$^{-1}$

42. Reaction of Tetrachlorobenzyne with 1-N,N-Dimethylaminonaphthalene:

A stirred solution of pentachlorophenyl lithium was treated with 1-N,N-dimethylaminonaphthalene (50.0 g) as explained earlier in experiment 2. The reaction mixture on work up and purification by column chromatography [silica gel, 10% ether in light petroleum] gave: 1-N,N-dimethylamino-tetrachloroethenoanthracene[5,6,7,8-tetrachloro-9,10-dihydro-9-N,N-dimethyl-amino-9,10-ethenoanthracene] (2-53):

(30.5 g, 77%) m.p. 196-97° (from ethanol)

(Found: C, 56.1; H, 3.4; N, 3.5%; $C_{18}H_{13}Cl_4N$ requires, C, 56.1; H, 3.4; N, 3.65%). M$^+$ (Mass spectrometry): 385.

^{1}H n.m.r. τ(CDCl$_3$): 2.30-2.52 (m, 1H); 2.61-3.24 (m, 5H); 4.30-4.52 (m, 1H); 7.27 (s, 3H); and 7.29 (s, 3H).

73.

ν_{max}^{KBr}: 3080, 3030, 3020, 2970, 2890, 2860, 2820, 1630, 1482, 1460, 1445, 1375, 1350, 1280, 1252, 1190, 1170, 1130, 1110, 1060, 955, 940, 925, 878, 835, 825, 805, 768, 708, 690, 660, and 630 cm.$^{-1}$

43.   Catalytic Hydrogenation of 9-N,N-Dimethylamino-tetrachloroetheno-anthracene (2-53):

A solution of 9-N,N-dimethylaminotetrachloroethenoanthracene (2-53) (1.0 g, 2.596 mmole) was catalytically reduced using palladised charcoal (10%, 40 mg) by the usual method as explained earlier. The residue on purification gave: 5,6,7,8-tetrachloro-9,10-dihydro-9-N,N-dimethylamino-9,10-ethanoanthracene (2-54): (1.0 g, 99%) m.p. 144-45° (from ethanol). (Found: C, 55.7; H, 3.8; N, 3.6%; $C_{18}H_{15}Cl_4N$ requires, C, 55.8; H, 3.85; N, 3.6%).

$M.^+$ (Mass spectrometry): 387.

^1H n.m.r. $\tau(CDCl_3)$: 2.30-2.51 (m, 1H); 2.55-2.95 (m, 3H); 5.15 (m, 1H); 7.08 (s, 6H); and 8.02-8.52 (m, 4H).

ν_{max}^{KBr}: 3080, 3030, 2970, 2890, 2880, 1460, 1442, 1375, 1350, 1252, 1170, 1130, 1060, 955, 925, 875, 805, 768, 708 and 660 cm.$^{-1}$

44.   Preparation of 2,2-Ethylenedioxy-1-methoxytetrachlorobenzobarrelene-[5,6,7,8-tetrachloro-1,4-dihydro-1-methoxy-2,2^1(1H)-spiro[1,3]dioxolane-1,4-ethenonaphthalene] (2-55):

A solution of 1-methoxytetrachlorobenzobarrelen-2-one (2-17) (5.0 g, 14.79 mmole) in ethane-1,2-diol (24.0 ml) and dichloromethane (100 ml) was treated with freshly distilled boron trifluoride etherate (25.0 ml) and maintained at room temperature for 60 h. The reaction mixture was diluted with dichloromethane (50 ml), washed with water (2 x 50 ml), saturated sodium chloride solution (2 x 30 ml) and dried ($MgSO_4$-Na_2CO_3). The solvent was evaporated under reduced pressure and the residue was purified to give (i) 2,2-ethylenedioxy-1-methoxytetrachlorobenzobarrelene (2-55);

(4.8 g, 85%) m.p. 185-86° (from ethanol).

M^{+} (Mass spectrometry): 296.

^{1}H n.m.r. τ(CDCl$_3$): 3.11-3.51 (m, 2H); 5.45-5.62 (m, 1H);

5.62-6.2 (m, 4H); 6.38 (s, 3H); 7.81-8.42 (dq, 2H, $\underline{J}$ = 12 Hz).

ν_{max}^{KBr}: 3025, 3000, 2980, 2965, 2915, 2855, 1635, 1445, 1380, 1362, 1325,

1300, 1268, 1228, 1190, 1140, 1130, 1080, 1070, 1050, 1015, 970, 950, 875,

840, 745, 698, and 684 cm.$^{-1}$

(ii) Unchanged starting material (0.6 g, 10%), characterized by
comparison with authentic sample.

45.   Preparation of 2,2-Ethylenedioxy-6-methyl-1-methoxytetrachloro-
benzobarrelene[5,6,7,8-tetrachloro-1,4-dihydro-1-methoxy-10-methyl-2,2-
(1H)-spiro[1,3]dioxolane-1,4-ethenonaphthalene] (2.56):

A solution of 6-methyl-1-methoxytetrachlorobenzobarrelen-2-one (2-20)
[5.0 g, 14.25 mmole] was subjected to ketalization as explained in
experiment 44. The crude product on purification gave: 2,2-ethylene-
dioxy-6-methyl-1-methoxytetrachlorobenzobarrelene (2-56):

(5.3 g, 95%), m.p. 116-17° (from ethanol).

(Found: C, 48.2; H, 3.4%; C$_{16}$H$_{14}$Cl$_4$O$_3$ requires, C, 48.5; H, 3.5%);

M^{+} (Mass spectrometry): 310.

^{1}H n.m.r. τ(CDCl$_3$): 3.02-3.53 (m, 1H); 5.61-5.92 (m, 1H); 6.12 (s, 3H);

6.12-6.65 (m, 4H); 8.16-8.52 (m, 1H); and 8.72 (s, 3H).

ν_{max}^{KBr}: 3095, 2985, 2940, 2905, 2850, 1630, 1455, 1375, 1360, 1318, 1260,

1182, 1140, 1108, 1038, 970, 940, 825, 745, and 695 cm.$^{-1}$

46.   Preparation of 3,3-Ethylenedioxy-1-methoxytetrachlorobenzo-
barrelene[5,6,7,8-tetrachloro-1,4-dihydro-1-methoxy-3,3'-(1H)-spiro-
[1,3]dioxolane-1,4-ethenonaphthalene (2-57):

A solution of 1-methoxytetrachlorobenzobarrelen-3-one (2-18)
[10.0 g, 29.58 mmole] was subjected to ketalization as explained in
experiment 44. The crude product on purification gave: 3,3-ethylenedioxy-
1-methoxytetrachlorobenzobarrelen-3-one (2-57):

(10.0, 88%), m.p. 129-30° (from ethanol).

(Found: C, 47.1; H, 3.1%; $C_{15}H_{12}Cl_4O_3$ requires C, 47.1; H, 3.15%).

$M.^{\dot{+}}$ (Mass spectrometry): 296.

^1H n.m.r. $\tau(CDCl_3)$: 3.17 (dd, 1H, $\underline{J}$ = 1.6 Hz); 3.32-3.61 (m, 1H); 5.51 (dd, 1H, $\underline{J}$ = 1.6 Hz); 5.78-6.12 (m, 4H); 6.38 (s, 3H); and 7.82 (q, 2H, $\underline{J}$ = 12 Hz).

ν_{max}^{KBr}: 3020, 3010, 2980, 2960, 2910, 2895, 2850, 1632, 1480, 1448, 1380, 1365, 1325, 1290, 1250, 1222, 1212, 1182, 1155, 1115, 1085, 1055, 1000, 960, 980, 820, 790, 750, 720, 690, and 655 cm.$^{-1}$

47. Preparation of 3,3-Ethylenedioxy-5-methyl-1-methoxytetrachlorobenzo-barrelene[5,6,7,8-tetrachloro-1,4-dihydro-1-methoxy-9-methyl-3,3(1H)-spiro-[1,3]dioxolane-1,4-ethenonaphthalene] (2-58):

A solution of 5-methyl-1-methoxytetrachlorobenzobarrelen-3-one (2-19) [10.0 g, 28.41, mmole] was subjected to ketalization as explained in experiment 44. The crude product on purification gave: 3,3-ethylenedioxy-5-methyl-1-methoxytetrachlorobenzobarrelene (2-58):

(10.0 g, 89%), m.p. 155-56° (from ethanol).

(Found: C, 48.6; H, 3.6%; $C_{16}H_{14}Cl_4O_3$ requires, C, 48.5; H, 3.55%).

$M.^{\dot{+}}$ (Mass spectrometry): 310.

^1H n.m.r. $\tau(CDCl_3)$: 3.55-3.78 (m, 1H); 5.7-5.9 (d, 1H, $\underline{J}$ = 2.2 Hz); 5.9-6.22 (m, 4H); 6.43 (s, 3H); 7.62-8.15 (q, 2H, $\underline{J}$ = 15 Hz); 7.95-8.22 (d, 3H, $\underline{J}$ = 2.2 Hz).

ν_{max}^{KBr} : 3030, 2995, 2970, 2950, 2910, 2845, 1443, 1370, 1360, 1325, 1285, 1260, 1218, 1140, 1105, 1095, 1055, 1005, 948, 870, 760, and 670 cm.$^{-1}$

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CHAPTER THREE

Dehalogenation of Benzobicyclic Systems

Dehalogenation of Benzobicyclic Systems:

Introduction:

Many metals have been used in a variety of solvents as reductants for dechlorination of a large number of perchlorinated systems derived from hexachlorobenzene or hexachlorocyclopentadiene. The reduction is usually assumed to occur at the surface of the metal and the reactivity of this surface is maintained by the presence of the solvent, which re-dissolves the products and acts as the transport medium for the substrate to the metal surface. Of the olefin-forming β-eliminations which do not involve hydrogen as one of the leaving groups, dehalogenations are the most common. With the exception of fluorine, as the leaving group, they can be induced with a variety of reducing agents.

Since Perkin initially reported an iodide-promoted elimination of coumarin dibromide,[1] many reductants have been utilized. These include metals like zinc,[2] sodium,[3] lithium,[4] cadmium,[5] magnesium,[5] copper,[5] aluminium,[5] etc. and a variety of nucleophilic reagents like thiolate,[6] acetate,[7] and phosphite,[8] etc. The majority of the reactions involving these reagents are homogeneous, and they offer a more realistic challenge to the kineticist than the heterogeneous metal reductions, yet few mechanistic studies have been reported.

Recently, the dehalogenation of alkyl and aryl halides has been the subject of considerable discussion.[9-14] It has been reported that the de-chlorination of halogenated alkanes particularly the chloroethanes or chloropropanes proceeds through an E2 concerted mechanism.[15] The de-chlorination on a metal surface has interest in connection with the stereo-selectivity and activity which depend on the kind of metal ion. In the present work, substantial amounts of benzobicyclic derivatives were required in connection with studies of acid-catalysed rearrangements.

These compounds are accessible by means of the elegant procedures of Wittig and co-workers,[16] which involve the addition of benzyne to the appropriate reactant. Similarly a number of other methods have been introduced by Cristol, Tanida, Stiles, and Barkhash and their co-workers.[17,18,19,20] However, these reactions yield comparatively small amounts of the desired products. In order to scale up the amounts of the desired adducts, alternative methods were designed.

Discussions and Results:

The smooth dehalogenation of isodrin, aldrin, and their related epoxides prompted a brief examination of other highly chlorinated compounds by means of lithium and t-butanol, which proceeds readily in refluxing tetrahydrofuran.[21] The geminal, allylic and even the bridge-head chlorine atoms can be replaced by hydrogen with ease as described previously.[22] The reaction provides a good synthetic route to several systems containing fused bicycloheptane rings, which are only with difficulty accessible by other means.[23]

Examples of dehalogenations with alkoxide bases appear in the literature but are best known with bromo-compounds.[24] Examples of nucleophilic attack on chlorine by bases are not by any means so well known but this seems to be the most reasonable explanation of the observations described by a number of authors.[25] It is generally assumed that a carbanion intermediate is formed by attack at the dichloromethano-bridge involving direct attack on chlorine, which is then protonated extremely rapidly in the presence of alcohols, but more slowly in their absence. This allows the possibility of stereomutation and might explain the two isomers isolated in the dechlorination of isodrin with the sodium hydride-dimethylsulphoxide reagent.[26] Assuming that stereo-mutation is not important, the formation of the carbanion is then determined by steric factors favouring the approach of the nucleophile to the chlorinated periphery of the molecule from the anti side of the dichloro-methylene bridge. This would seem a reasonable explanation since the same stereochemistry was obtained in the dechlorination of isodrin derivatives where alternative arguments involving repulsion of a tetra-hedral carbanion lobe syn to an adjacent π-bond cannot apply. The presence of two chlorine atoms at the corners of the cage structure might be expected to promote the approach of alkoxide ion. A number of papers

have been published on homoenolisations in this type of compound.[27]

Pilgrim and Ohse[28] have discussed the use of trivalent phosphorous compounds for the dechlorination of highly chlorinated ketones. According to the method, highly chlorinated ketones undergo rapid α,β-dechlorination when treated with equivalent amount of triphenyl phosphine, triphenyl phosphite, or trialkyl phosphite. The reaction between trialkyl phosphites and α-haloketones (Perkow reaction) has been considerably expanded in scope since its discovery, although the reagent seems to have limited scope in the case of the aromatic systems. [29]

The stereochemistry of reductive dehalogenation has been examined employing three representative reducing agents, dissolving metal (zinc-acetic acid), homogeneous transition metal cation (chromous acetate), and catalytic reduction (Pd-C). The system chosen for study was 1,2,3,4,7,7-hexachloro-5-endo--acetoxy-bicyclo[2.2.1]hept-2-ene (3-1), which possesses vinyl, geminal and bridgehead chlorines. The authors have studied mono-dechlorination paying particular attention to the two geminal chlorine atoms on the bridging methano-group.[30]

[3-1]   [3-2]   [3-3]   [3-4]
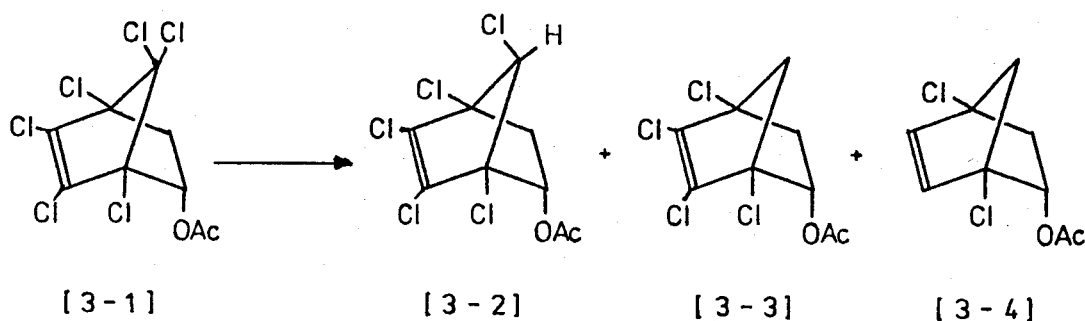
The authors[31] suggested that zinc reduction of chlorinated compounds proceeds with a rather high degree of stereospecificity to give a mixture of variously dechlorinated products. Brewster[32] interprets this as indicative of a mechanism involving attack of the electron-rich metal surface on the chlorine atom to produce a carbanion which is immediately protonated from the rear by the solvent. No direct chemical evidence was found for the presence of either a free radical or carbanion intermediate.

Chromous acetate in acetic acid gave almost the same results as zinc-acetic acid reduction.[33] Castro and Kray[34] proposed a mechanism involving carbenes as intermediates in the reduction process.

Catalytic reduction (Pd-C) of chlorinated bicyclic compounds has been reported in various preparative schemes although these systems are subject to steric hindrance.[35] Wilcox[36] noted the hydrogenation of double bond followed by elimination and reduction of hydrogenolysis of the chlorines on the two carbon bridge. Heaney and co-workers[37] in this laboratory observed that the olefinic double bond of the bicyclic systems was selectively reduced when palladium on charcoal in ethanol and hydrazine hydrate was used for the reductive dechlorination.

In a related study, Wilcox and co-workers[38] have examined the stereochemistry involved in the dechlorination of 1,2,3,4,7,7-hexachloro-bicyclo[2.2.1]heptane. A number of reagents have been used for selective dechlorination purposes. The two chlorines in the dichloromethano-group of the hexachlorobicyclo[2.2.1]heptane (3-5) were removed by treatment with zinc-acetic acid to give a low yield (∿29%) of 1,2,3,4-tetrachloro-bicyclo[2.2.1]heptane (3-7). An additional product obtained was found to contain five chlorine atoms and was isolated in 40% yield (Scheme 3-1).

Reagents : (i) Zn-AcOH , (ii) Ni-H$_2$/KOH , (iii) Li-^{t}BuOH/ T.H.F.
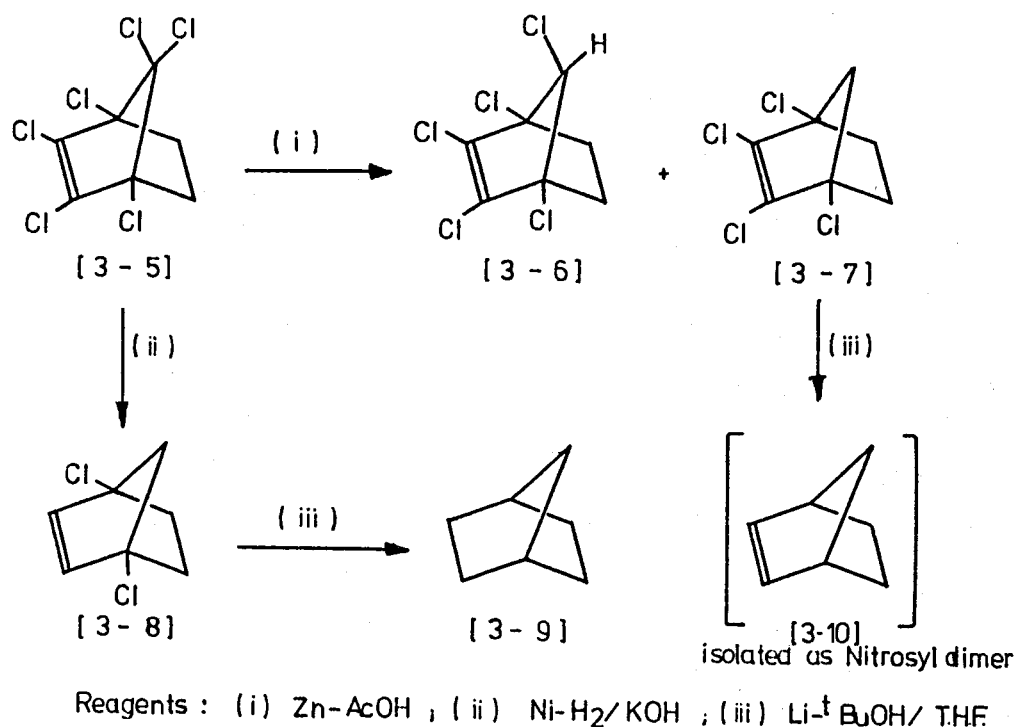
[Scheme 3-1]

The structure of the pentachlorobicyclo[2.2.1]heptane (3-5) was assigned on the basis of chemical and spectral evidence. The hexachloro-cycloheptane (3-5) was converted to 1,4-dichlorobicyclo[2.2.1]heptane (3-8) in 82% yield by reduction with Raney nickel in the presence of base. The reaction probably proceeds by a consecutive series of reductions and eliminations. Reduction of 1,4-dichlorobicycloheptane (3-8) with lithium and t-butanol in tetrahydrofuran, gave norbornane, thereby estab-lishing the skeleton of 1,4-dichlorobicyclo[2.2.1]heptane, by comparison with an authentic sample prepared by several other synthetic sequences.[39] Corroborative evidence is provided by the removal of all four of the chlorines, using the Winstein reduction procedure, to give bicycloheptene[2,10] (isolated as the nitrosyl chloride dimer).

84.

The same authors[30,38] have demonstrated the use of various
reducing agents for the selective removal of the chlorine atoms, present
under different environments, without affecting or rearranging the
remainder of the molecule.

Diels-Alder addition of tetrachlorocyclopentadiene-dimethyl ketal
(3-11) to endo-5-norbornene carboxylic acid (3-12) produces 5,6,7,8-
tetrachloro-9,9-dimethoxy-1,4:5,8-dimethane-1,2,3,4,5,5a,8,8a-octahydro-
naphthalene-endo-2-carboxylic acid (3-13). Ketal cleavage, cheletropic
loss of carbon monoxide, and aromatization affords the endo-carboxylic
acid (3-16), which was dechlorinated by reaction with Ni-Al alloy and
alkali to give benzonorbornene-endo-2-carboxylic acid (3-17). The clean
retention of stereochemistry in the reaction sequence was suggested to
be of value in the general synthesis of alicyclic substituted benzo-
norbornenes.[41] Decarboxylation of the acid (3-17) resulted in the
formation of benzonorbornene in an excellent yield (Scheme 3-2).

[3 - 11]   [3 - 12]   [3 - 13]

[3 - 15]   [3 - 14]

[3-15] $\longrightarrow$ [3 - 16] [3 - 17]

[3- 67]
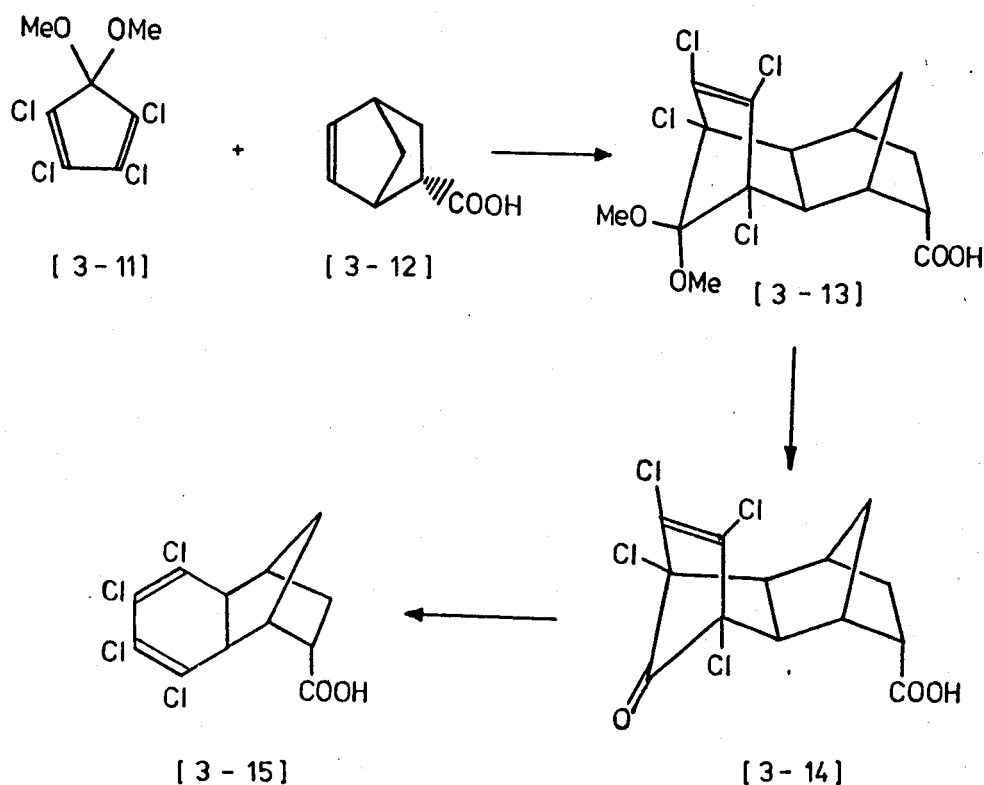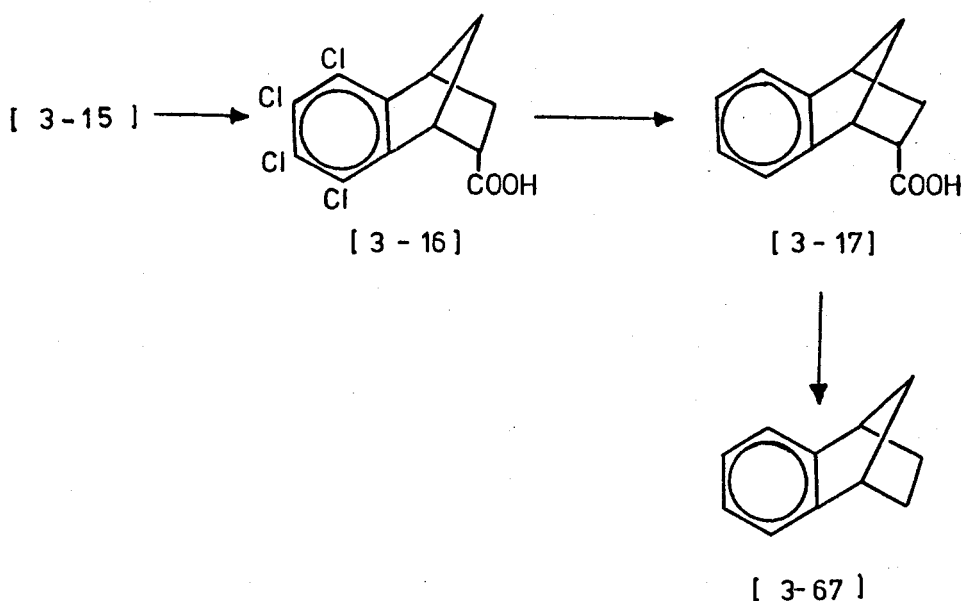
[Scheme 3-2]

MacKenzie[42] reported the preparation of some polychlorinated benzonorbornenes, initially derived from the Diels-Alder addition of 5,5-dimethoxytetrachlorocyclopentadiene with norbornadiene. This route gave 5,6,7,8-tetrachlorobenz n orbornene (3-18), and 2,3-dibromo-5,6,7,8-tetrachlorobenznorbornene (3-19), and in addition 5,6,7,8-tetrachloro-benzonorbornadiene (3-20) was obtained.[43] Bruck[44] treated these compounds with lithium and t-butanol in tetrahydrofuran, in the hope that dehalogenation would provide alternative routes to benzonorbornene derivatives.
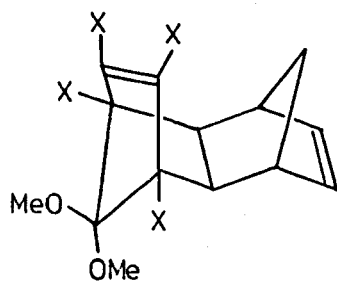
[3-18]

X = Cl
X = H
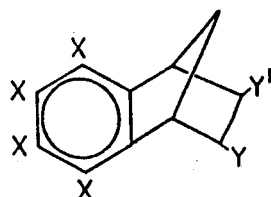
[3 - 19]

X = Cl, Y= Y'= H
X = Cl, Y= Y'= Br
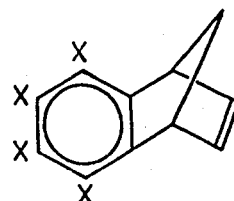
[3 - 20]

X = Cl
X = H

The synthesis of 5-substituted bicyclo[2.1.1]hexenes via the dehalogenation of 2,3-dichlorobicyclo[2.1.1]-hexenes has been described by Wiberg and his co-workers.[45] Bicyclo[2.1.1]hexene derivatives are of interest in connection with studies of double bond participation and of thermal rearrangements.[46]

A short synthetic route to 7-substituted bicyclo[2.2.1]hept-2-enes has been developed, by the dechlorination of 1,2,3,4,7,7-dimethoxytetra-chlorobicyclo[2.2.1]-heptene (3-21).[47] The previous literature preparation of bicyclo[2.2.1]heptan-2-one (3-23) made use of the oxidation of bicyclo[2.2.1]heptanol, which resulted in a mixture of ketones.[48] Because of the complexity of the reaction, it loses its feasibility as a general method of synthesis.

[3 - 21] [3 - 22] [3 - 23]

X = Cl
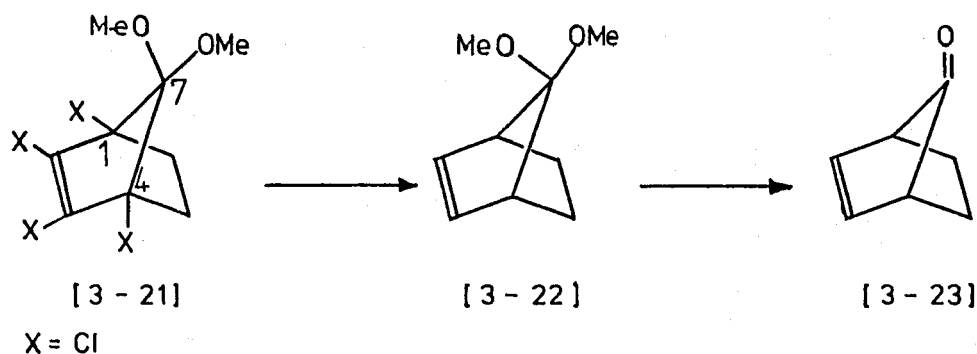
[Scheme 3-3]

A variety of perchlorinated systems derived from hexachlorocyclo-pentadiene have been reported in literature.[49] Cage-like structures have been obtained by dechlorination of their chlorinated precursors using sodium and t-butanol in tetrahydrofuran. No structural reorganis-ation was observed.[50,51]

OMe ⟶ OMe

[3 - 24] [3 - 25]
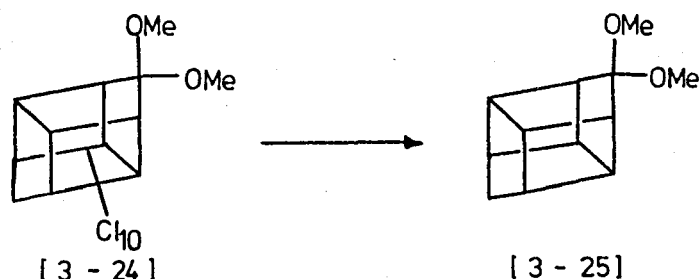
A large number of other examples[52] exist in the literature where other dechlorinating agents have been used, again without any structural changes. For instance, Bryce Smith and co-workers[53] used magnesium in the presence of tertiary alcohols as the dechlorinating agent. According to the published procedures the process involves alkoxide-promoted formation of an organomagnesium complex which is followed by alcoholysis. The use of Ni-Al alloy in the presence of strong base has been frequently made in certain cases for the dechlorination of cyclic compounds, containing carboxylic groups.[54]

The use of sodium-liquid ammonia for the dechlorination purposes has been unsuitable for bicyclic systems.[55] The existing literature does not contain any example where use has been made of sodium-liquid NH_3 for the dehalogenation of barrelene systems. Magnesium amalgam in glyme led to a slow elimination of halogen.[56] Disodium phenanthrene was found to effect dehalogenation relatively effectively at low temperature.[45] Since we required large amounts of benzobarrelene derivatives (Table I) which would be easily accessible by dechlorinating the related tetrachloro-benzobarrelenes,[57] we decided to examine the dechlorination process in detail.

Benzobarrelene (3-30) is a molecule of considerable potential interest, but studies of its chemistry have been few on account of its relative unavailability. Neither of the existing synthetic routes, the

cycloaddition of maleic anhydride to β-naphthol[58] or the addition of benzyne to benzene,[59,60] is suitable for large scale preparations. However, Heaney and co-workers[61] have reported a high yield preparation, which consisted of the reductive dechlorination of tetrachlorobenzobarrelene, obtained from the Diels-Alder cycloaddition of tetrachlorobenzyne with benzene.

The dehalogenation of a variety of alkenyl chlorides[62] using alkali metals and t-butanol in tetrahydrofuran, suggested this approach. The present chapter in this thesis is based on the previously published note on dechlorination,[61] and is concerned with its mechanistic pathway and in establishing its scope and limitations.

Recently, Jefford and co-workers[63] reported on alternative large scale preparation of benzobarrelene (3-30). The authors claimed this method does have flexibility with respect to the preparation of aromatic substituted derivatives. However, the method needs further improvement and evaluation before becoming of general use for the preparation of substituted benzobarrelenes.

The method involves the addition of dichlorocarbene to benzonorbornadiene (3-26)[64] to give a rearranged adduct which on reductive dechlorination affords benzo[6,7]bicyclo[3.2.1]octa-2,6-diene (3-28).[65] The dechlorination of the adduct was effected by sodium and t-butanol in anhydrous ether, to give an overall yield of 80%. Bromination of the hydrocarbon (3-28) in dichloromethane gave the di-antibromo-adduct (3-29) in quantitative yield. The bromination brings about the skeletal rearrangement and provides the functionality which permits the easy introduction of two double bonds. Stereospecific brominations with rearrangement have been observed for the analogues, benzonorbornadiene (3-26)[66] and benzo[7,8]bicyclo[4.2.1]nona-2,7-diene[67] and present no particular mechanistic problems.

The double dehydrobromination of the bromoanalogue (3-29) was achieved with surprising efficiency using the classical method of potassium-tert-butoxide in tetrahydrofuran to give pure benzobarrelene after sublimation. In overall, this route allows straight forward synthesis of benzobarrelene (3-30) and its derivatives from benzonorbornadiene (3-26) in four steps. In terms of a comparison of the overall yields it is evident that we must take into account the steps involving the aryne. In the reaction of benzyne with cyclopentadiene this is 66% and tetrachlorobenzyne with benzene 68%. However, this method does offer a good route for isotopically labelling the bicyclic skeleton at certain specific positions.[63] (Scheme 3-4).
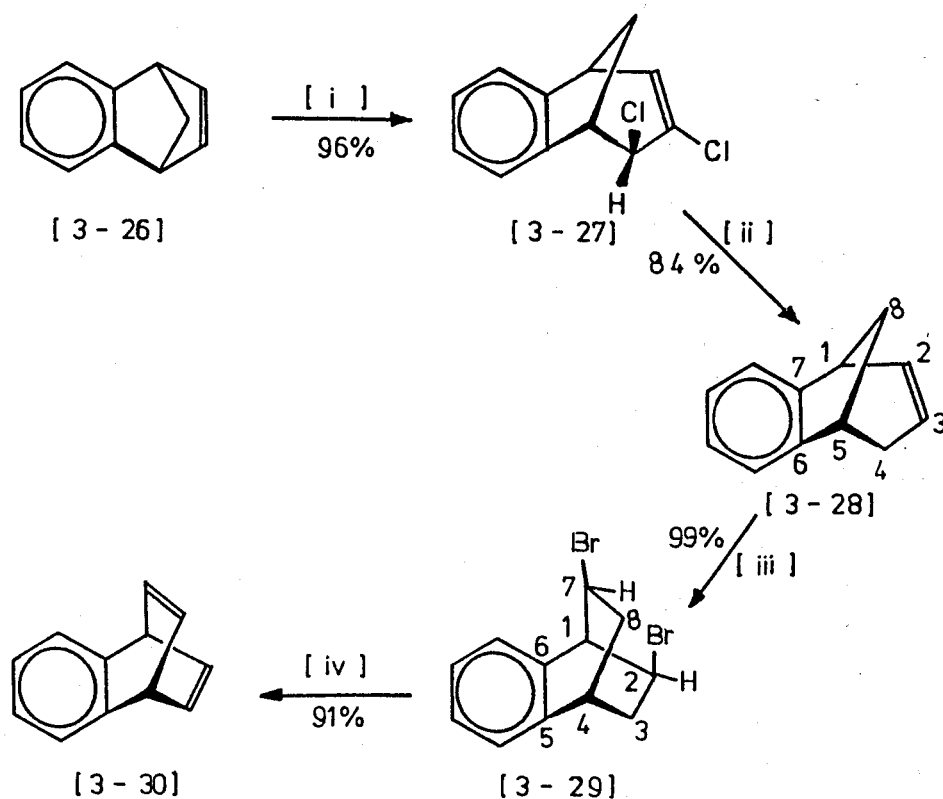
Reagents : [i] :CCl$_2$; [ii] Na -^{t}BuOH / (C$_2$H$_5$)$_2$O ; [iii] Br$_2$, CH$_2$Cl$_2$, -20° ; [iv] K-^{t}BuOH / THF.

[Scheme 3-4]

90.

The labelling can be achieved by using labelled dichlorocarbene. Alternatively, several deuteriated benzonorbornadienes are known,[68] which could serve as precursors to deuteriated benzobarrelenes.

In the present study, the dehalogenation of tetrachlorobenzobarrelene derivatives was investigated using sodium metal and t-butyl alcohol as the reducing system. The substituted 1-methoxytetrachlorobenzobarrelene derivatives were prepared as explained in the second chapter, according to the method of Heaney and co-workers.[57] The generality of the procedure is exemplified by the examples given in the Table 3-1. The end point in the dechlorination is usually clearly indicated when the precipitated sodium chloride becomes purple. This is assumed to be due to the presence of free electrons (sodium atoms) in the crystal lattice.
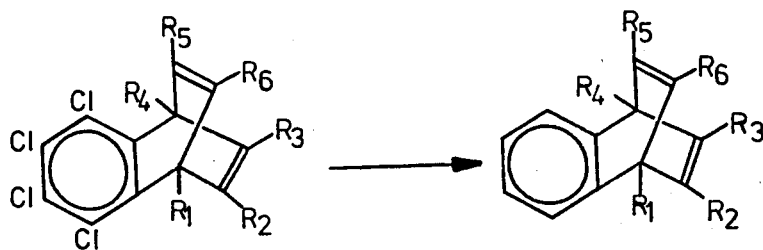
Reagents : K –^{t}BuOH / T.H.F.

(Table 3-1)

Substituents (Anisole)	No.	R_1	R_2	R_3	R_4	R_5	R_6	Yield %
-	(3-31)	-OMe	H	H	H	H	H	98
2-Methyl-	(3-32)	-OMe	Me	H	H	H	H	93
2,3-Dimethyl-	(3-33)	-OMe	Me	Me	H	H	H	93
2,5-Dimethyl-	(3-34)	-OMe	Me	H	H	Me	H	95
3,5-Dimethyl	(3-35)	-OMe	H	Me	H	Me	H	98
2,6-Dimethyl-	(3-36)	-OMe	Me	H	H	H	Me	96
2,3,5-Trimethyl-	(3-37)	-OMe	Me	Me	H	Me	H	93
2,3,5,6-Tetramethyl-	(3-38)	-OMe	Me	Me	H	Me	Me	95
2,6-Dimethyl-	(3-39)	$-OSiMe_3$(H)	Me	H	H	H	Me	72
(Benzene)								
-	(3-30)	H	H	H	H	H	H	90
1,3,5-Trimethyl-	(3-40)	Me	H	Me	H	Me	H	97
1-^{t}Butyl-	(3-41)	$-C(Me)_3$	H	H	H	H	H	93
2-^{t}Butyl-	(3-42)	-H	$-C(Me)_3$	H	H	H	H	94
1,3,5-tri-^{t}Butyl-	(3-43)	$-C(Me)_3$	H	$-C(Me)_3$	H	$-C(Me)_3$	H	97
N,N-Dimethylamino-	(3-44)	$-NMe_2$	H	H	H	H	H	87
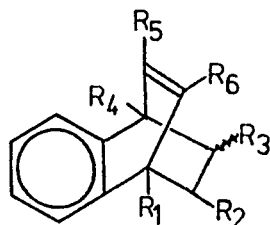
Table (continued)

Substituents	No.	R_1	R_2	R_3	R_4	R_5	R_6	Yield %
(Anisole Ketals)								
2,2-Ethylenedioxy-	(3-45)	-OMe	(ethylenedioxy)	H	H	H	H	96
2,2-Ethylenedioxy-3-methyl-	(3-46)	-OMe	(ethylenedioxy)	Me	H	H	H	94
2,2-Ethylenedioxy-6-methyl-	(3-47)	-OMe	(ethylenedioxy)	H	H	H	Me	96
3,3-Ethylenedioxy-	(3-48)	-OMe	H	(ethylenedioxy)	H	H	H	94
3,3-Ethylenedioxy-5-methyl-	(3-49)	-OMe	H	(ethylenedioxy)	H	Me	H	98

The tetrachlorobenzobarrelene derivatives were heated under reflux with sodium metal (as wire) and t-butyl alcohol in tetrahydrofuran in the ratio (1:1:3:40 w/w) until most of the sodium metal turns into purple sodium chloride (approximately 10-12 hrs) and the unreacted shining sodium metal starts floating on the surface of the mixture. Excess of sodium was removed by adding methanol. Use of large excess of sodium was avoided in order to check further reduction by the metal. It was found that the purple sodium chloride contained a large amount of sodium entrapped in its crystal lattice. Volumetric analysis on one sample of purple sodium chloride showed that it contained approximately 26.8% active sodium which was found to be capable of carrying out dechlorination by itself. An experiment using tetrachloro-benzobarrelene (2-47) and purple sodium chloride in tetrahydrofuran containing t-butanol under identical conditions but in the absence of sodium metal, gave a 7% yield of the dechlorinated product.

It was observed that the dechlorination process can be easily initiated either by the addition of a catalytic quantity of sodium chloride or a few drops of 1,2-dichloroethane. The process of dechlorination once started proceeds very rapidly until most of the halogen reacts with sodium to give sodium chloride. Purple sodium chloride in itself is an efficient reaction initiator and helps in using up the last traces of any unreacted

halogen compound present in the system.

A large number of tetrachlorobenzobarrelene derivatives containing various substituents at the bridgehead as well as the olefinic double bonds were subjected to similar treatment of dechlorination and it was observed that the metal ions do not attack the olefinic double bond or reorganise the molecule under investigation except that the four chlorines were replaced by four hydrogens. In the case of substituted 1-methoxytetrachlorobenzobarrelene derivatives, the presence of oxygen atom (-OMe) did not show any direct or indirect effect on the olefinic double bond. In most of the cases >90% of the dechlorinated material was recovered, after purification. Even when oxygen was replaced with a nitrogen atom, no unusual effect by the hetero-atom was observed. For example, when 1-N,N-dimethyl-aminotetrachlorobenzobarrelene (2-35) was dechlorinated using the standard method, one product, 1-N,N-dimethylaminobenzobarrelene (3-44) was obtained in 94% yield. (Scheme 3-5). The spectral data of these two compounds were found to be identical except for the expected changes due to the fact that four chlorines were replaced by four hydrogens.

[2 - 35]   [3 - 44]

[Scheme 3 - 5]
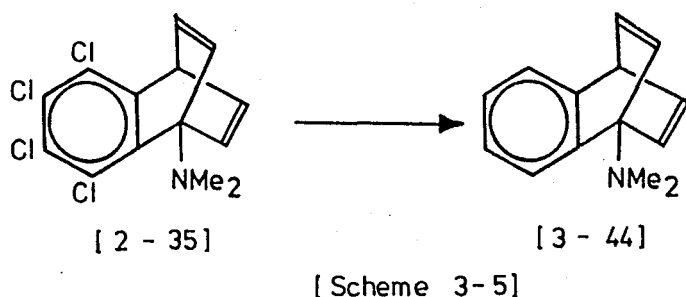
Similarly the dechlorination of 1,2,3,4-tetrachloro-9,10-dihydro-9-N,N-dimethylamino-9,10-ethenoanthracene (2-53) or 1,2,3,4-tetrachloro-9,10-dihydro-9-methoxy-9,10-ethenoanthracene (2-52) gave quantitative yields of 9,10-dihydro-9-N,N-dimethylamino-9,10-ethenoanthracene (3-50) or 9,10-dihydro-1-methoxy-9,10-ethenoanthracene (3-51), respectively.
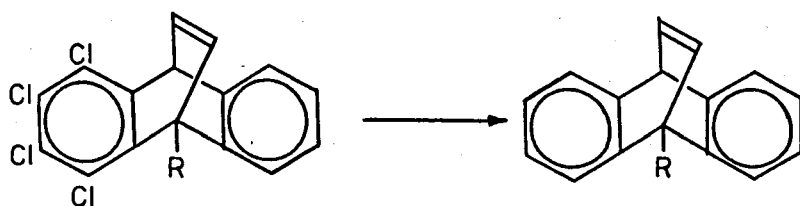
Table II

No.	R	Yield %
[3-50]	$-NMe_2$	100
[3 51]	$-OMe$	100

When 2,6-dimethyl-1-trimethylsilyloxytetrachlorobenzobarrelene (2-15) was dechlorinated using sodium in tetrahydrofuran containing t-butanol, only 2,6-dimethyl-1-hydroxybenzobarrelene (3-53) was recovered. The approach seems to be effective in obtaining bridgehead hydroxy compounds, but the reason of desilylation is not fully understood. Presumably, during working up of the reaction acid helps in cleaving the -O-Si bond. The overall yield of 2,6-dimethyl-1-hydroxybenzo-barrelene (3-53) was 94%. Even this type of dehalogenation did not show any effect on the remainder of the molecule, further proving the versatility of this reagent system for dechlorination purposes (Scheme 3-6).

[2-15]   [3-52]   [3-53]

[Scheme 3-6]

95.
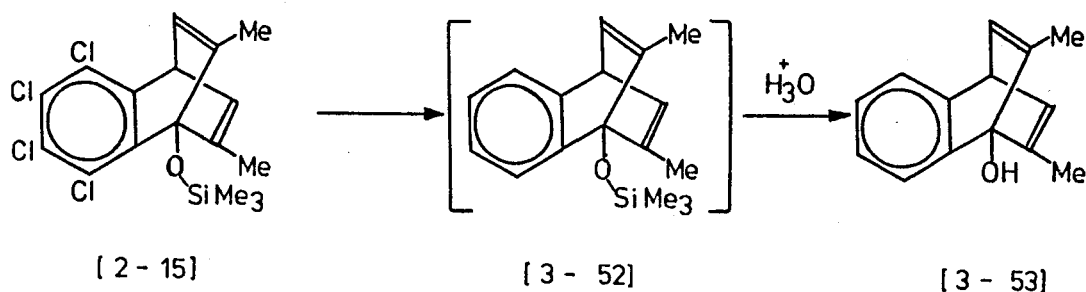
1,3,5-Tri-tert-butylbenzobarrelene (3-54) was obtained in 97% yield by dechlorinating 1,3,5-tri-tert-butyltetrachlorobenzobarrelene (2-51) using the standard technique. The catalytic reduction of 1,3,5-tri-tert-butylbenzobarrelene (3-54) using palladium on charcoal under a positive pressure of hydrogen, surprisingly gave a single product in which only one of the double bonds was reduced, over a period of three hours. We therefore decided to leave the sample, under the same conditions for a much longer period (~ 48 h). The second double bond remained unreduced. An attempted catalytic hydrogenation using Adam's catalyst did not result in reduction of the second olefinic double bond. It is most probable that the bulky size of the substituents (at position 3 and 5) effectively protects the second double bond. These results suggest that the stereochemistry of the compound (3-55) is as shown in the Scheme 3-7.

[2 - 51]   [3 - 54]

[3 - 55]

[Scheme   3 - 7]

96.
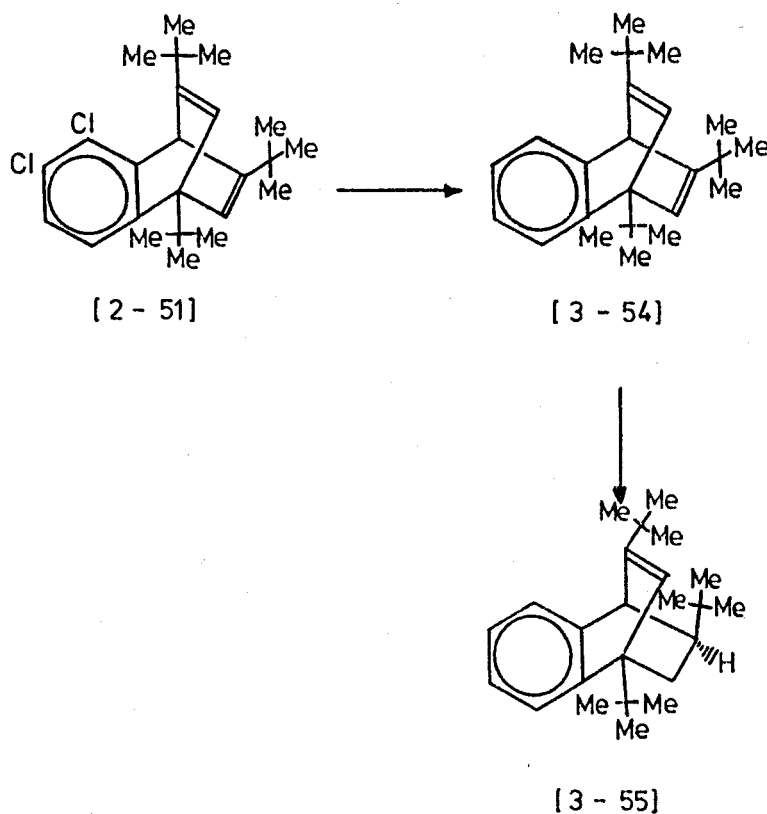
In order to obtain further information on this point the mesitylene adduct, 1,4-dihydro-1,3,10-trimethyl-1,4-ethenonaphthalene (3-56), obtained from its chloro-analogue (2-48) by dechlorination, was subjected to catalytic reduction using palladium on charcoal under a positive pressure of hydrogen and gave a single product in 100% yield, in which both the olefinic double bonds were reduced.

[3 - 56]   [3 - 57]
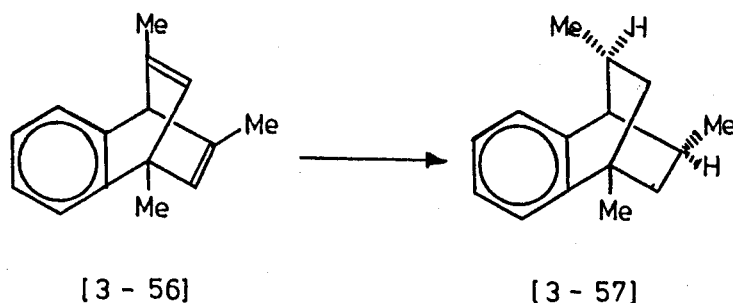
On the basis of data available, a plausible mechanistic pathway has been suggested, which fulfils the necessary requirements.

Two mechanisms have been put forward for this type of dechlorination, both requiring the solvent to supply the proton which replaces the lost halogen. The experimental evidence obtained in the present work differs from that reported previously in literature.[69]

Sargent[10] has cogently summarized the evidence supporting the suggested mechanisms for the dehalogenation of aryl halides involving radical anions. Adapting his conclusions to the present reaction leads to the following sequence. The initially formed radical anion eliminates a halide ion in the rate limiting reaction (equation 2). The aryl radical so formed is reduced (equation 3) to an aryl anion by the alkali metal as shown or possibly by the radical anion formed in the reaction (equation 3).

97.

The suggested mechanism can be formulated as (equation 1 to 6):

$$[Na\cdot \longrightarrow Na^+] \qquad [3.1]$$

$$Na^+ \qquad NaCl \qquad [3.2]$$

$$Na\cdot \longrightarrow Na^+ \qquad Na^+ \qquad [3.3]$$

$$Na^+ + HS \longrightarrow \qquad + \bar{S}Na^+ \quad [3.4]$$

$$+ Na^+\bar{S} \longrightarrow X \qquad Na^+ \qquad [3.5]$$

$$Na^+\bar{S} + H_2O \longrightarrow SH + NaOH \qquad [3.6]$$
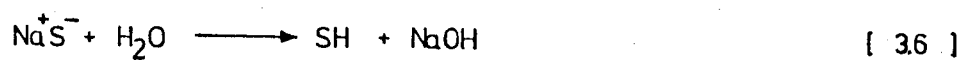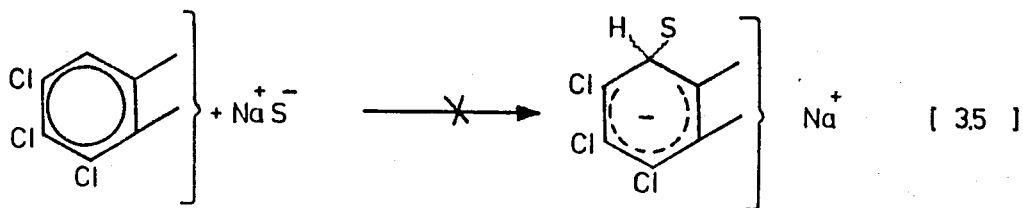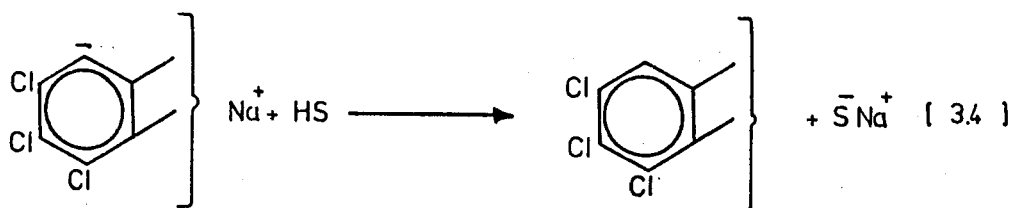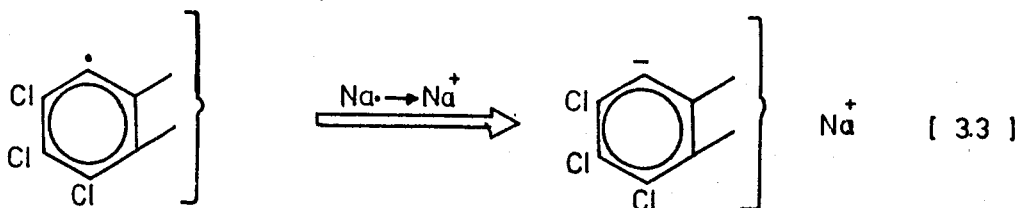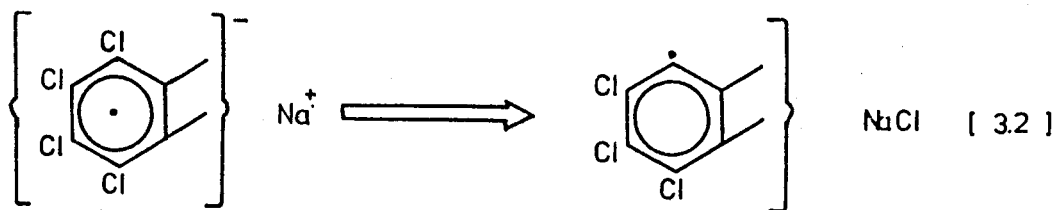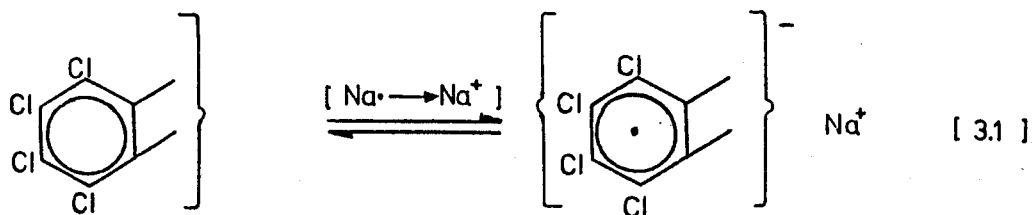
[HS : Solvent]

The systems selected by Sargent and Smith and co-workers[70,71] for the study were the reductive dimerization of substituted aryl imines. Thus o-chlorobenzylideneaniline (3-58) was treated with sodium and lithium in diethyl ether (D.E.E.). The system not only serves as the aryl halide undergoing dehalogenation but also provided the functional group to capture the reactive intermediates arising from the solvent. According to Sargent, the abstraction of an α-hydrogen from the solvent (Hs) (which is ether) generates the chlorine free Schiff base and the solvent derived anion as shown in equation 4. The last anion then adds to either of the two Schiff bases present in solution (equation 8) while the aryl anion also undergoes a competitive dimerization (equations 7 to 9).[72]

[3-58]

$$Na^{+}S^{\ominus} + Ar\ CH = N.Ph \longrightarrow Ar\ \underset{\underset{S}{|}}{CH}\ \overset{\ominus}{N}\ Ph.Na^{\ominus} \qquad - (3.8)$$

or

$$2Ar\ CH = N.Ph + 2\ Na \longrightarrow (Ph\ \underset{\underset{|}{}}{CH}\ \bar{N}.Ph)_2 2\ Na^{\ominus} \qquad - (3.9)$$
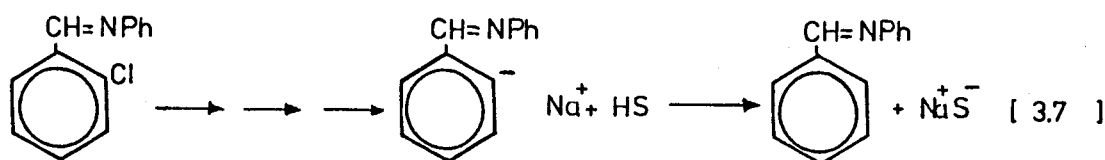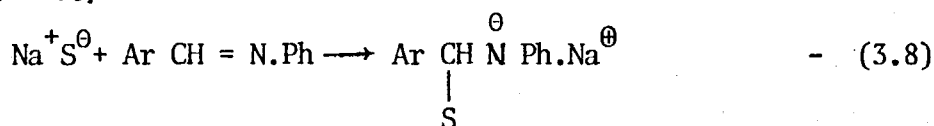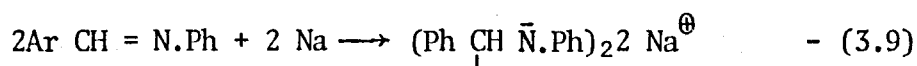
Our hypothesis of proton supply differs from the suggested mechanism. According to our findings the proton comes from t-butanol. Since the tertiary alcohols do not react with sodium metal very easily under ordinary conditions, the sodium reacts more vigorously in the presence of equivalent amount of halogen or halogen derivatives. So presumably what happens is that the sodium salt of an aryl anion (equation 3) is formed, which abstracts a proton from t-butanol to give sodium ^{t}butoxide as the by-product, along with the sodium chloride, which on work up (addition of water) gives t-butanol and alkali. The reaction can be represented as (equations 10 and 11).

$$\left[\begin{array}{c} \overset{-}{\underset{Cl}{\overset{Cl}{\bigcirc}}} \end{array}\right] \quad Na^{\overset{+}{\cdot}} + H-O^tBu \longrightarrow \left[\begin{array}{c} \overset{Cl}{\underset{Cl}{\overset{Cl}{\bigcirc}}} \end{array}\right] + Na^{+} \overset{-}{O}^tBu \qquad [\ 3.10\ ]$$

$$Na\overset{\ominus\ominus}{O}^tBu + H_2O \longrightarrow {}^tBuOH + NaOH \qquad (3.11)$$
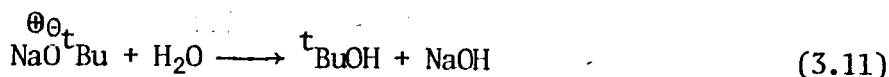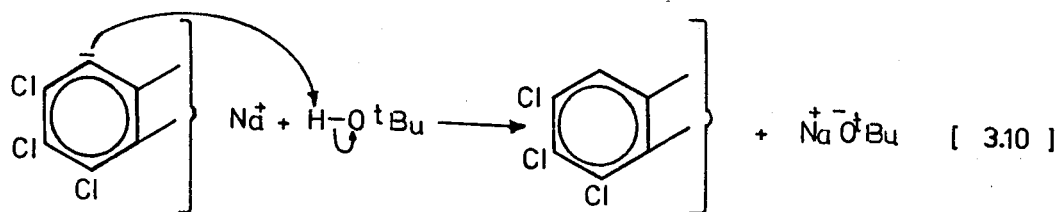
The extreme rapidity of electron transfer reactions[73] supports the formation of anionic intermediates. The behaviour described here agrees with the conclusions of Garst[74] and of Sargent,[10] who on the basis of apparently excellent supportive evidence, deduced that the radicals formed on dehalogenation are largely reduced to anions prior to any other reaction. However, it is possible that, under the reaction conditions employed, the intermediate radical anion formed from chloro-derivative and sodium might not collapse to chloride ion and aryl radical until it had diffused to a region remote from the sodium. Abstraction of hydrogen by the radical would then occur prior to further reduction. However, it is very difficult to define precisely how the reduction proceeds.

Further supporting evidence against hydrogen abstraction of the solvent by the aryl radical was obtained by using deuteriated solvents. The dechlorination of tetrachlorobenzobarrelene (2-47) and 2,3-dimethyl-1-methoxytetrachlorobenzobarrelene (2-3) was effected by sodium in tetrahydrofuran using $\underline{O}$-[^2H]-t-butanol. In both the cases deuteriated products were obtained. Mass spectrometry showed that the total deuterium incorporation in tetradeuteriobenzobarrelene (3-59) was 91.2%, the amount of individual contribution of deuterium in the molecule was as d_0, 9.8%; d_1, 14.61; d_2, 29.22; d_3, 27.45; and d_4, 18.80 mole %. The amount of unlabelled species was very high since the deuteriated $\underline{t}$-butanol used was very old. We decided to repeat the experiment using the fresh batch of deuteriated $\underline{t}$-butanol and another derivative of the benzobarrelene system. 2,3-Dimethyl-1-methoxytetrachloro-

-benzobarrelene (2-3) was then subjected to dechlorination using freshly distilled deuteriated $\underline{t}$-butanol (98.5%, by wt.), the overall deuterium incorporation in the molecule was 97.5%. Since the total amount of deuterium in deuteriated $\underline{t}$-butanol was 98.5%, we can presume that the loss of deuterium in the deuteriated molecule was caused by the presence of non-deuteriated $\underline{t}$-butanol. The calculations of deuterium incorporation are as follows:
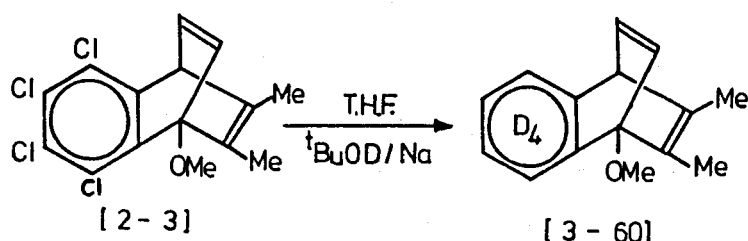
When M^+ is considered as the fragment of mass ignoring the other fragments M-1, M-2 etc. the isotope is $\underline{1}$ mass unit heavier than the light one.

Peak heights (arbitary units) in unlabelled standard.

Mass:	M	M+1	M+2	M+3	M+4	M+5
Intensity:	1.00	0.240	0.300	0.004	0.002	0.000

Peak heights (scale divisions) in labelled sample:

Mass:	M	M+1	M+2	M+3	M+4	M+5
Intensity:	60	180	480	900	995	150

-(A)

The peak at M^+, 60 div., is due to only unlabelled species.

Compute contributions of unlabelled species to the peaks at M, M+1, M+2 etc. by multiplying the peak height at M^+ with the abundance values of the standard:

60 x 1.00 = 60.00; 60 x 0.240 = 14.40; 60 x 0.03 = 1.80;

60 x 0.004 = 0.240; 60 x 0.002 = 0.120   -(B)

Subtract (B) from (A):

60.00	180.00	480.00	900.000	995.000	
-60.00	-14.40	- 1.80	- 0.240	0.120	
00.00	165.60	478.20	899.760	994.880	- (C)

The peak height at M+1 due to singly labelled species is thus 165.60 div., compute the contributions of singly labelled species:

165.60 ;   165.60 x 0.240 = 39.744; 165.60 x 0.03 = 4.968;

165.60 x 0.004 = 0.6624; 165.60 x 0.002 = 0.3312

- (D)

Subtract (D) from (C):

165.60	478.20	899.760	994.880	150.00	
-165.60	-39.74	- 4.968	- 0.662	- 0.33	
000.00	438.46	894.792	994.218	149.67	-(E)

The peak height at M+2 due to the double labelled species is 438.46 div., compute contributions of doubly labelled species:

438.46   ; 438.46 x 0.24 = 105.23; 438.46 x 0.03 = 13.154;

438.46 x 0.004 = 1.754; 438.46 x 0.002 = 0.877 - (F)

Subtract (F) from (E) :

438.46	894.792	994.218	149.670	
-438.46	-105.230	13.154	1.754	
0.00	789.562	981.064	147.916	- (G)

The peak height at M+3 due to triply labelled species is 789.562 div., compute contributions of triply labelled species:

102.

789.562   ;   789.562 x 0.24 = 189.49; 789.562 x 0.03 = 23.68;

789.562 x 0.004 = 3.16   - (H)

Subtract (H) from (G) :

789.562   981.064   147.916

-789.562   -189.490   -23.680

0.000   791.574   124.236

——————   ——————   ——————   - (I)

The peak height at M+4 due to tetra labelled species is 791.574 div.,

compute contributions of tetra labelled species:

791.574   ;   791.574 x 0.24 = 189.97   - (J)

Subtract (J) from (I) :

791.574   124.236

-791.574   -189.970

0.000   -65.734

——————   ——————   - (K)

No species containing more than four heavy isotopes are present.

The sum of all corrected intensities is :

60.00 + 165.60 + 438.46 + 789.56 + 791.57 = 2245.19.

The distribution in mole percent is :

$\frac{60.00}{2245.19}$ x 100 = 2.67 mole % unlabelled species.

$\frac{165.60}{2245.19}$ x 100 = 7.37 mole % singly labelled species.

$\frac{438.46}{2245.19}$ x 100 = 19.53 mole % doubly labelled species.

$\frac{789.56}{2245.19}$ x 100 = 35.17 mole % triply labelled species.

$\frac{791.57}{2245.19}$ x 100 = 35.26 mole % tetra labelled species

Total amount of deuterium present is 97.33%.

These results are, at least, precise to two significant figures since

the data are not very accurate. The amount of deuterium present in the

103.

molecule was further cross-checked by calculating the deuterium incorporation at fragments $[M^+-26]$, loss of acetylene ($CH{\equiv}CH$) and$[M^+-54]$, loss of dimethyl-acetylene $[CH_3-C{\equiv}C-CH_3]$. Thus the calculations of deuterium incorporation agree with that already reported e.g. at $[M^+-26]$ the amount of deuterium was 97.73% and at $[M^+-54]$, 97.60% deuterium was present.

In another experiment $[^2H_8]$tetrahydrofuran was diluted with freshly distilled tetrahydrofuran(1:1 ratio) and used as the solvent, for the dechlorination of 2,3-dimethyl-1-methoxytetrachlorobenzobarrelene (2-3) using sodium and t-butanol. Mass spectrometry of the dechlorinated product showed no trace of deuterium in the molecule, which indicates that the solvent does not take part in the reaction. Further evidence of the proton supply by the t-butanol was obtained, by attempting to carry out the dechlorination of tetrachlorobenzobarrelene (2-47) without using the t-butanol, unchanged starting material was obtained in 90% yield, even after 60 h. Perhaps the polarity and boiling point of the solvent plays a significant role in the rate of dechlorination. For example, when the dechlorinations were carried out in tetrahydrofuran, 90-100% yields of the dehalogenated products were obtained, whereas only 50% conversion was achieved when diethyl ether was used as a solvent. No purple sodium chloride was obtained when diethyl ether was used as the solvent.

In a similar related study Cheng[11] suggested that the aryl radical produced in reaction 3.2 could remove the hydrogen atom from the solvent. The resulting solvent radical would be expected to be reduced to the solvent anion. An attempt was made to assess this possibility by conducting the reaction in mixtures of tetrahydrofuran and diethyl ether, should hydrogen removal be effected by radicals then the ratio of solvent containing products would reflect the relative reactivity of the two ethers towards radicals. Controlled g.l.c. of solvent systems at the intermediate

stages showed no evidence of the presence of any other products.

In order to establish the scope of the method we decided to de-chlorinate 1,4-dihydro-1,4-epoxytetrachloronaphthalene (2-40) obtained from the Diels-Alder reaction of tetrachlorobenzyne with furan. Dechlor-ination of the molecule using the standard conditions, gave partial reduction of the double bond resulting in a mixture of saturated and unsaturated products.[37] The overall yield of the dechlorinated products was 97%, which were separated by preparative t.l.c. to give 1,4-dihydro-1,4-epoxynaphthalene (3-61) (40%) and 1,2,3,4-tetrahydro-1,4-epoxy-naphthalene (3-62) (47%)[76] (Scheme 3-8).

[2- 40]   [3 - 61]   [3 - 62]
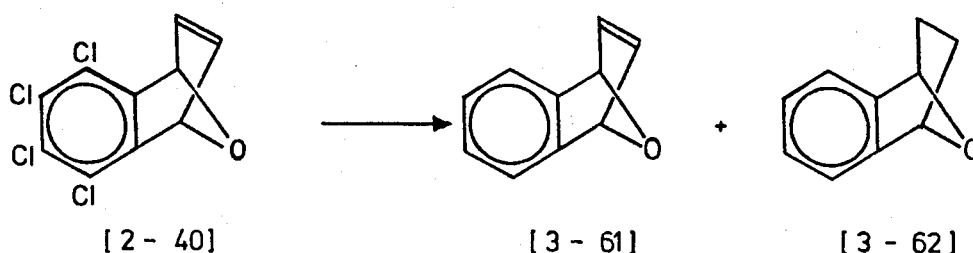
[Scheme   3-8]

At first the reason for this reduction could not be understood, so we decided to carry out a series of dechlorinations of the products containing a hetero-atom at the position seven of the molecule. 5,6,7,8-Tetrachloro-1,4-dihydro-1,4-N-methyliminonaphthalene (2-41) on dechlorination gave a mixture of the products, 1,4-dihydro-1,4-N-methyliminonaphthalene (3-63) (38%) and 1,2,3,4-tetrahydro-1,4-N-methyliminonaphthalene (3-64) (50%).[77] (Scheme 3-9). Further evidence of the reduction of olefinic double bond were obtained by dechlorinating a number of similar products as reported in Table III.

[2 - 41]   [3 - 63]   [3 - 64]

[Scheme   3-9]

105.
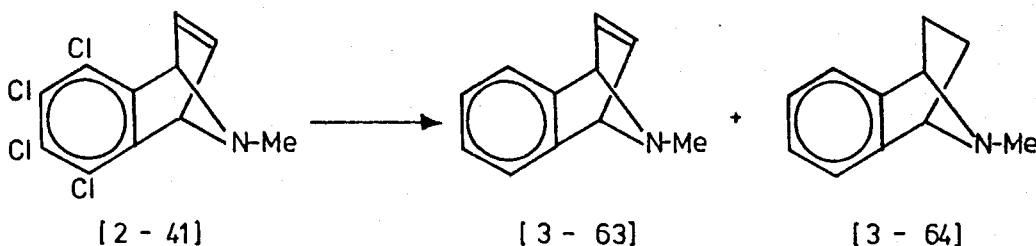
Having shown that several 1,4-disubstituted derivatives, containing a hetero-atom at the seven position, give a mixture of saturated and unsaturated products on dechlorination, we decided to dechlorinate tetrachlorobenzonorbornadiene (2-36) under the same conditions. Tetrachlorobenzonorbornadiene (2-36), obtained by decomposing the 2-carboxytetrachlorobenzenediazonium tetrafluoroborate in the presence of cyclopentadiene on dechlorination gave benzonorbornadiene (3-67)[78] in 87% yield, which was also verified by means of physical data reported in the literature.

[2-36]   [3-67]
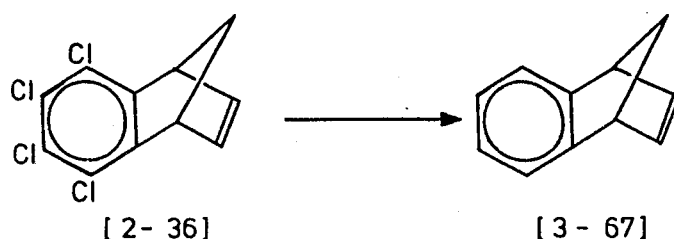
N.m.r. studies on the crude reaction mixture showed no traces of the reduced product, benzonorbornene.

[I]   [II]
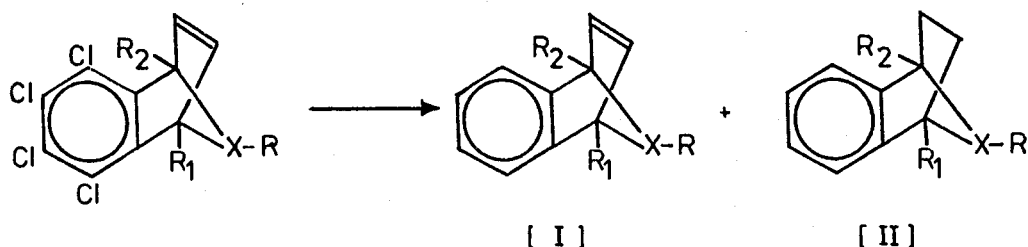
(Table 3-3)

Substituents	No.	Product	X	R	R_1	R_2	Yield (%)
Furan adduct	(3-61)	I	O	H	H	H	40
	(3-62)	II	O	H	H	H	47
N-Methylpyrrole adduct (3-63)		I	N	Me	H	H	38
	(3-64)	II	N	Me	H	H	50
1,2,5-Trimethylpyrrole adduct	(3-65)	I	N	Me	Me	Me	35
	(3-66)	II	N	Me	Me	Me	47

The ratio of these saturated and unsaturated reaction products were not constant, varying considerably from reaction to reaction, and apparently depending upon the amount of sodium used in the reduction. The adduct obtained from tetrachlorobenzyne with 6,6-dimethylfulvene by Diels-Alder reaction,[79] when subjected to dechlorination, gave just one product, the 7-isopropylidenebenzonorbornadiene (3-68) in 94% yield, which further verifies the earlier results. From all the work reported above, it appears that in some way a hetero-atom helps in the reduction of the olefinic double bond. The compounds containing a five membered ring were more prone to the reduction than six membered rings.

[2 - 38]   [3 - 68]
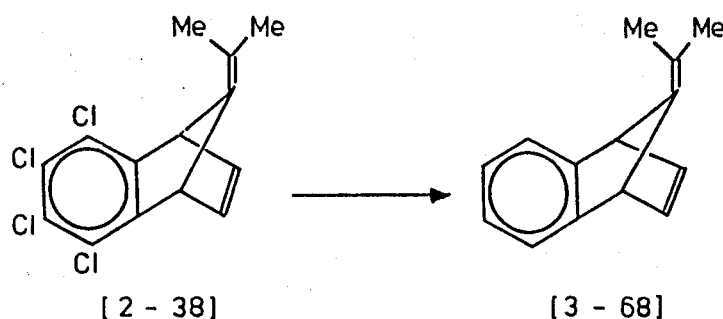
In the case of 7,7-dimethoxyoctachlorobenzonorbornadiene (2-44),
dechlorination according to the procedure given above, gave partial
reduction of the double bond.[80] The mixture was separated by extraction
with aqueous silver nitrate solution, to give 7,7-dimethoxybenzonorbornadiene
(3-69) (66%) and 7,7-dimethoxybenzonorbornene (3-70) (12%) [Scheme 3-10].

[2 - 44]   [3 - 69]   [3 - 70]

[Scheme 3-10]
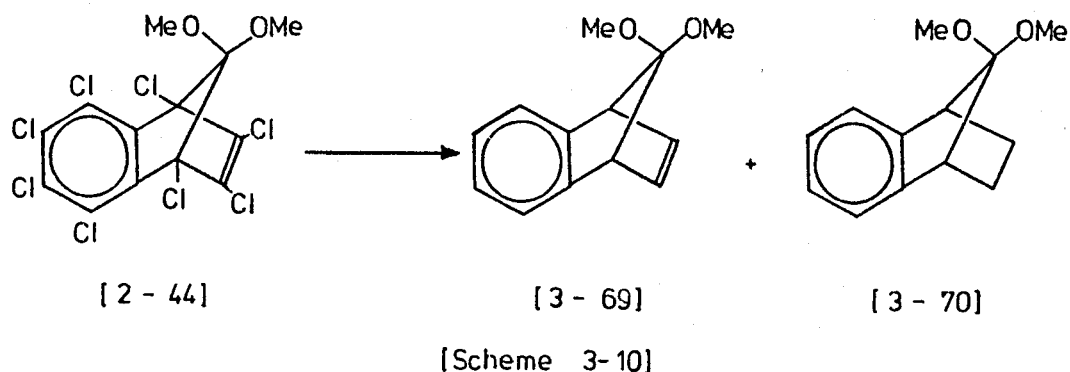
A number of other similar examples exist in the literature,[81] where
the reduction of the double bond has been observed, when the hetero-atom
(e.g. oxygen) is present in the very close vicinity of the double bond.
For example, the tetrachloroketal, (3-71), a readily available adduct of

[3 - 71]   [3 - 72]
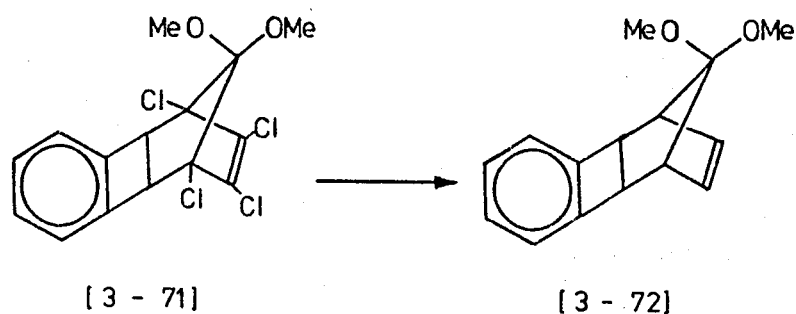
benzocyclobutadiene with 5,5-dimethoxytetrachlorocyclopentadiene and the
corresponding ketal (3-71) were dechlorinated. The standard methods were
used for the dechlorination and only 20% of the reduced product was obtained.[82]

108.

Recently Warrener and co-workers [85] in their studies of the synthesis of isobenzofulvene from 7-methylenebenzonorbornadiene (3-68) have successfully utilized sodium and t-butanol for the dechlorination purposes without effecting the stereochemistry of the molecule (3-73). The reaction is summarized in Scheme 3-11.
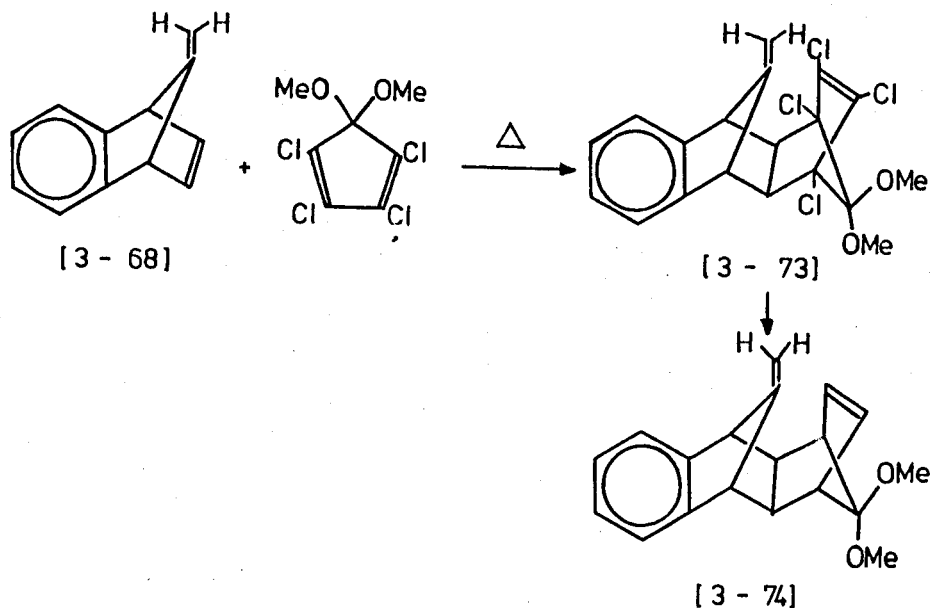
[Scheme 3-11]

A number of mechanisms could be postulated for the catalytic reduction of the olefinic double bond, during the dechlorination process, when a hetero-atom (X=N, O etc.) is present at position-7 of the ring system or when it is present in the very close vicinity of the double bond.
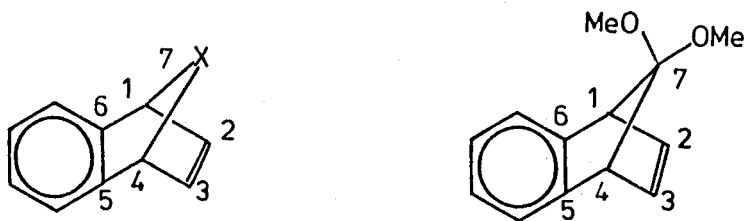
The available evidence indicates the indirect participation of the π-electron cloud of the 2,3-olefinic double bond with the lone pair of electrons of the hetero-atom present at position-7. The electrostatic charge flowing around the hetero-atom (O or N), presumably delocalized the effect of the π-electron interaction of p-orbitals of the 2,3-olefinic double bond during the metal attack thus making it more susceptible to the reduction process, without actually taking part in the reaction. This is achieved, by the overlap of p-orbitals at the reaction centre with the adjacent π-electron system, which in turn may overlap the p-electrons.
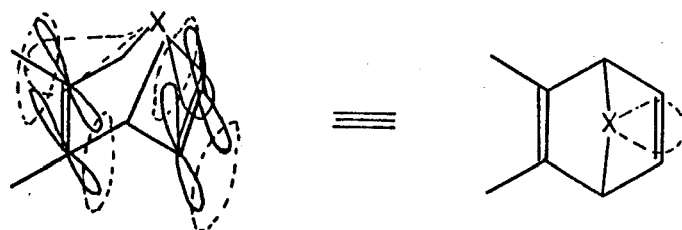
Although no definite evidence is yet available on the question of how the olefinic double bond gets reduced, it is assumed that the sodium metal attacks the polarized 2,3-olefinic double bond, forming a radical anion. This radical anion then abstracts a proton from the system leaving behind alkyl radical. The existing radical is then further reduced by sodium metal to alkyl anion, which abstracts another proton from the nearby source. The mechanism for the reaction can be summarized as follows (Equations 12 to 16):

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$$Na\bullet \longrightarrow Na^+ \qquad\qquad Na^+ \qquad [\ 3.12\ ]$$

$$Na^+ +\ H\text{--}S \longrightarrow \qquad\qquad +\ Na^+S^- \quad [\ 3.13\ ]$$

$$Na\bullet \longrightarrow Na^+ \qquad\qquad Na^+ \qquad [\ 3.14\ ]$$

$$Na^+ +\ H\text{--}S \longrightarrow \qquad\qquad +\ Na^+S^- \quad [\ 3.15\ ]$$

$$Na^+S^- +\ H_2O \longrightarrow NaOH\ +\ HS \qquad\qquad [\ 3.16\ ]$$
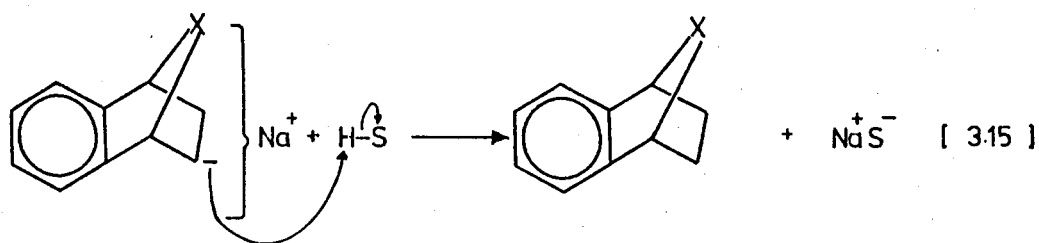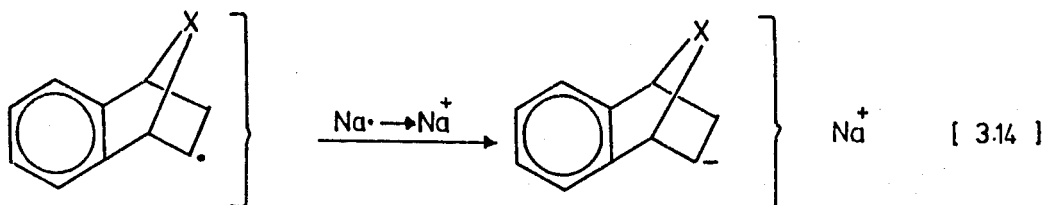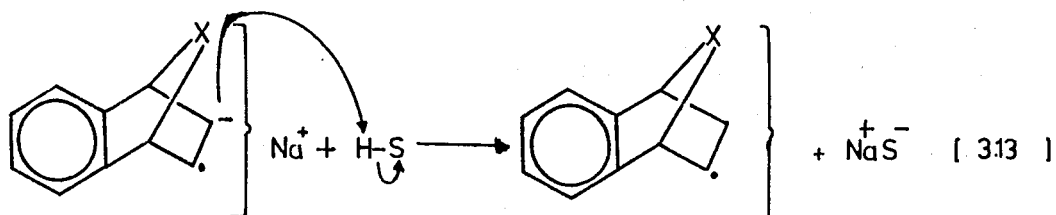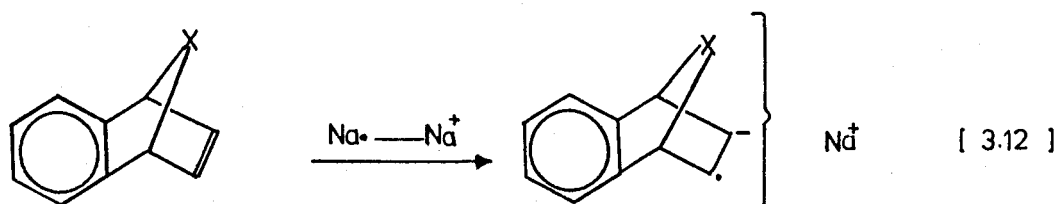
[X = N, O ; HS = Solvent]

The extreme rapidity of the electron transfer reactions again indicates an anionic intermediate. Similar reduction of the olefinic double bond was observed when the oxygen (-OMe) was present in very close proximity of the double bond. Thus when 7,7-dimethoxyoctachlorobenzonorbornadiene (2-44) was subjected to dechlorination, a mixture of saturated and unsaturated compounds was obtained. Presumably the remote oxygen participation was of

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the same type as that explained earlier, the lone pair electrons assisting the metal to attack the double bond to form a radical anion. Once the process is initiated reaction proceeds rapidly as explained with or without the assistance of the oxygen.

[3 - 75]   [3 - 70]
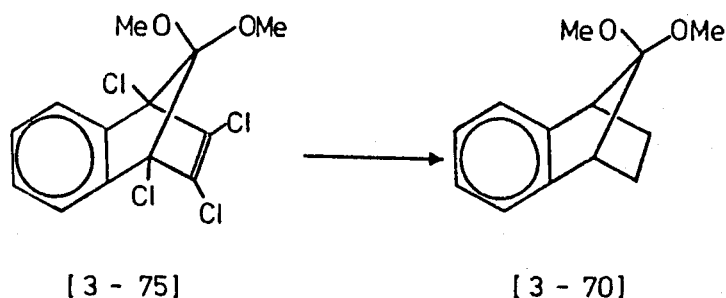
This phenomenon of olefinic double bond reduction, during dechlorination, still needs further examination because of its unique behaviour. Since the presence of a hetero-atom in the barrelene system behaves differently than in norbornadiene systems, further evidence was sought by dechlorinating systems like the ketals of benzobarrelenones,in which a hetero-atom (e.g. O) was present in the close proximity of the double bond. These systems showed no reduction of the double bond. Thus 3,3-ethylenedioxy-5-methyl- -1-methoxytetrachlorobenzobarrelene (2-58) on dechlorination gave 3,3-ethylenedioxy-5-methyl-1-methoxybenzobarrelene (3-49) in 95% yield, no traces of any other reduced product was found.

[2 - 58]   [3 - 49]
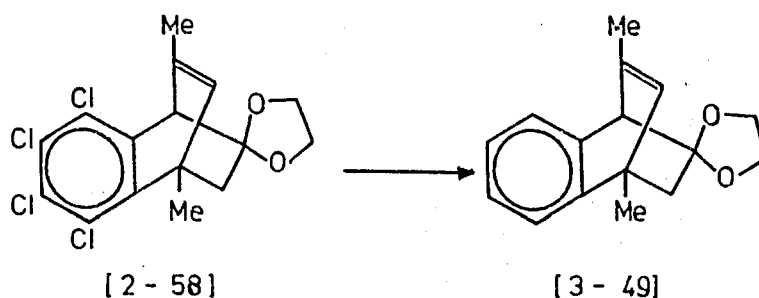
Similarly other ketals derived from benzobarrelenone system showed no unusual behaviour on dechlorination. It was further observed that aromatic systems containing a heteroatom undergo dechlorination smoothly, although the yields were low as compared to the hydrocarbon systems. For example, when 4,7-dichloro-8-hydroxyquinoline (3-76) was subjected to the standard dechlorination treatment, 66% yield of 8-hydroxyquinoline (3-77) was obtained. The spectral data for the product agreed with that of an authentic sample.

[3 - 76]   [3 - 77]
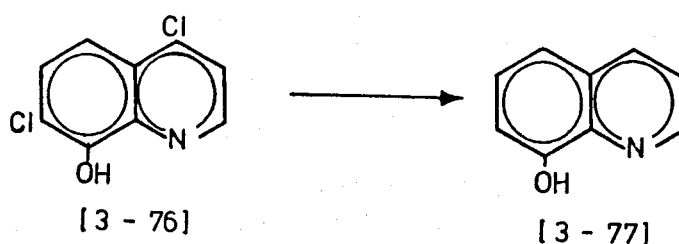
In order to compare the suitability of the dechlorinating agent against a number of other reagents suggested by various research groups, we decided to try a number of other dechlorinating agents on our systems. For example, magnesium and propan-2-ol was used for dechlorination of tetrachlorobenzobarrelene (2-47) by refluxing in decahydronaphthalene as a solvent as suggested by Bryce Smith and co-workers.[53] Only 2% yield of the dechlorinated product was obtained. The major drawback of the system was the solubility.

[2 - 47]   [3 - 30]

$$R.Hal. + Mg + R'.OH \longrightarrow RH + R'.OMgHal.$$
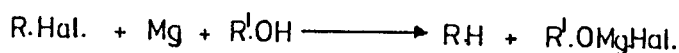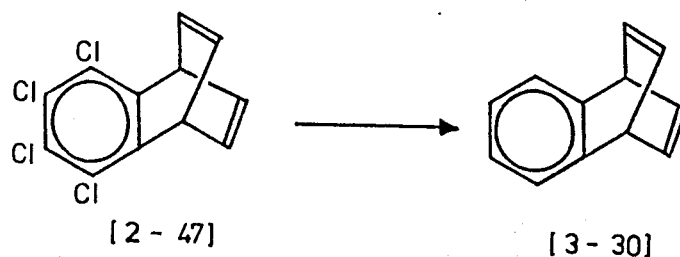
The use of Ni-Al alloy in alkali, suggested by Wilt and co-workers,[54] was found equally unsuitable for our systems. Dechlorination of tetrachlorobenzobarrelene (2-47) using Ni-Al alloy in strong potassium hydroxide gave benzobarrelene in 3.5% yield.

Use of palladium on charcoal and hydrazine hydrate has been frequently made by a number of research workers,[83] for the dechlorination of aromatic systems. In the case of bicyclic systems, the reduction of the olefinic double bond has been frequently encountered. Thus the dechlorination of 1-methoxytetrachlorobenzobarrelene (2-1) resulted in the formation of saturated product, the 1-methoxy-1,4-ethanotetralin (3-78), when heated under reflux with 5% Pd/C in ethanol and hydrazine hydrate. The spectral data for the product, 1-methoxy-1,4-ethanotetralin (3-78), were identical to those reported by Jablonski[84] (Scheme 3-12).

[2 - 1]   [3 - 78]
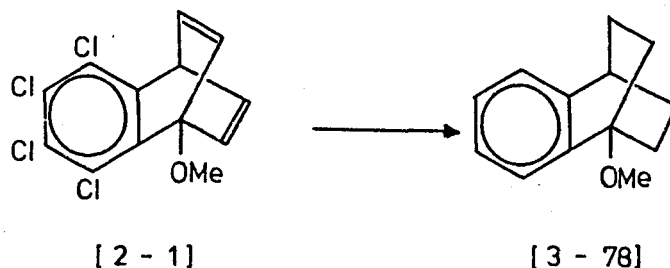
[Scheme 3-12]

On the other hand, the dechlorination of tetrachloronaphthalene derivatives was successfully carried out by using Pd/C and hydrazine hydrate. For example, when α-[3-methyl-5,6,7,8-tetrachloronaphthyl]-acetic acid (2- 59) was heated with 5% palladium on charcoal and hydrazine hydrate in ethanol, a quantitative yield of α-[3-methylnaphthyl]-acetic acid (3-79) was obtained. The use of these reagents under ideal conditions showed no reduction and has been successfully employed for the

dechlorination of a large number of similar substituted aromatic systems. The mechanistic pathway is not fully understood.

[2 - 59]   [3 - 79]
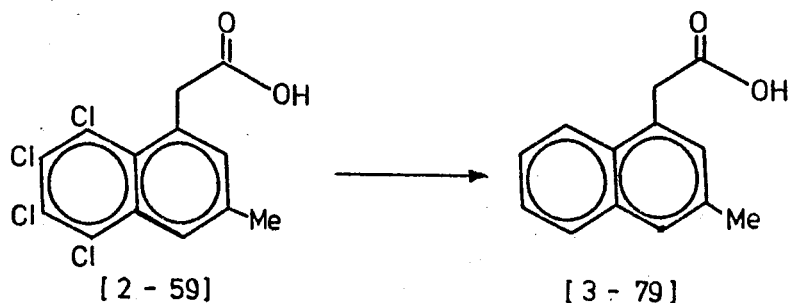
Finally the dechlorination of few other ketals in which the alkyl groups were present at position 1 and 3 or 5 of the barrelene skeleton using the sodium-t-butanol-THF system confirmed the versatility of this method. The various results are as shown in Table IV.
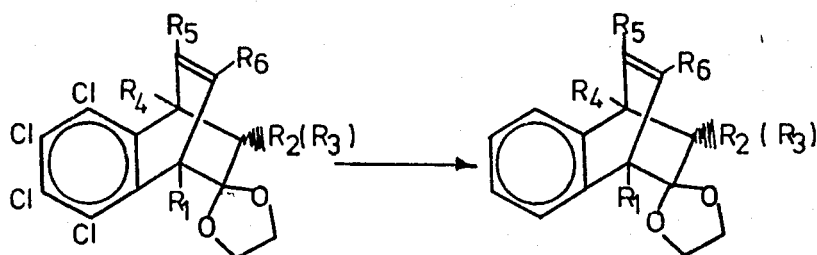
Table IV

No.	R_1	R_2	(R_3)	R_4	R_5	R_6	Yield %
			Product				
(3-80)	Me	Me	(Me or H)	H	H	H	92
(3-81)	Me	H	(H)	H	Me	H	84
(3-82)	H	H	(H)	Me	H	Me	94

The 1,3-dimethylbenzobarrelenones (3-83) were obtained by the dechlorination and deketalization of its chloro-analogue (2-9). The ^{1}H n.m.r. spectrum of the product suggested that only one isomer was present with an endo methyl group. The catalytic reduction of the

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olefinic double bond with 10% palladium on charcoal in ethanol, under a positive pressure of hydrogen revealed that it was a mixture of two isomers in the ratio 95:5 [Scheme 3-13]. The major product did have the methyl group in an endo location. The two isomers could not be separated because of their close R_f values.

[3 - 83]   [3 - 84]   [3 - 85]
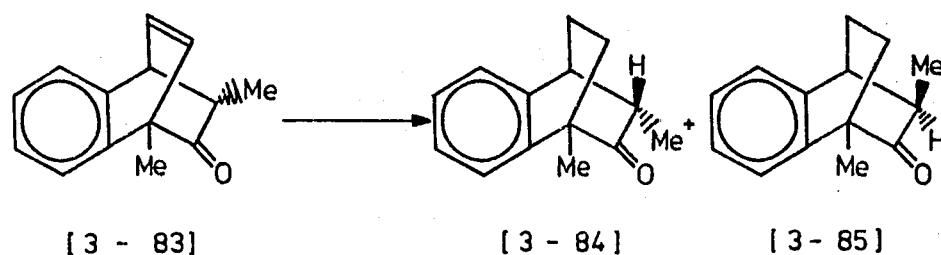
[Scheme 3-13]

In conclusion it can be said that the stereochemistry of dehalogenation varies widely with the type of reductant used. For a reaction which has been studied in the recent years, in more detail from a kinetic view, all the possible types of reaction intermediates have been suggested. These include radical, carbanion, and carbonium ion intermediates, and also a concerted single-step process. The use of sodium and t-butanol in tetrahydrofuran for the dechlorination purposes has been found most suitable for the bicyclic systems. The reagent has a number of advantages over a large number of other dehalogenating agents. The present dehalogenating agents can be utilized even for the removal of halogens from the system containing hetero-atoms and the most important thing is that the reaction completion can be observed visually which helps in knowing the reaction time and saving the molecule from further attack of the metal.

EXPERIMENTAL

Experimental Section:

General Procedures:

The general procedures are as described in Chapter two.

1. Preparation of 1-Methoxybenzobarrelene [1,4-dihydro-1-methoxy-1,4-ethenonaphthalene] (3-31):

A solution of 1-methoxytetrachlorobenzobarrelene (2-1) (10.0 g, 31.05 mmole) in tetrahydrofuran (50 ml) was added dropwise to a vigorously stirred suspension of sodium metal (as a wire, 11.0 g, 460 mmole) in tetrahydrofuran (400 ml) containing t-butanol (33 g) over a period of 0.5 h, while maintaining the temperature ca. 70°. The reaction mixture was heated under reflux for 8 hr. The reaction mixture was cooled to room temperature and methanol (50 ml) was carefully added. The resulting mixture was poured onto crushed ice (ca. 500 g) and extracted with ether (3 x 200 ml). The combined ether extracts were dried (Mg SO$_4$) and evaporated under reduced pressure. The residual mass was purified by column chromatography (silica gel, light petroleum) to give 1-methoxybenzobarrelene (3-31): (5.40 g, 98%) m.p. 37-38° (from ethanol) (lit.[61] m.p. 37-38°). Spectral data agreed with those previously reported.[61]

2. Preparation of 2-Methyl-1-methoxybenzobarrelene [1,4-dihydro-1-methoxy-2-methyl-1,4-ethenonaphthalene] (3-32):

A solution of 2-methyl-1-methoxytetrachlorobenzobarrelene (2-2) (10.0 g, 29.76 mmole) in tetrahydrofuran (50 ml) was added dropwise to a vigorously stirred suspension of sodium metal (11.0 g, 460 mmole) in tetrahydrofuran (400 ml) containing t-butanol (33.0 g), while maintaining the temperature at ca. 70°. The reaction was completed as explained in experiment no. 1 to give 2-methyl-1-methoxybenzobarrelene (3-32): (5.5 g, 93%) b.p. 122-123°/4.5 m.m. Hg.

(Found: C, 84.7; H, 7.0%; C$_{14}$H$_{14}$O requires, C, 84.84; H, 7.07%);

M$^+$ (Mass spectrometry): 198.

^{1}H n.m.r. τ(CDCl$_3$): 2.42-3.32 (m, 6H); 3.54-3.82 (m, 1H); 5.26-5.52 (m, 1H); 6.19 (s, 3H); and 8.27 (d, 3H, J = 2.6 Hz).

ν_{max}^{oil}: 3060, 3020, 2980, 2950, 2840, 1590, 1450, 1325, 1220, 1160, 1130, 1080, 1050, 1000, 890, 800, 770, 745 and 665 cm.$^{-1}$

3. Preparation of 2,3-Dimethyl-1-methoxybenzobarrelene [1,4-dihydro-1-methoxy-2,3-dimethyl-1,4-ethenonaphthalene] (3-33):

A solution of 2,3-dimethyl-1-methoxytetrachlorobenzo-barrelene (2-3) (10.0 g, 28.57 mmole) in tetrahydrofuran (50 ml) was added dropwise to a vigorously stirred suspension of sodium metal (11.0 g, 460 mmole) in tetra-hydrofuran (400 ml), containing t-butanol (33.0 g) at ca. 70°. The reaction was completed as explained in experiment no. 1 to give 2,3-dimethyl-1-methoxybenzobarrelene (3-33):

(5.6 g, 93%), m.p. 80-81° (from ethanol).

(Found: C, 84.6; H, 7.7%; $C_{15}H_{16}O$ requires, C, 84.9; H, 7.55%);

M^+ (Mass spectrometry): 212. ^{1}H n.m.r. τ (CDCl$_3$): 2.55-2.80 (m, 1H); 2.80-3.32 (m, 5H); 5.62 (dd, 1H, $\underline{J}$ = 2.2 Hz, $\underline{J}$ = 1.6 Hz); 6.2 (s, 3H); 8.27 (q, 3H, $\underline{J}$ = 1.5 Hz); and 8.29 (q, 3H, $\underline{J}$ = 1.5 Hz).

ν_{max}^{KBr}: 3065, 3020, 2960, 2940, 2910, 2840, 1603, 1445, 1380, 1360, 1340, 1323, 1230, 1215, 1160, 1080, 1042, 992, 940, 900, 870, 845, 815, 760, 712, 675, and 650 cm.$^{-1}$

4. Preparation of 2,5-Dimethyl-1-methoxybenzobarrebene [1,4-dihydro-1-methoxy-2,9-dimethyl-1,4-ethenonaphthalene] (3-34).

A solution of 2,5-dimethyl-1-methoxytetrachlorobenzobarrelene (2-4) (100.0 g, 30.0 mmole) in tetrahydrofuran (50 ml) was added to a suspension of sodium metal (11.0 g, 460 mmole) in tetrahydrofuran (400 ml) containing t-butanol (33.0 g) at 70°. The reaction was worked up as explained in experiment no. 1 to give 2,5-dimethyl-1-methoxybenzobarrelene (3-34):

(5.6 g, 95%), b.p. 118-120°/0.3 m.m. Hg.

(Found: C, 84.5; H, 7.5%; $C_{15}H_{16}O$ requires, C, 84.90; H, 7.55%);

M^+ (Mass spectrometry): 212.

^{1}H n.m.r. τ(CDCl$_3$): 2.49-2.75 (m, 1H); 2.75-3.26 (m, 3H); 3.31-3.51

    (m, 1H); 3.55-3.80 (m, 1H); 5.55-5.80 (dd, 1H, $\underline{J}$ = 2.2 Hz);

    6.18 (s, 3H); and 7.83-8.25 (m, 6H).

ν_{max}^{oil}: 3065, 3020, 2965, 2935, 2870, 2850, 2830, 1460, 1440, 1375, 1300,

    1250, 1235, 1160, 1100, 1080, 1020, 910, 850, 750, 715, and 635 cm.$^{-1}$

5.   Preparation of 3,5-Dimethyl-1-methoxybenzobarrelene[1,4-dihydro-1-

methoxy-3,9-dimethyl-1,4-ethenoanphthalene] (3-35):

    A solution of 3,5-dimethyl-1-methoxytetrachlorobenzobarrelene (2-10)

(10.0 g, 30.0 mmole) in tetrahydrofuran (50 ml) was added to a stirred

suspension of sodium metal (11.0 g, 460 mmole) in tetrahydrofuran (400

ml), containing $\underline{t}$-butanol (33.0 g) at $\underline{ca}$. 70°. The reaction was worked

up as explained in experiment no. 1 to give 3,5-dimethyl-1-methoxybenzo-

barrelene (3-35):

(5.8 g, 98%), m.p. 69-70° (from ethanol).

(Found: C, 84.80; H, 7.5%; C$_{15}$H$_{16}$O requires, C, 84.90; H, 7.55%);

M^{+} (Mass spectrometry); 212.

^{1}H n.m.r. τ(CDCl$_3$): 2.55-3.32 (m, 4H); 3.48-3.68 (m, 2H); 5.78-6.02

    (m, 1H); 6.26 (s, 3H); 7.92-8.2 (d, 6H, $\underline{J}$ = 2.2 Hz).

ν_{max}^{KBr}: 3075, 3060, 3020, 2970, 2960, 2930, 2840, 1660, 1440, 1375, 1300,

    1285, 1275, 1250, 1185, 1160, 1130, 1100, 1070, 1025, 980, 970,

    905, 840, 808, 760, 760, 730, and 640 cm.$^{-1}$

6.   Preparation of 2,6-Dimethyl-1-methoxybenzobarrelene[1,4-dihydro-1-

methoxy-2,10-dimethyl-1,4-ethenonaphthalene] (3-36) :

    A solution of 2,6-dimethyl-1-methoxytetrachlorobenzobarrelene (2-8)

(10.0 g, 30.0 mmole) in tetrahydrofuran (50 ml) was added to a suspension

of sodium metal (11.0 g, 460 mmole) in tetrahydrofuran (400 ml), containing

t-butanol (33.0 g) at $\underline{ca}$. 70°. The reaction mixture was completed as

explained in experiment no. 1 to give 2,6-dimethyl-1-methoxybenzobarrelene (3-36):

(5.8 g, 96%), m.p. 74-76° (from ethanol).

(Found: C, 84.9; H, 7.6%; $C_{15}H_{16}O$ requires, C, 84.87; H, 7.6%);

$M^{\cdot+}$ (Mass spectrometry): 212.

^1H n.m.r. $\tau(CDCl_3)$: 2.59 (q, 1H); 3.03 (m, 3H); 3.62 (dq, 2H, $|\underline{J}|$ = 6.2 Hz; $|\underline{J}|$ = 2.2

Hz); 5.56 ($\underline{t}$, 1H, $\underline{J}$ = 6.2 Hz); 6.07 (s, 3H); and 8.08 (s, 6H).

ν^{KBr}_{max}: 3040, 2960, 2920, 2840, 1440, 1292, 1280, 1220, 1150, 1075, 1024,

880, 810, 748, and 675 cm.$^{-1}$

7. Preparation of 2,3,5-Trimethyl-1-methoxybenzobarrelene[1,4-dihydro-

-1-methoxy-2,3,9-trimethyl-1,4-ethenonaphthalene] (3-37);

A solution of 2,3,5-trimethyl-1-methoxytetrachlorobenzobarrelene

(2-12) (10.0 g, 27.47 mmole) in tetrahydrofuran (50 ml) was added to a

stirred suspension of sodium metal (11.0 g, 460 mmole) in tetrahydrofuran

(400 ml), containing $\underline{t}$-butanol (33.0 g) at $\underline{ca}$. 70°. The reaction was

worked up as explained in experiment no. 1 to give 2,3,5-trimethyl-1-

methoxybenzobarrelene (3-37):

(5.8 g, 94%), m.p. 56-57° (from ethanol).

(Found: C, 84.4; H, 8.1%; $C_{16}H_{18}O$ requires, C, 84.9; H, 7.8%);

$M^{\cdot+}$ (Mass spectrometry); 226.

^1H n.m.r. $\tau(CDCl_3)$: 2.61-3.32 (m, 4H); 3.39-3.56 (m, 1H); 5.91

(d, 1H, $\underline{J}$ = 2.2 Hz); 6.24 (s, 3H); 7.98-8.14 (d, 3H, $\underline{J}$ = 1.6 Hz);

and 8.15-8.36 (m, 6H).

ν^{KBr}_{max}: 3080, 3055, 2980, 2940, 2850, 1600, 1502, 1460, 1420, 1385, 1325,

1305, 1287, 1264, 1205, 1175, 1158, 1125, 1098, 1030, 1000, 940,

840, 763, 730, 722, 660, and 630 cm.$^{-1}$

8. Preparation of 2,3,5,6-Tetramethyl-1-methoxybenzobarrelene[1,4-

dihydro-1-methoxy-2,3,9,10-tetramethyl-1,4-ethanonaphthalene] (3-38):

A solution of 2,3,5,6-tetramethyl-1-methoxytetrachlorobenzobarrelene

(2-14) (10.0 g, 26.45 mmole) in tetrahydrofuran (50 ml) was added to a

stirring suspension of sodium metal (11.0 g, 460 mmole) in tetrahydrofuran (400 ml) containing t-butanol (33.0 g) at ca. 70°. The reaction mixture was worked up as explained in experiment no. 1 to give 2,3,5,6-tetra-methyl-1-methoxybenzobarrelene (3-38):

(6.05 g, 95%), m.p. 111-112° (from ethanol).

(Found: C, 85.1; H, 8.3%; $C_{17}H_{20}O$ requires, C, 85.00; H, 8.33%);

$M^{+\cdot}$ (Mass spectrometry): 240.

^1H n.m.r. $\tau(CDCl_3)$: 2.6-2.8 (m, 1H); 2.82-3.32 (m, 3H); 6.02 (s, 1H); 6.12 (s, 3H); and 8.24 (s, 12H).

ν_{max}^{KBr}: 3070, 3035, 2985, 2935, 2860, 2850, 1455, 1445, 1385, 1305, 1278, 1240, 1180, 1145, 1092, 1005, 940, 868, 780, 750, 675, and 650 cm.$^{-1}$

9.　Preparation of 2,6-Dimethyl-1-hydroxybenzobarrelene[1,4-dihydro-1-hydroxy-2,10-dimethyl-1,4-ethenonaphthalene] (3-39):

A solution of 2,6-dimethyl-1-trimethylsilyloxytetrachlorobenzo-barrelene (2-15) (2.50 g, 6.127 mmole) in tetrahydrofuran (25 ml) was added to a stirred suspension of sodium metal (3.0 g, 123 mmole) in tetrahydrofuran (400 ml) containing t-butanol (9.0 g) at ca. 70°. The reaction mixture was worked up as explained in experiment no. 1 to give 2,6-dimethyl-1-hydroxybenzobarrelene (3-39);

(900 mg, 72%), m.p. 95-96° (from ethanol).

(Found: C, 84.6; H, 7.1%; $C_{14}H_{14}O$ requires, C, 84.84; H, 7.07%;

$M^{+\cdot}$ (Mass spectrometry): 198.

^1H n.m.r. $\tau(CDCl_3)$: 2.32-2.92 (m, 6H); 6.49 (m, 1H), 7.7 (s, 6H); and 8.12 (broad hump, 1H);

ν_{max}^{KBr}: 3450, 3060, 3040, 2960, 2920, 2850, 1600, 1475, 1445, 1405, 1382, 1348, 1320, 1310, 1220, 1180, 1080, 1025, 945, 890, 875, 840, 765, 760, 742, and 700 cm.$^{-1}$

10. Preparation of 9,10-Dihydro-9-N,N-dimethylamino-9,10-etheno-anthracene (3-50):

A solution of 1,2,3,4-tetrachloro-9,10-dihydro-9-N,N-dimethylamino-9,10-ethenoanthracene (2-53) (10.0 g, 26.0 mmole) in tetrahydrofuran (30 ml) was dechlorinated using sodium metal (11.0 g, 460 mmole) in tetra-hydrofuran (400 ml) containing t-butanol (33.0 g) at ca. 70°. The reaction mixture on work up as explained in experiment no. 1 gave 9,10-dihydro-9-N,N-dimethylamino-9,10-ethenoanthracene (3-50):

(5.6 g, 87%), m.p. 184-185° (from ethanol).

(Found: C, 87.4; H, 6.9; N, 5.5%; $C_{18}H_{17}N$ requires C, 87.41; H, 6.93; N, 5.66%); M^{+} (Mass spectrometry): 247.

^{1}H n.m.r. τ(CDCl$_3$): 2.35-2.62 (m, 2H); 2.65-3.28 (m, 8H); 4.95-5.15 (m, 1H); and 7.05 (s, 6H).

ν_{max}^{KBr}: 3080, 3030, 2990, 2950, 2850, 1608, 1590, 1470, 1455, 1330, 1300, 1245, 1230, 1180, 1170, 1108, 1085, 1022, 988, 945, 915, 880, 840, 810, 770, 760, 740, 685, and 650 cm.$^{-1}$

11. Catalytic reduction of 9,10-Dihydro-9-N,N-dimethylamino-9,10-ethenoanthracene (3-50^{1}):

A suspension of palladised charcoal (10%, 40 mg) in a solution of 9-N,N-dimethylamino-9,10-ethenoanthracene (3-50) (1.0 g, 4.04 mmole) in ethyl alcohol-ethyl acetate (50:10 ml) was stirred at room temperature under one atmosphere of hydrogen for 8 h. The catalyst was removed by filtration and the filtrate was evaporated under reduced pressure. The residue on purification gave 9,10-dihydro-9-N,N-dimethylamino-9,10-ethanoanthracene (3-50^{1}):

(980 mg, 98%), m.p. 146-147° (from ethanol).

(Found: C, 86.4; H, 7.7; N, 5.5%; $C_{18}H_{19}N$ requires, C, 86.7; H, 7.68; N, 5.62%).

M^+ (Mass spectrometry): 249.

^{1}H n.m.r. τ(CDCl$_3$): 2.35-2.62 (m, 2H); 2.65-3.05 (m, 6H); 5.84 (d, 1H, $\underline{J}$ = 2.2 Hz); 6.97 (s, 6H); and 8.32 (s, 4H).

ν_{max}^{KBr}: 3080, 3040, 2950, 2888, 2840, 2800, 1590, 1485, 1475, 1455, 1340, 1320, 1208, 1194, 1155, 1055, 1030, 985, 945, 882, 785, 765, and 732 cm.$^{-1}$

12. Preparation of 9,10-Dihydro-9-methoxy-9,10-ethenoanthracene (3-51):

A solution of 1,2,3,4-tetrachloro-9,10-dihydro-9-methoxy-9,10-ethenoanthracene (2-52) (10.2 g, 27.0 mmole) in tetrahydrofuran (50 ml) was subjected to dechlorination by the usual method as explained in experiment no. 1. The crude product on purification gave: 9,10-dihydro--9-methoxy-9,10-ethenoanthracene (3-51):

(5.6 g, 88%), m.p. 181-82° (from ethanol).

(Found: C, 87.1; H, 6.1%; C$_{17}$H$_{14}$O requires, C, 87.18; H, 5.98%);

M^+ (Mass spectrometry): 234.

^{1}H n.m.r. τ(CDCl$_3$): 2.37-3.25 (m, 10H); 4.95 (dd, 1H, $\underline{J}$ = 7.2 Hz; $\underline{J}$ = 2.2 Hz); and 6.04 (s, 3H).

ν_{max}^{KBr}: 3080, 3050, 3030, 2995, 2975, 2955, 2850, 1603, 1470, 1455, 1330, 1298, 1248, 1230, 1180, 1135, 1110, 1085, 1045, 1020, 998, 936, 915, 880, 840, 770, 760, and 685 cm.$^{-1}$

13. Preparation of Benzobarrelene[1,4-Dihydro-1,4-ethenonaphthalene] (3-30):

A solution of tetrachlorobenzobarrelene (2-47) (10.0 g, 35.0 mmole) in tetrahydrofuran (50 ml) was added to a stirred suspension of sodium metal (11.0 g, 460 mmole) in tetrahydrofuran (400 ml) at $\underline{ca}$. 70°. The reaction mixture was worked up on completion as explained in experiment no. 1 to give benzobarrelene (3-30).

(7.5 g, 90%), m.p. 64-65° (from ethanol) (lit.[61] m.p. 65-66°).
Spectral data agreed with those previously reported.

14. Preparation of Tetradeuteriated benzobarrelene[5,6,7,8-tetra-deuterio-1,4-dihydro-ethanonaphthalene] (3-59):

A solution of tetrachlorobenzobarrelene (2-47) (1.0 g, 3.5 mmole) in tetrahydrofuran (10 ml) was added to a stirred suspension of sodium metal (1.1 g, 46.0 mmole) in tetrahydrofuran (30 ml) containing $\underline{O}$-[^{2}H]-$\underline{t}$-butanol (3.0 g) at $\underline{ca}$. 70°. The reaction mixture was worked up after 12 hours as explained above to give tetradeuteriobenzobarrelene (3-59).
(770 mg, 91.2%), m.p. 65-66° (from ethanol), deuterium incorporation in the molecule was : d_o, 9.8%; d_1, 14.61; d_2, 29.22; d_3, 27.45; and d_4, 18.80 mole percent.

15. Preparation of 1,3,5-Trimethylbenzobarrelene[1,4-dihydro-1,3,9-trimethyl-1,4-ethenonaphthalene] (3-40):

A solution of 1,3,5-trimethyltetrachlorobenzobarrelene (2-48) (10.0 g, 30.0 mmole) in tetrahydrofuran (50 ml) was dechlorinated using sodium metal (11.0 g, 460 mmole) in tetrahydrofuran (400 ml) at $\underline{ca}$. 70°. The reaction mixture on work up as explained in experiment no. 1 gave 1,3,5-trimethylbenzobarrelene (3-40):

(5.70 g, 97%), m.p. 85-86° (from ethanol)

(Found: C, 92.0; H, 7.9%; $C_{15}H_{16}$ requires C, 92.0; H, 8.0%)

M^+ (Mass spectrometry): 196.

^{1}H n.m.r. τ(CDCl$_3$): 2.71-2.98 (m, 2H); 3.0-3.25 (m, 2H); 3.97 (m, 2H);

5.84 (m, 1H); 8.09 (s, 3H); 8.12 (s, 3H); and 8.14 (s, 3H).

ν_{max}^{KBr}: 3050, 2980, 2970, 2940, 2915, 2890, 2860, 1455, 1445, 1380, 1308,

1275, 1265, 1192, 1110, 1025, 840, 815, 755, 748, 730, and 650 cm.$^{-1}$

16. Preparation of 1-<u>t</u>-Butylbenzobarrelene [1,4-dihydro-1-<u>t</u>-butyl-1,4-

ethenonaphthalene] (3-41):

A solution of 1-<u>t</u>-butyltetrachlorobenzobarrelene (2-50) (2.5 g,

7.2 mmole) in tetrahydrofuran (25 ml) was dechlorinated using sodium

metal (3.0 g) in tetrahydrofuran (100 ml) at <u>ca</u>. 70°. The reaction

mixture was worked up on completion as explained earlier to give 1-<u>t</u>-

butylbenzobarrelene (3-41):

(1.4 g, 93%), m.p. 60-61° (from ethanol)

M$^+$ (Mass spectrometry): 210.

^{1}H n.m.r. τ(CDCl$_3$): 2.5-2.92 (m, 4H); 2.98-3.26 (m, 4); 4.56-4.82 (m,

1H); 8.48 (s, 6H); and 8.94 (s, 3H).

ν_{max}^{KBr}: 3065, 3025, 2968, 2935, 2905, 2870, 1603, 1496, 1462, 1448, 1392,

1365, 1315, 1268, 1252, 1160, 1115, 1030, 995, 905, 835, 825, 785,

765, 738, 718, 698, and 652 cm.$^{-1}$

17. Preparation of 2-<u>t</u>-Butylbenzobarrelene [1,4-dihydro-2-<u>t</u>-butyl-1,4-

ethenonaphthalene] (3-42):

A solution of 2-<u>t</u>-butyltetrachlorobenzobarrelene (2-49) (7.5 g,

21.6 mmole) in tetrahydrofuran (50 ml) was dechlorinated using sodium

metal (8.5 g, 350 mmole) in tetrahydrofuran (300 ml) at <u>ca</u>. 70° by the

usual method as explained above to give 2-<u>t</u>-butylbenzobarrelene (3-42):

(4.25 g, 94%),b.p. 105-106/0.2 m.m. Hg.

(Found: C, 91.7; H, 8.5%; C$_{16}$H$_{18}$ requires C, 91.43; H, 8.57%).

M$^+$ (Mass spectrometry): 210.

^{1}H n.m.r. τ(CDCl$_3$): 2.42-2.88 (m, 4H); 2.92-3.32 (m, H); 3.66 (dd, 1H,

$\underline{J}$ = 6.2 Hz; $\underline{J}$ = 2.2 Hz); 4.55-4.82 (m, 2H); and 8.68 (s, 9H).

ν_{max}^{oil}: 3085, 3035, 2980, 2945, 2920, 2885, 1635, 1603, 1470, 1398, 1370, 1325, 1258, 1225, 1152, 1110, 1060, 1030, 960, 915, 855, 835, 803, 760, 725, and 660 cm.$^{-1}$

18.   Preparation of 1,3,5-Tri-$\underline{t}$-butylbenzobarrelene [1,4-dihydro-1,3,9-tri-$\underline{t}$-butyl-1,4-ethanonaphthalene] (3-43):

A solution of 1,3,5-tri-$\underline{t}$-butyltetrachlorobenzobarrelene (2-51) (10.0 g, 21.74 mmole) in tetrahydrofuran (50 ml) was dechlorinated using sodium metal (11.0 g, 460 mmole) in tetrahydrofuran (400 ml) at $\underline{ca}$. 70°. The reaction was completed and worked up as explained in experiment no. 1 to give 1,3,5-tri-$\underline{t}$-butylbenzobarrelene (3-43):

(6.80 g, 97%), m.p. 139-140° (from ethanol).

(Found: C, 89.4; H, 10.2%; $C_{24}H_{34}$ requires, C, 89.4; H, 10.5 %);

M^{+} (Mass spectrometry): 322.

^{1}H n.m.r. $^{\tau}$(CDCl$_{3}$): 2.41-2.62 (m, 1H); 2.78-2.96 (m, 1H); 3.06-3.28 (m, 2H); 3.72 (d, 2H, $\underline{J}$ = 2.2 Hz); 5.26 (m, 1H); 8.48 (s, 6H); 8.73 (s, 3H); and 8.95 (s, 18H).

ν_{max}^{KBr}: 3085, 3015, 2965, 2915, 2875, 1598, 1465, 1455, 1392, 1364, 1308, 1283, 1235, 1203, 1135, 1065, 1025, 958, 922, 840, 788, 752, 740, 678, and 625 cm.$^{-1}$

19.   Catalytic hydrogenation of 1,3,5-Tri-t-butylbenzobarrelene (3-43):

A suspension of palladised charcoal (10%, 20 mg) in a solution of 1,3,5-tri-$\underline{t}$-butylbenzobarrelene (3.43) (1.0 g, 3.105 mmole) in ethyl alcohol (50 ml) and ethyl acetate (10 ml) was stirred at room temperature under a positive pressure of hydrogen for 12 h. The catalyst was removed by filtration and the filtrate was evaporated under reduced pressure. The residual material was purified by column chromatography (alumina, light petroleum 40-60°) to give 1,2,3,4-tetrahydro-1,3,9-tri-$\underline{t}$-butyl-1,4-

-ethenonaphthalene (3-43[1]):

(1.0 g, 99%); m.p. 75-76° (from ethanol).

(Found: C, 89.4; H, 11.4%; $C_{24}H_{36}$ requires, C, 88.9; H, 11.1%).

M^{+} (Mass spectrometry): 324.

[1]H n.m.r. τ(CDCl$_3$): 2.38-2.55 (m, 1H); 2.78-3.15 (m, 3H); 3.85 (d, 1H, $\underline{J}$ = 2.2 Hz); 6.16 (s, broad hump, 1H) 8.25-8.74 (m, 3H); 8.58 (s, 6H); 8.78 (s, 3H); 8.98 (s, 9H); 9.14 (s, 9H).

ν_{max}^{KBr}: 3110, 3075, 2970, 2915, 2880, 1480, 1465, 1395, 1368, 1320, 1232, 1198, 1148, 1120, 1065, 1025, 937, 875, 862, 830, 755, 736, and 685 cm.$^{-1}$

20.   Preparation of 1-$\underline{N}$,$\underline{N}$-Dimethylaminobenzobarrelene[1,4-dihydro-1-$\underline{N}$,$\underline{N}$-dimethylamino-1,4-ethenoanphthalene] (3-44):

A suspension of 1-$\underline{N}$,$\underline{N}$-dimethylaminotetrachlorobenzobarrelene (10.0 g, 20.0 mmole) in tetrahydrofuran (50 ml) was dechlorinated by the usual method using sodium metal (11.0 g, 460 mmole) in tetrahydrofuran (400 ml) at $\underline{ca}$. 70° to give 1-$\underline{N}$,$\underline{N}$-dimethylaminobenzobarrelene (3-44):

(5.12 g, 87%), m.p. 68-69° (from ethanol)

M^{+} (Mass spectrometry): 197.

[1]H n.m.r. τ(CDCl$_3$): 2.52-2.96 (m, 4H); 3.12-3.5 (m, 4H); 5.51 (s, 1H); and 7.02 (s, 6H).

ν_{max}^{KBr}: 3090, 3065, 3035, 2960, 2930, 2870, 2860, 2820, 1600, 1505, 1455, 1372, 1355, 1295, 1248, 1215, 1192, 1160, 1118, 1075, 1030, 990, 945, 862, 750, 730, and 692 cm.$^{-1}$

21.   Preparation of Benzonorbornadiene[1,4-dihydro-1,4-methanonaphthalene] (3-67):

A solution of tetrachlorobenzonorbornadiene (2-36) (1.2 g, 4.29 mmole) in tetrahydrofuran (30 ml) was dechlorinated by the usual method using sodium metal (1.5 g, 63.0 mmole) in tetrahydrofuran (60 ml) containing $\underline{t}$-butanol (4.0 g) at $\underline{ca}$. 70° to give benzonorbornadiene (3-67).

(0.51 g, 83%), m.p. 82-83° (from ethanol) (lit.[16] m.p. 82.5-83°).

The spectral data agreed with those previously reported.

22. Preparation of 9,9-Dimethoxybenzonorbornadiene[1,4-dihydro-9,9-dimethoxy-1,4-methanonaphthalene] (3-69):

A solution of 9,9-dimethoxyoctachlorobenzonorbornadiene (2-44) (4.78 g, 10.0 mmole) in tetrahydrofuran (30 ml) was dechlorinated by the usual method using sodium metal (7.5 g, 314 mmole) in tetrahydrofuran (150 ml) containing t-butanol (21.0 g) at ca. 70° to give 9,9-dimethoxy-benzonorbornadiene (3-69):

(1.34 g, 66%), m.p. 42-44°C (from ethanol) (lit.[80] m.p. 45-46°).

Spectral data agreed with those previously reported, and 1,2,3,4-tetra-hydro-9,9-dimethoxy-1,4-methanonaphthalene (3-69[1]):

(0.24 g, 12%), m.p. 48-50° (from ligroin 40-60°) (lit.[80] m.p. 54-55°).

Spectral data agreed with those reported previously.

23. Preparation of 7-Isopropylidenebenzonorbornadiene[1,4-dihydro-9-isopropylidene-1,4-methanonaphthalene] (3-68).

A solution of 7-isopropylidenetetrachlorobenzonorbornadiene (2-38) (10.0 g, 31.25 mmole) in tetrahydrofuran (50 ml) was added to a suspension of sodium metal (11.0 g, 460 mmole) in tetrahydrofuran (350 ml) containing t-butanol (33.0 g) at ca. 70° by the usual method as explained earlier. The reaction mixture was worked up as in experiment no. 1 to give 7-iso-propylidenebenzonorbornadiene (3-68).

(5.3 g, 93%), m.p. 91-92° (from ethanol) (lit.[79] 94°).

Spectral data agreed with those previously reported.

24. Preparation of 1,4-Dihydro-1,4-epoxynaphthalene (3-61).

A solution of 1,4-dihydro-tetrachloroepoxynaphthalene (2-40) (7.5 g, 26.60 mole) in tetrahydrofuran (40 ml) was dechlorinated by the usual method using sodium metal (8.5 g, 355 mmole) in tetrahydrofuran (300 ml),

containing t-butanol (22.5 g) at ca. 70°. The reaction mixture on work up
gave a mixture of products, which were separated by column chromatography,
to give: (i) 1,4-dihydro-1,4-epoxynaphthalene (3-61):

(1.55 g, 40%), b.p. 78-80°/4 m.m. (lit.[78] m.p. 49-51°)

Spectral data agreed with those previously reported.

(ii) 1,2,3,4-tetrahydro-1,4-epoxynaphthalene (3-62):

(1.81 g, 47%), b.p. 80-82°/4 m.m. (lit.[78] m.p. 55-56°).

Spectral data agreed with those previously reported.

25. Preparation of 1,4-Dihydro-1,4-N-methyliminonaphthalene (3-63):

A solution of 1,4-dihydro-1,4-N-methyliminotetrachloronaphthalene
(2-41) (6.0 g, 20.34 mmole) was dechlorinated by the usual method using
sodium metal (6.6 g, 276 mmole) and t-butanol (18.9 g) in tetrahydro-
furan (400 ml) at ca. 70°. The reaction mixture on work up gave a mixture
of products which were separated by column chromatography to give

(i) 1,4-dihydro-1,4-N-methyliminonaphthalene (3-63):

(1.25 g, 38%), b.p. 157-58° (lit.[76] b.p. 157-58°).

Spectral data agreed with those previously reported.

(ii) 1,2,3,4-tetrahydro-1,4-N-methyliminonaphthalene (3-64):

(1.6 g, 50%), b.p. 135-36°/4mm. (lit.[76] b.p. 135-36°/4mm.).
with
Spectral data agreed/those previously reported.

26. Preparation of 1,4-Dihydro-1,4,9-trimethyliminonaphthalene (3-65):

A solution of 1,4,9-trimethyliminotetrachloronaphthalene (2-42)
(6.0 g, 18.58 mmole) in tetrahydrofuran (50 ml) was dechlorinated by
using sodium metal (6.6 g, 276 mmole) in tetrahydrofuran (300 ml)
containing t-butanol (20 g) at ca. 70°. The reaction mixture on work
up gave a mixture of products which were separated by column chromatography
to give (i) 1,4-dihydro-1,4,9-trimethyliminonaphthalene (3-65):

(1.25 g, 35%), m.p. 45-46° (lit.[75] m.p. 47-48°).

Spectral data agreed with those previously reported.

(ii) 1,2,3,4-tetrahydro-1,4,9-trimethyliminonaphthalene (3-66):

(1.64 g, 47%), m.p. 41-42° (lit.[75] m.p. 42-43°).

Spectral data agree with those previously reported.

27. Preparation of 2,2-Ethylenedioxy-1-methoxybenzobarrelene[1,4-dihydro-1-methoxy-2,2'(1H)-Spiro[1,3]dioxolane-1,4-ethenonaphthalene] (3-45):

A solution of 2,2-ethylenedioxy-1-methoxytetrachlorobenzobarrelene (2-55) [4.0 g, 10.47 mmole] in tetrahydrofuran (20 ml) was subjected to dechlorination by the usual method as explained in experiment no. 1. The crude product on purification gave: 2,2-ethylenedioxy-1-methoxybenzobarrelene (3-45):

(2.4 g, 96%), m.p. 120-21° (from ethanol).

(Found: C, 74.3; H, 6.6%; $C_{15}H_{16}O_3$ requires, C, 73.75; H, 6.60%).

M^+ (Mass spectrometry): 158 (86 loss).

^1H n.m.r. τ(CDCl$_3$): 2.42-2.92 (m, 4H); 3.02-3.51 (m, 2H); 5.45-6.25 (m, 5H); 6.38 (s, 3H); and 7.81-8.42 (m, 2H).

ν_{max}^{KBr}: 3080, 3025, 3003, 2990, 2958, 2910, 2850, 1615, 1465, 1362, 1321, 1265, 1244, 1172, 1130, 1085, 1052, 1040, 1025, 1010, 965, 925, 875, 795, 780, 735, and 698 cm.$^{-1}$

28. Preparation of 2,2-Ethylenedioxy-6-methyl-1-methoxybenzobarrelene [1,4-dihydro-1-methoxy-10-methyl-2,2(1H)-Spiro[1,3]dioxolane-1,4-ethano-naphthalene] (3-47):

A solution of 2,2-ethylenedioxy-1-methoxytetrachlorobenzobarrelene (2-56) [4.0 g, 10.10 mmole] in tetrahydrofuran (20 ml) was subjected to dechlorination by the usual method as explained in experiment no.1. The crude product on purification gave: 2,2-ethylenedioxy-6-methyl-1-methoxy-benzobarrelene (3-47):

(2.5 g, 96%), m.p. 85-86° (from ethanol).

(Found: C, 74.2; H, 6.9%; $C_{16}H_{18}O_3$ requires C, 74.39; H, 7.02%),

M.$^+$ (Mass spectrometry): 172 (loss 86)

^{1}H n.m.r. τ(CDCl$_3$): 2.38-3.12 (m, 4H); 3.28 (dq, 1H, $\underline{J}$ = 6.2 Hz; $\underline{J}$ = 2.2 Hz);

5.6-5.96 (m, 1H); 5.97-6.42 (m, 4H); 6.12 (s, 3H); 7.46-8.12 (m, 2H);

and 8.32 (d, 3H, $\underline{J}$ = 2.2 Hz).

ν_{max}^{KBr}: 3060, 3030, 2995, 2970, 2930, 2910, 2840, 1622, 1450, 1378, 1362,

1324, 1288, 1249, 1217, 1180, 1140, 1105, 1080, 1050, 954, 875, 820, 780,

748, 715, 685, and 654 cm.$^{-1}$

29. Preparation of 3,3-Ethylenedioxy-1-methoxybenzobarrelene [1,4-dihydro-
-1-methoxy-3,3(1H)-Spiro[1,3]-dioxolane-1,4-ethenonaphthalene] (3-48):

A solution of 3,3-ethylenedioxy-1-methoxytetrachlorobenzobarrelene

(2-57) [8.0 g, 20.94 mmole] in tetrahydrofuran (30 ml) was subjected to

dechlorination by the usual method as explained in experiment no. 1. The

crude product on purification gave: 3,3-ethylenedioxy-1-methoxybenzobarrelene

(3-48):

(4.80 g, 94%) m.p. 124-125° (from ethanol)

(Found: C, 73.4; H, 6.0%; C$_{15}$H$_{16}$O$_3$ requires C, 73.75; H, 6.60%).

M.$^+$ (Mass spectrometry): 158 (loss 86).

^{1}H n.m.r. τ(CDCl$_3$): 2.45-3.02 (m, 4H); 3.12-3.56 (m, 2H); 5.85-6.16

(m, 4H); 6.11-6.24 (m, 1H); 6.32 (s, 3H); 7.70 (d, 1H, $\underline{J}$ = 15 Hz);

and 8.17 (d, 1H, $\underline{J}$ = 15 Hz).

ν_{max}^{KBr}: 3080, 3035, 2995, 2958, 2905, 2850, 1615, 1473, 1358, 1325, 1265, 1248,

1222, 1174, 1138, 1102, 1075, 1055, 1022, 970, 958, 888, 855, 770, 735, 695,

and 675 cm.$^{-1}$

30. Preparation of 3,3-Ethylenedioxy-5-methyl-1-methoxybenzobarrelene [1,4-
dihydro-1-methoxy-9-methyl-3,3'-(1H)-Spiro[1,3]dioxolane-1,4-ethenonaphthalene
(3-49):

A solution of 3,3-ethylenedioxy-5-methyl-1-methoxytetrachlorobenzo-

barrelene (2-58) [8.0 g, 20.20 mmole] in tetrahydrofuran (30 ml) was subjected

to dechlorination by the method as explained in experiment no.1. The crude product on purification gave: 3,3-ethylenedioxy-5-methyl-1-methoxy-benzobarrelene (3-49):

(5.11 g, 98%) m.p. 118-20° (from ethanol).

(Found: C, 74.3; H, 6.9%; $C_{16}H_{18}O_3$ requires C, 74.42; H, 6.97%).

$M.^+$ (Mass spectrometry): 172 (loss 86).

^1H n.m.r. $\tau(CDCl_3)$: 2.2-2.45 (m, 1H); 2.45-3.05 (m, 3H); 3.65-3.85 (m, 1H); 5.91 (d, 1H, $\underline{J}$ = 2.2 Hz); 5.99-6.32 (m, 4H); 6.49 (s, 3H); 7.85 (q, 2H, $\underline{J}$ = 15 Hz); 8.13 (d, 3H, $\underline{J}$ = 2.2 Hz).

ν_{max}^{KBr}: 3070, 3050, 2980, 2950, 2910, 2890, 2840, 1460, 1445, 1375, 1332, 1318, 1260, 1208, 1172, 1110, 1095, 1048, 1022, 948, 908, 875, 855, 798, 760, and 648 cm.$^{-1}$

31. Preparation of 2,2-Ethylenedioxy-1,3-dimethylbenzobarrelene[1,4-dihydro-1,3-dimethyl-2,2(1H)-Spiro[1,3]dioxolane-1,4-ethenonaphthalene] (3-81):

A solution of 2,2-ethylenedioxy-1,3-dimethyltetrachlorobenzobarrelene(2-[2.0 g, 5.26 mmole] in tetrahydrofuran (20 ml) was subjected to dechlorination by the usual method as explained in experiment no. 1. The crude product on purification gave: 2,2-ethylenedioxy-1,3-dimethylbenzobarrelene[3-83]:

(1.22 g, 92%), m.p. 142-43° (from ethanol)

$M.^+$ (Mass spectrometry): 142 (loss 99).

^1H n.m.r. $\tau(CDCl_3)$: 2.55-2.95 (m, 4H); 3.31 (t, 1H, $\underline{J}$ = 7.2 Hz); 3.75 (dd, 1H, $\underline{J}$ = 1.6 Hz); 5.85-6.32 (m, 4H); 6.36-6.57 (m, 1H); 7.68-8.12 (m, 1H); 8.38 (s, 3H); and 9.37 (d, 3H, $\underline{J}$ = 7.2 Hz).

ν_{max}^{KBr}: 3060, 3025, 2990, 2975, 2885, 2840, 1620, 1475, 1455, 1375, 1350, 1320, 1290, 1265, 1215, 1190, 1155, 1092, 1070, 1030, 990, 960, 898, 818, 792, 760, 725, 695, and 660 cm.$^{-1}$

32. Preparation of 1,3-Dimethylbenzobarrelen-2-one[1,4-dihydro-1,3-dimethyl-1,4-ethenonaphthalen-2(1H)-one] (3-84):

A solution of the ketal (3-83) [1.0 g, 4.125 mmole] in tetrahydrofuran

132.

(4.0 ml) and hydrochloric acid (2N, 15ml) was stirred at room temperature for 4 h. The reaction mixture on work up gave 1,3-dimethylbenzobarrelen-2-one (3-84) (780 mg, 96%) m.p. 80-81°

^{1}H n.m.r. τ(CDCl$_3$): 2.59-2.94 (m, 4H); 3.24 (t, 1H, $\underline{J}$ = 7.2 Hz);

3.78 (dd, 1H, $\underline{J}$ = 2.2 Hz, $\underline{J}$ = 1.6 Hz); 6.12 (m, 1H); 7.62-7.96 (m, 1H);

8.30 (s, 3H); and 9.24 (d, 3H, $\underline{J}$ = 7.2 Hz).

ν_{max} 3060, 3030, 2980, 2940, 2880, 1728, 1610, 1470, 1455, 1380, 1345, 1310, 1280, 1255, 1210, 1185, 1155, 1145, 1090, 1065, 1045, 1028, 980, 960, 895, 810, 770, 752, 695, and 660 cm.$^{-1}$

33. Preparation of 2,2-Ethylenedioxy-1,5-dimethylbenzobarrelene[1,4-dihydro-1,9-dimethyl-2,2(1H)-Spiro[1,3]dioxolane-1,4-ethenonaphthalene] (3-81):

A solution of 2,2-ethylenedioxy-1,5-dimethyltetrachlorobenzo-barrelene (2- 59) [2.0 g,526 mmole] in tetrahydrofuran (80 ml) was subjected to dechlorination by the usual method as explained in experiment no.1. The crude product on purification gave:

2,2-ethylenedioxy-1,5-dimethylbenzobarrelene (3-81):

(1.05 g, 84%) m.p. 111-112° (from ethanol) (Found: C, 79.7; H, 7.4%; C$_{16}$H$_{18}$O$_2$ requires C, 79.3; H, 7.43%).

[M$^+$ -86] (Mass spectrometry): 156.

^{1}H n.m.r. τ (CDCl$_3$). 2.6-3.05 (m, 4H); 4.02-4.22 (m, 1H); 5.81-6.3 (m, 4H);

6.43 (dq, 1H, $\underline{J}$ = 6.2 Hz; J = 2.2 Hz), 7.85-8.6 (m, 2H); 8.1 (d, 3H,

J = 1.6 Hz), 8.4 (s, 3H).

ν_{max} KBr. 3015, 2970, 2940, 2880, 1480, 1460, 1435, 1380, 1340, 1310, 1270, 1160, 1115, 1090, 1060, 1030, 950, 895, 850, 807, 760, and 745 cm^{-1}.

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CHAPTER FOUR

The Acid-Catalysed Rearrangements of some Methyl-Substituted 1-Methoxybenzo-barrelenes.

Introduction:

Despite extensive investigations of reactions of benzobarrelenes which involve carbonium ions and their rearrangements,[1] it has not been possible to define precisely the character of the solvolytic transition states or the structures of all of the product-forming intermediates.[2] Recent studies have been concerned with structurally rigid precursors of various designs and the mechanisms of the rearrangements of 1-methoxybenzobarrelenes.[3] The structures of the products may be understood as a consequence of a number of shifts within the C̲-protonated molecules. Each shift produces presumably a more stable carbo-cation and eventually the result is the formation of an oxonium salt. The stabilization of the carbo-cation by the oxygen leads to the corresponding ketones.[4] It is possible that demethylation of a methoxonium salt is the final step in certain of the reactions.

The effect on the rearrangements of alkyl substitution is considerable.[5] Extensive alkylation stabilizes the carbocations to such an extent that equilibrium mixture(s) of products may be formed from rapidly interconverting cations. Hart and his co-workers[6] have successfully shown that the related ketone (4-1) can be equilibrated in an acidic medium with three isomeric ketones [(4-2), (4-3), and (4-4)]. Presumably the relatively similar energies of the carbocations is the result of the presence of a large number of alkyl groups [Scheme 4-1].

[4 - 1]

[4 - 2]

[4 - 3]

[4 - 4]
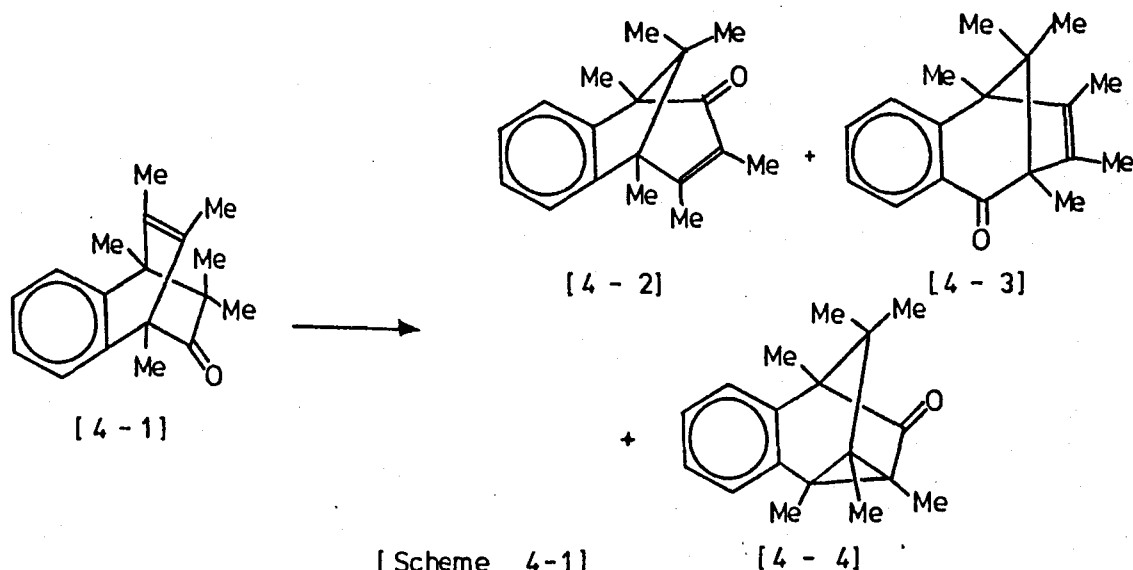
[Scheme 4-1]

Earlier attempts to study some of the aspects of the rearrangements using less extensively methylated 1-methoxytetrafluorobenzobarrelenes could answer only a few questions.[1,7] It seemed reasonable that sulphuric acid could protonate one of the double bonds and that the methoxy-group would direct the rearrangement. Rearrangements of this type are well known in simpler systems.[2] The primary rearrangement products are, in some cases, subject to secondary reactions under the acidic conditions required for the protonation, although under milder conditions the reactions can be monitored and stopped after primary rearrangement. Alkyl substitution not only enhances the reactivity of the benzobarrelenes, but also increases the lability of the products.[8]

Earlier investigations[2,9] involving acid-catalysed rearrangement reactions of 1-methoxybenzobarrelenes have been shown to yield, in general, three isomeric ketones [e.g. (4-5) ⟶ (4-6), and (4-8)] [Scheme 4-2]. The product ratio of these isomeric ketones appeared to be dependent upon the reaction medium and the temperature. The reactions are extremely rapid in strong acids and a number of mechanistic pathways operate, thus making any kinetic measurements difficult. The mechanisms of these transformations have been investigated using deuteriated solvents,[10] [²H]labelled derivatives of 1-methoxybenzobarrelenes,[1] solvolytic reactions of certain tosylates,[11] attempted equilibration experiments,[3] and [¹⁴C]labelling experiments.[12]

$X_4 = F_4$ (4-5)	(4-6)	(4-7)	(4-8)
$X_4 = Cl_4$ (4-9)	(4-10)	(4-11)	(4-12)
$X_4 = H_4$ (4-13)	(4-14)	(4-15)	(4-16)

[Scheme 4-2]

141.
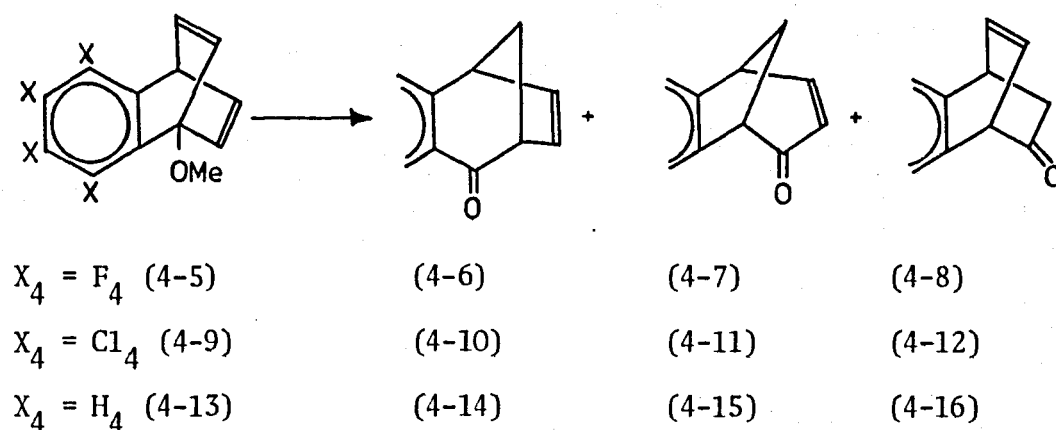
The results of these studies show that the olefinic double bond of the benzobarrelene system can be easily protonated in a strongly acidic medium giving rise to a carbocation either at position (C-2) or (C-3). Protonation at (C-3) leads to the formation of the aryl ketones [(4-6), (4-10) or (4-14)] and the αβ-unsaturated ketones [(4-7), (4-11) or (4-15)], in which the former products result from [1,2]alkenyl shifts, whereas the latter products arise from [1,2]aryl shifts.[1,3] The stability of this carbocation presumably depends upon the substitution pattern although no evidence of any direct intervention has been found [Scheme 4-3].

$X_4 = F_4$ [4-6]
$X_4 = Cl_4$ [4-10]
$X_4 = H_4$ [4-14]

$X_4 = F_4$ [4-5]
$X_4 = Cl_4$ [4-9]
$X_4 = H_4$ [4-13]

$X_4 = F_4$ [4-7]
$X_4 = Cl_4$ [4-11]
$X_4 = H_4$ [4-15]
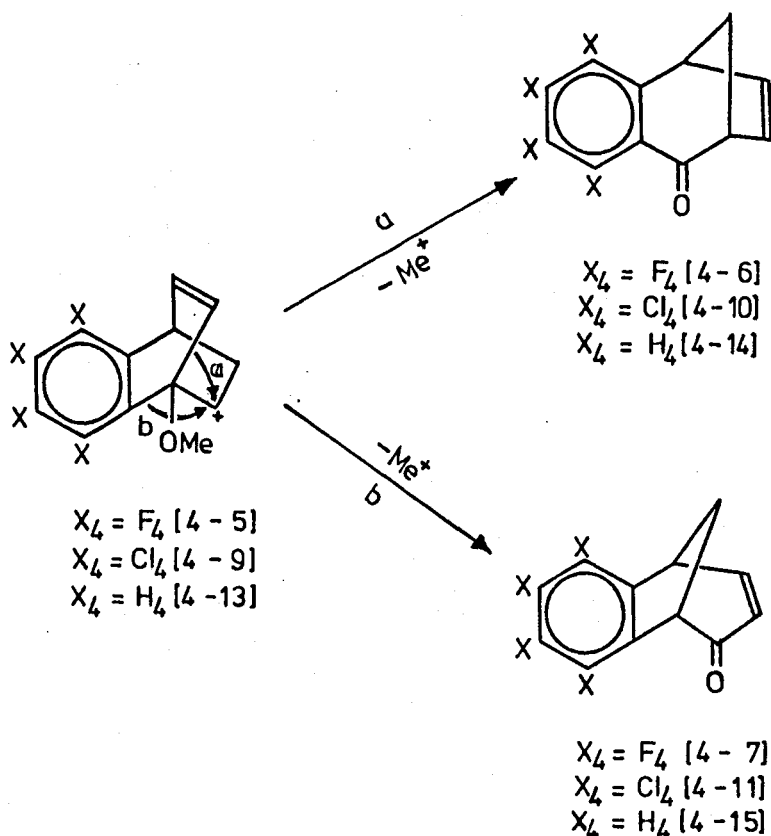
[Scheme 4-3]

Further evidence was obtained from the solvolysis of the 2-exo-tosylate (4-17) and the 2-endo-tosylate (4-18): each tosylate produces only one product [(4-6) and (4-7)] respectively in acidic media.[13]

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The stereospecificity suggests that the reaction is either ·concerted [equation 4-1] or possibly involves a bridged ion (A) whose breakdown is governed by the methoxy-group [equation 4-2].

[4-17]   [4-7]   [4.1]

[4.17] ⟶ [A] ⟶ [4.7] [4.2]·
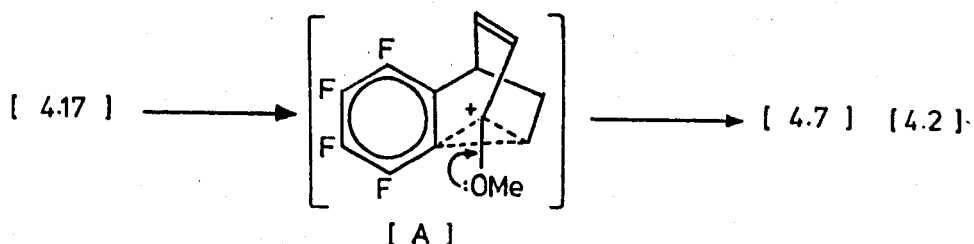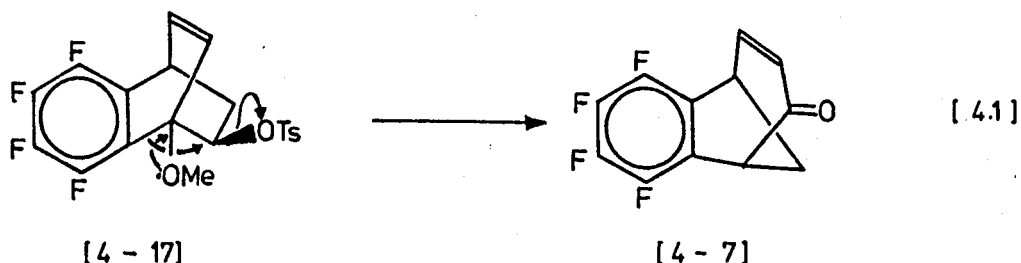
A study of the solvolysis of the 2-endo-tosylate (4-18) in glacial acetic acid containing acetic anhydride and sodium acetate led to the formation of the vinyl ketone (4-6) in 92% yield [equation 4-3].

[4-18]   [4-6]   [4.3]
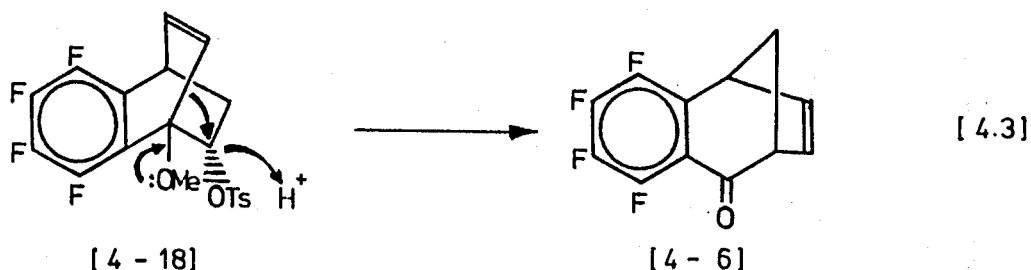
The precise nature of the intermediates which lead to the formation of the aryl ketones [(4-6), (4-10) or (4-14)] or the αβ-unsaturated ketones

[(4-7), (4-11), or (4-15)] is still unknown.

In the solvolysis of the 2-endo-tosylate (4-18) one might expect some anchimeric assistance from the other double bond to form a bridged ion (B), which by the analogy to Tanida's[14] work could be solvolysed to give the tricyclic-derivative (4-19), but, as expected, this was not observed in our systems [equation 4-4].

[4 - 18]   [B]

[4 - 6]   [4.4]
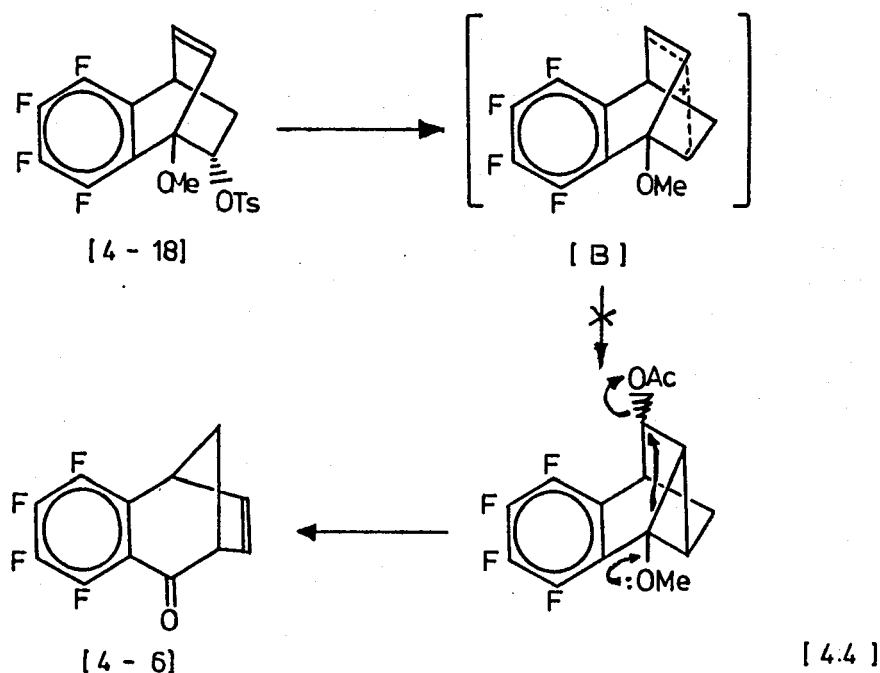
Protonation at (C-2) results in the formation of the benzobarrelenones-[(4-8), (4-12) or (4-16)] as shown in Scheme 4-4.

The nature of the rearrangement evidently involves complex pathways and is not fully understood. Deuterium labelling studies have established that the initial rearrangement is from the carbocation at (C-3). These experiments further indicate that at least two distinct pathways lead to the formation of the benzobarrelenones [(4-8), (4-12), or (4-16)] and the ratio of these isomers varied depending on the strength of the

$X_4 = F_4$ [4 - 8]
$X_4 = Cl_4$ [4 -12]
$X_4 = H_4$ [4 -16]
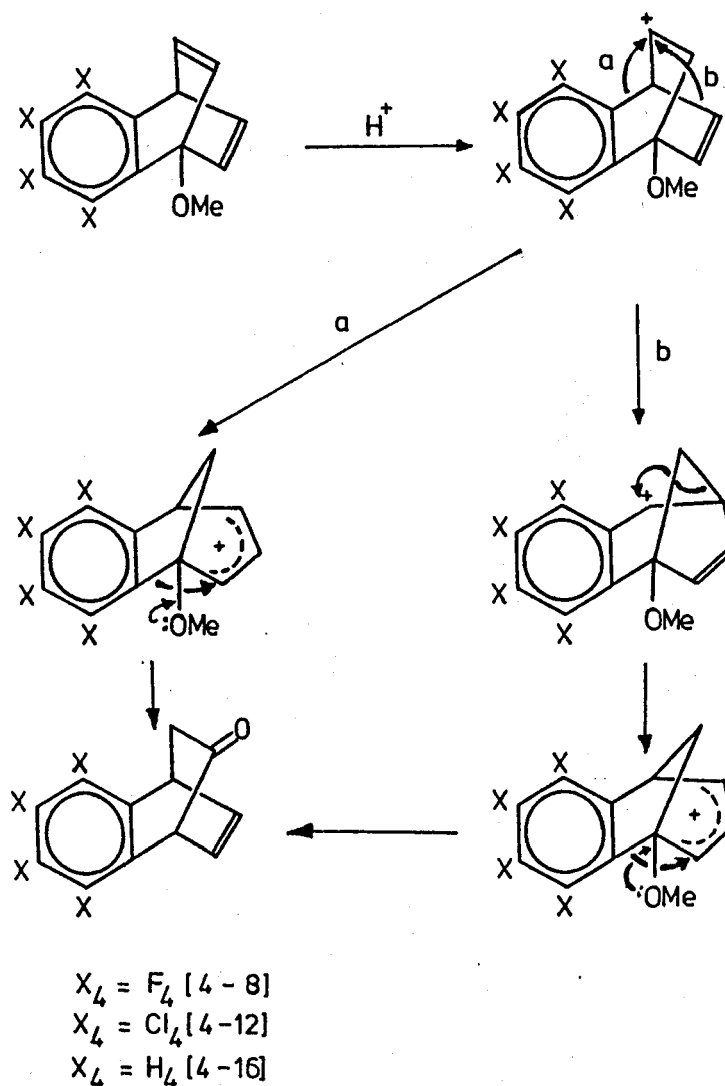
[Scheme 4-4]

protonating media. A significant feature of these rearrangements is that (C-1) of the 1-methoxybenzobarrelenes becomes the (C-2) of the benzobarrelenone systems.

Two other proposals were put forward by other groups of workers and may be easily discarded on a variety of grounds.

Barkhash and his co-workers[15] in their studies suggested a mechanism involving ionization by loss of an O-protonated methoxy-group,

145.

followed by solvolysis of an anti-Bredt allyl cation, which in turn followed by protonation and finally hydride shift to give a benzobarrelenone (4-8) [Scheme 4-5]:
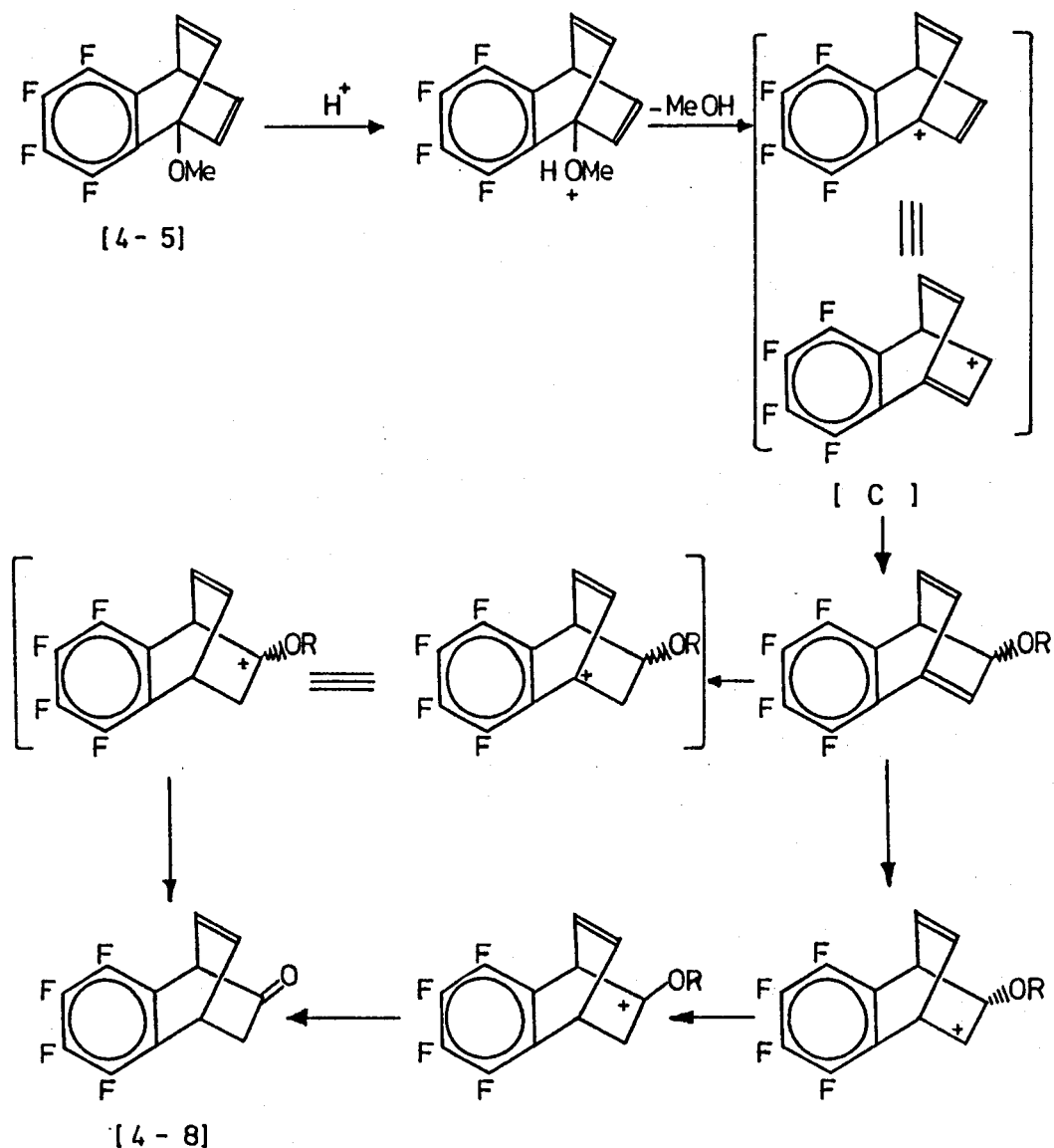
[Scheme 4-5]

In this case the protonation of the methoxy group followed by loss of methanol to give bridgehead cation would be expected to be a slow process,

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giving rise to a highly energetic carbocation[C] at the bridgehead position. The nature of such hot cations is still not fully understood. This mechanism was excluded on the basis of deuterium labelling studies.

In the other proposal,[16] the mechanism is analogous to the rearrangements of epoxides and acyclic ketones. The key step would involve a [1,2]-methoxy shift followed by a [1,2]hydride shift [Scheme 4-6].

[Scheme 4-6]

147.
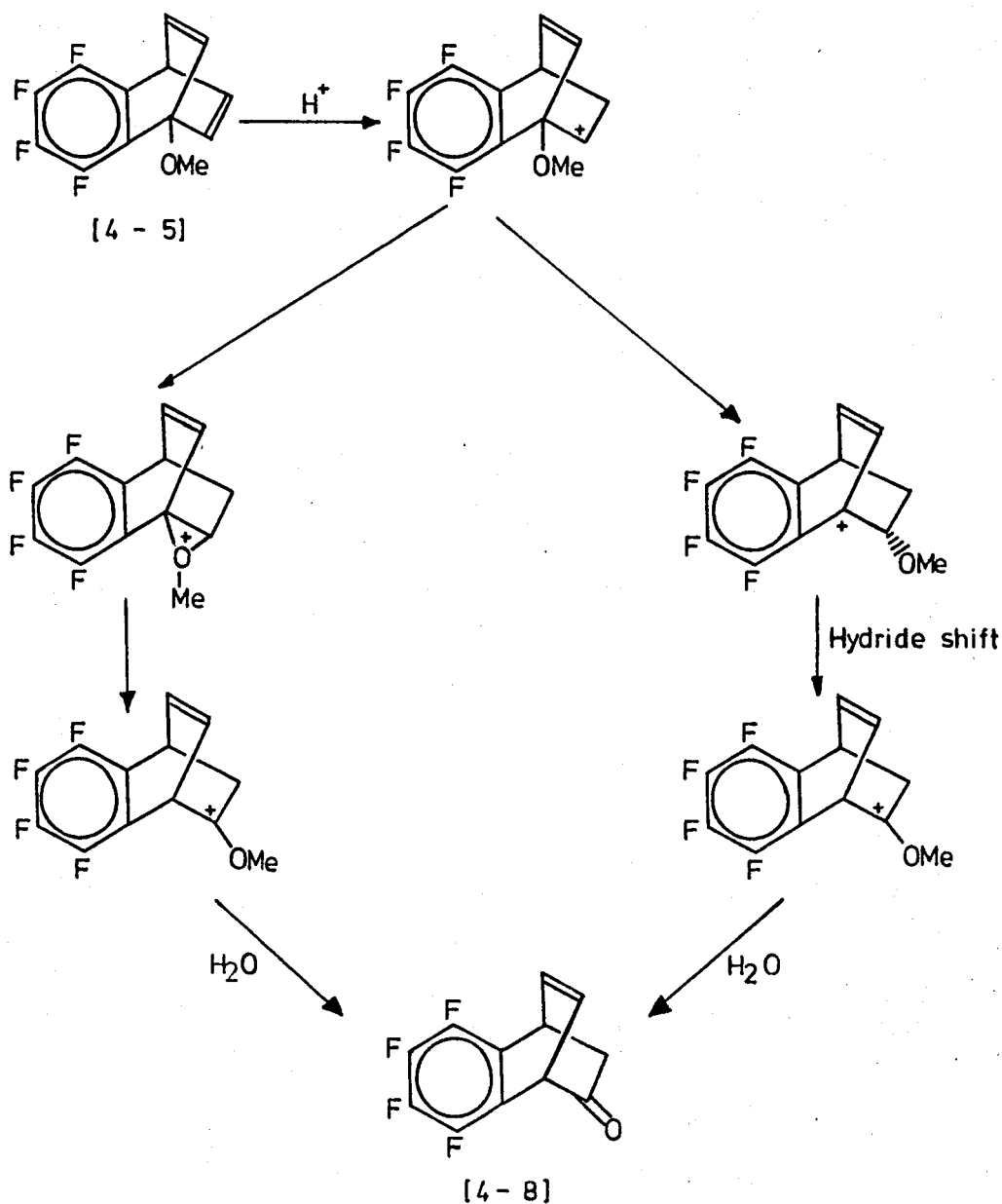
In the latter case, the great angle strain and the unfavourable stereo-electronic factors render this proposal unlikely. Furthermore, the deuterium labelling work also makes this proposal very unlikely.

Benzobarrelenones are usually moderately stable in strong acids. A labilizing factor seems to be the presence of an alkyl substituent on the etheno-bridge. It has been seen in a number of cases that the product determining protonation is directed by one of the alkyl groups,whereas the other methyl groups promote secondary reactions. On the basis of the above discussion the rearrangements of symmetrically substituted 1-methoxybenzobarrelenes appear simple at the first sight, but this is not the case. The reactions are complicated by the additional substitution rather than simplified.

Various examples exist in the literature which help in understanding some of the factors involved in the reaction pattern.[17] A 3-methyl-group helps in the formation of a benzobarrelenone, with retention of a bicyclo-[2.2.2]octane skeleton. On the other hand a 2-methyl group leads to the formation of aryl- and $\alpha\beta$-unsubstituted-ketones, in which the carbon skeleton is changed to that of a bicyclo[3.2.1]octane system.

The principal reason for undertaking the present study was to establish the effect - or hopefully the lack of fundamental effect - of the halogen atoms on the previously studied rearrangement reactions of the tetrahalo-geno-1-methoxybenzobarrelenes.

The present work involves the reactions of 2-methyl-(3-32); 2,3-dimethyl-(2-3) and (3-33); 2,5-dimethyl-(3-34); 2,6-dimethyl-(2-5), (2-8), and (3-36); 3,5-dimethyl-(2-10) and (3-35);2,3,5-trimethyl-(2-12) and (3-37); and 2,3,5,6-tetramethyl-(2-14) and (3-38), substituted 1-methoxybenzobarrelenes. The mechanisms of many of the reactions involving simple substitution patterns are quite clear. On the other hand reactions

of those compounds carrying a number of substituents, which result in secondary rearrangements, are still ambiguous.

Without doubt, in some reactions, sulphonation of the aromatic ring complicates the picture. These reactions are effectively hindered by the halogen substituents. These substituents confer a desirable degree of crystallinity on the products but they may affect the stability of any benzylic carbocations. The tetramethyl-substituted compounds (2-14) and (3-38) compare the two modes of rearrangement within one molecule because of the directing effect of the symmetrically substituted methyl-groups. We describe here a number of synthetically useful rearrangements in which the double bond is in a six-membered ring, but is located in a favourable geometry for interaction with the protonated ketones and which may result in unusual secondary rearrangements in strong acids.

Discussion and Results:

Using the established methods,[1,3] the treatment of 2-methyl-1-methoxybenzobarrelene (3-32) with trifluoroacetic acid at room temperature gave three isomeric ketones, the aryl ketone (4-19), the benzobarrelenone (4-21), and the $\alpha\beta$-unsaturated ketone (4-20). Conducting the reaction in boiling trifluoroacetic acid, all the three expected products were obtained, however, the product ratio was greatly changed. The three products were those expected from previous studies. Their structures were established from spectral data and elemental analyses.

Rearrangement of 2-methyl-1-methoxybenzobarrelene (3-32) in concentrated sulphuric acid gave the same three ketone types, in which the major product was the benzobarrelenone (4-21). When the rearrangement of the compound (3-32) was conducted in fluorosulphuric acid, the yield of the benzobarrelenone (4-21) was comparatively high. The [1]H n.m.r. spectrum analysis of the crude product showed less than 15% of either of the other ketones (4-19) and (4-20). These results show that the chlorine atoms which were present in the previous study[1,3] do not affect the pathways available for rearrangement (Scheme 4-7).

| [3 - 32] | [4 - 19] | [4 - 20] | [4 - 21] |
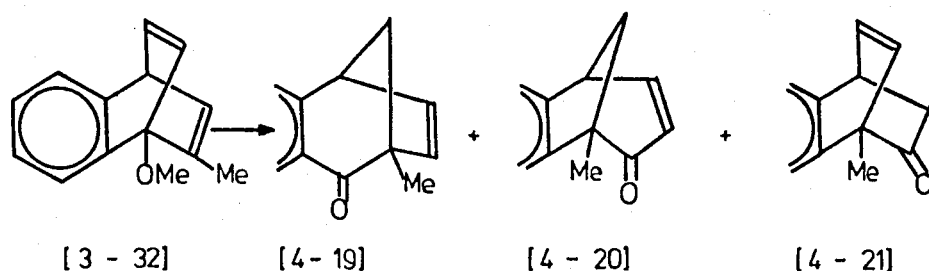
		(Product %)	
(i)	44	26	19
(ii)	4.6	31	19
(iii)	4.3	32	25
(iv)	13	12.7	34

Solvents: (i) CF_3COOH at 20°; (ii) CF_3COOH at 72°; (iii) Conc. H_2SO_4; (iv) $F.SO_3H$ at -70°.

(Scheme 4-7)

The acid-catalysed rearrangements of 2,3-dimethyl-1-methoxytetrachloro-
benzobarrelene (2-3) and its dehalogenated analogue (3-33) similarly showed no
unusual behaviour.

Rearrangement of 2,3-dimethyl-1-methoxytetrachlorobenzobarrelene (2-3)
and its dechlorinated analogue (3-33) in trifluoroacetic acid gave the aryl
ketones[(4-22), (4-28)], a mixture of benzobarrelenones [(4-23), (4-24),
(4-29), and (4-30)] and the $\alpha\beta$-unsaturated ketones [(4-25), (4-31)] [(Scheme
4-8)]. The two benzobarrelenones formed were those which result from
protonation of the tetra-substituted double bond followed by aryl migration.
The other benzobarrelenones [(4-26) and (4-32)] which were expected on the
basis of mechanistic speculations [Scheme 4-9], could not be traced. The
reaction was repeated by heating the compounds (2-3) and (3-33) under
reflux with trifluoroacetic acid and the results were similar except that
the ratios of two pairs of benzobarrelenones [(4-23), (4-24), (4-29), and
(4-30)] were changed.
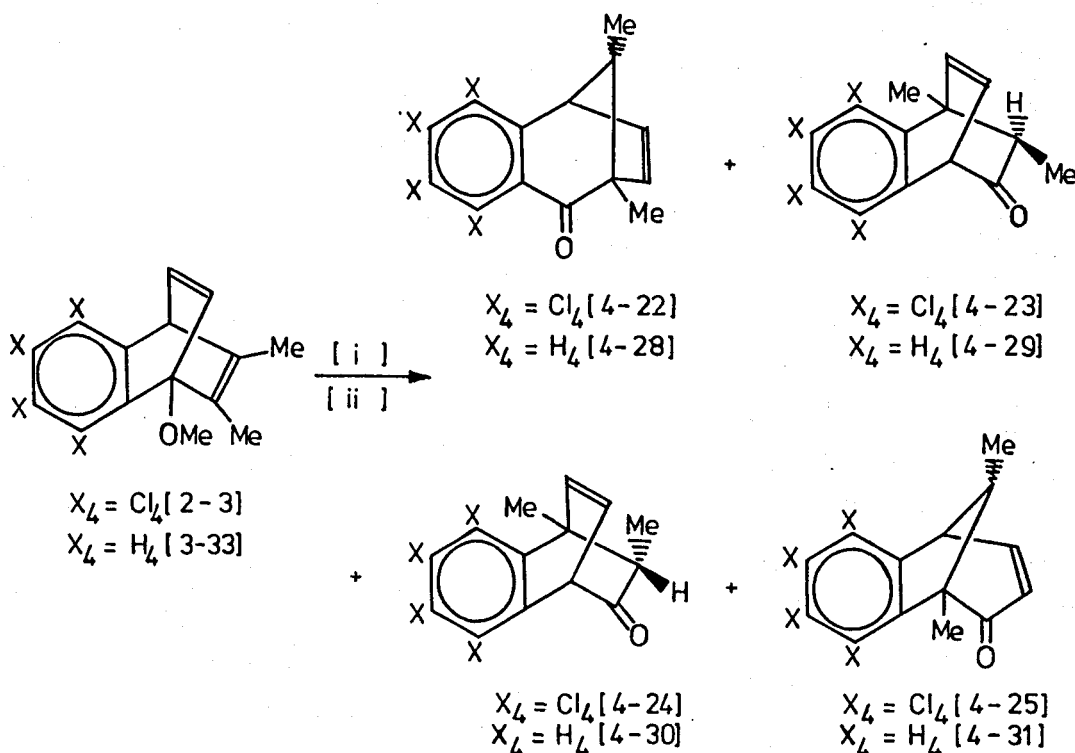
Solvents : [i] CF$_3$COOH ; [ii] Concentrated H$_2$SO$_4$.

[Scheme 4-8]

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The benzobarrelenones are presumably formed as shown in Scheme 4-9.

$X_4 = Cl_4$ [4 - 23]
$X_4 = Cl_4$ [4 - 24]
$X_4 = H_4$ [4 - 29]
$X_4 = H_4$ [4 - 30]

$X_4 = Cl_4$ [4 - 26]
$X_4 = Cl_4$ [4 - 27]
$X_4 = H_4$ [4 - 32]
$X_4 = H_4$ [4 - 33]

[Scheme   4 - 9]

152.
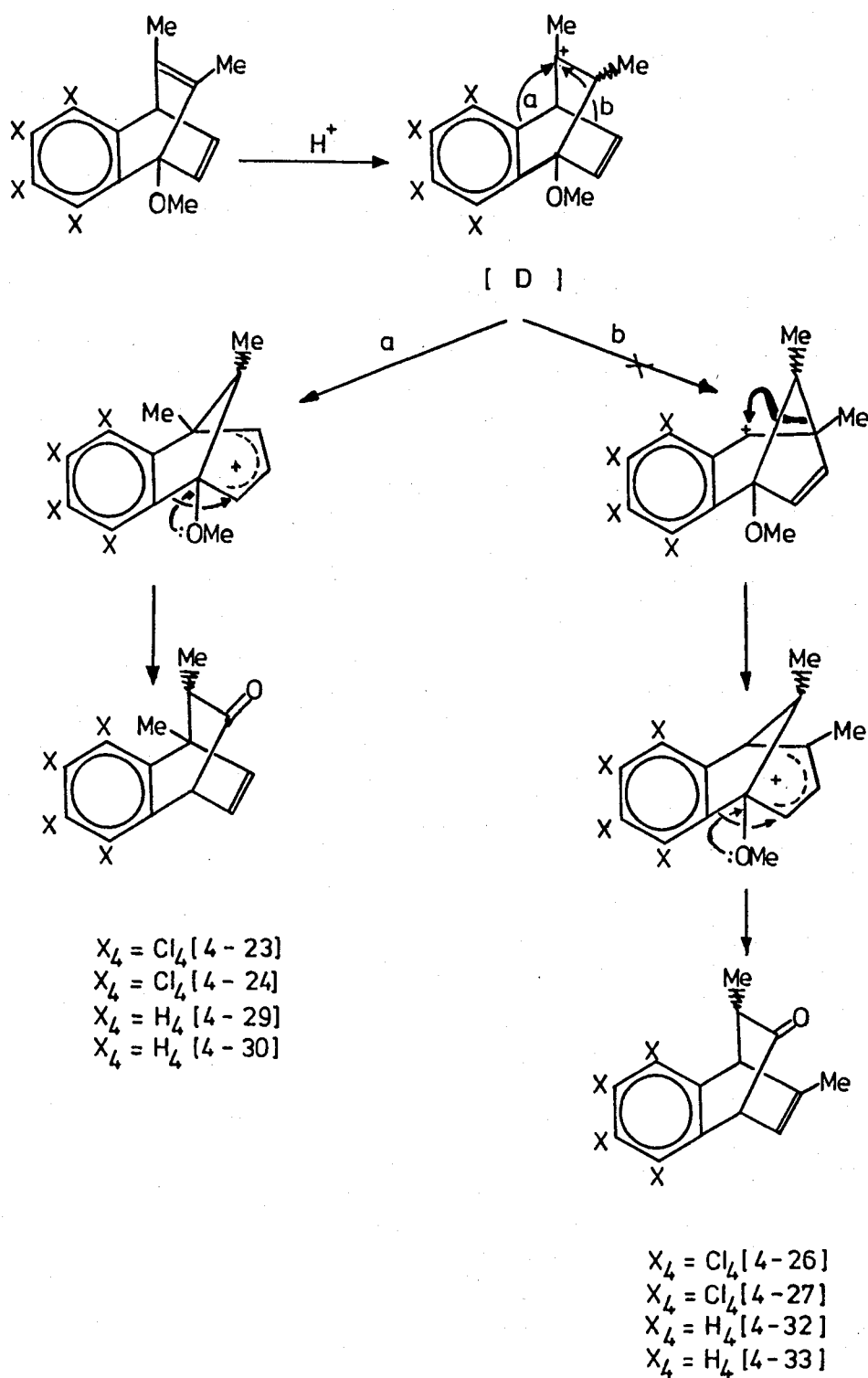
Treatment of 2,3-dimethyl-1-methoxytetrachlorobenzobarrelene (2-3) and its dechlorinated analogue (3-33) with concentrated sulphuric acid each gave the same four products. The crude reaction mixtures showed no trace of any other product in the ^{1}H n.m.r. spectra. However, the ratio of the benzobarrelenones to one another and to the other reaction products was not constant, varying considerably from reaction to reaction.

The stability of αβ-unsaturated ketones [(4-25), (4-31)] and the degradation of both the aryl ketones [(4-22), (4-28)] and the benzobarrelenones [(4-23), (4-24), (4-29), and (4-30)] to multitudinous uncharacterized products in strong acidic medium at longer time periods led us to the conclusion that these products do not undergo equilibration with one another.

The most plausible explanation for the formation of only two benzobarrelenones [(4-23) and (4-24)] instead of four benzobarrelenones from the same carbocation (D) during the solvolysis of the compound (2-3) in trifluoroacetic acid is the formation of an intermediate which then seems to govern the reaction pathway. In the solvolysis reaction, the carbocation (D) seems to undergo trifluoroacetolysis from the exo-face which is then followed by the 1,2-aryl shift (path a) instead of the 1,2-alkenyl shift (path b) giving rise to two benzobarrelenones [(4-23) and (4-24)]. The rate determining step cannot be assessed under the reaction conditions. However, the reaction products strongly suggest that the stereospecificity of these reactions is due to the intermediacy of the trifluoro-acetate (E) [Scheme 4-10].

The exo-endo rate ratio for trifluoroacetates (E) and (F) reveals the dramatic effect exerted by the exo-fused substituent in retarding the ionization rate for the endo-oriented leaving group. The only apparent explanation could be the steric destabilization of the bridged-ion formation, and the approach of the trifluoroacetate ion from the exo-face. It is also clear from the results that endo-attack by the trifluoroacetate ion

is being restricted by the participation of a phenonium ion as explained in Chapter one.

X = Cl, H.
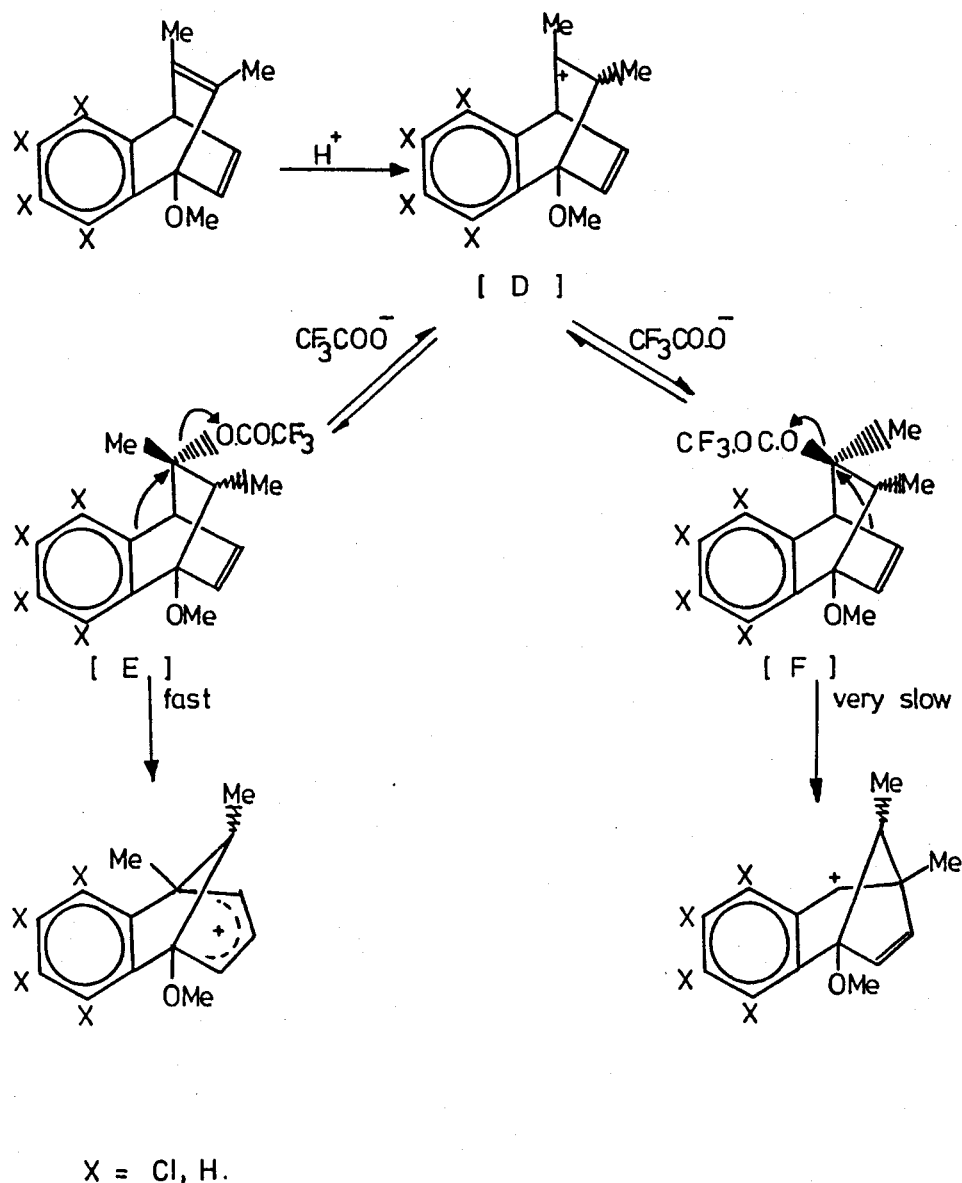
[Scheme 4-10]

This Scheme also recommends that the substitution pattern of the methyl groups help in stabilizing the positive charge either by hyperconjugation or induction or by both, thus enabling the direction of the reaction pathway.

2,6-Dimethyl-1-methoxybenzobarrelene:

The acid-catalysed rearrangement reactions of 2,6-dimethyl-1-methoxy-tetrahalogenobenzobarrelenes are treated as a special case in this thesis because of certain important features which need to be discussed in detail.

Treatment of 2,6-dimethyl-1-methoxytetrafluorobenzobarrelene (2-5) with boiling trifluoroacetic acid for a short period (1 h) gave only two products, the aryl ketone (4-34) (70%) and the αβ-unsaturated ketone (4-35) (24%). No benzobarrelenones could be detected. These results are in agreement with the proposed mechanism for the formation of aryl ketones (4-6, 4-10) and the αβ-unsaturated ketones (4-7, 4-11), from a common intermediate.[2] The protonation is evidently directed by the symmetrically substituted methyl groups [positions C-2 and C-6] to form the cation at C-2.

When the αβ-unsaturated ketone (4-35) was dissolved in concentrated sulphuric acid at room temperature in an attempt to equilibrate the system, only the unchanged starting material was recovered. Similarly in boiling trifluoroacetic acid the only product recovered even after 72 h was the unchanged starting material. However, when the aryl ketone (4-34) was heated under reflux with trifluoroacetic acid (24 h), the isomer with an exocyclic-methylene group (4-40) was obtained together with an unchanged aryl ketone (4-34) in a ratio of 1:1. That these ketones are present as an equilibrium mixture was established by heating the ketone (4-40) for 24 h under reflux in trifluoroacetic acid and which again gave a 1:1 mixture of (3-34) and (4-40) [Scheme 4-11].

[4 - 34]   [4 - 40]

[Scheme 4-11]

The rearrangement of 2,6-dimethyl-1-methoxytetrafluorobenzobarrelenene (2-5) in concentrated sulphuric acid at room temperature gave a complex mixture of products, but treatment with fluorosulphuric acid at -60° for 10 minutes gave a mixture of the aryl ketone (4-34) (64 %) and the αβ-unsaturated ketone (4-35) (26 %) along with a brown unidentifiable tar which could not be crystallised or analysed. The ratio of the two ketones varied and depended on the precise reaction conditions used.

Treatment of 2,6-dimethyl-1-methoxytetrafluorobenzobarrelene (2-5) with concentrated sulphuric acid (98%) at room temperature gave the aryl ketone (4-34) (5%), the αβ-unsaturated ketone (4-35) (28%) and a new ketone (65%) which was later shown on the basis of accumulated chemical and spectral data to be the sultone (4-41) [Scheme 4-14]. The formation of the sultone (4-41) could not be rationalised within the accepted mechanisms as a primary rearrangement product. It must be supposed to be a secondary product.

More surprising yet was the effect of the dilute sulphuric acid (ca. 80%) on 2,6-dimethyl-1-methoxytetrafluorobenzobarrelene (2-5), which still resulted in the formation of the sultone (4-41), although the yield of the αβ-unsaturated ketone (4-35) remained constant. No additional product could be obtained.

The reaction of the aryl ketone (4-34) or the exo-cyclic methylene compound (4-40) with concentrated sulphuric acid at room temperature and quenching with water gave exclusively the sultone (4-41) in 100%yield. It was clear that the sultone (4-41) could have been formed from the 2,6-dimethyl-1-methoxytetrafluorobenzobarrelene (2-5) by way of the aryl ketone (4-34) or via the exo-cyclic-methylene compound (4-40) and that this was most probably its provenance. however, needs further attention.

The correct assignment of the structure of sultone (4-41) is of fundamental importance to any discussion of the place which these molecules

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occupy in the rearrangements of the bicyclic systems under investigation. It is instructive to consider the spectral data for the sultone (4-41).

Mass spectrometry showed the molecular ion $M^{+\cdot}$ at m/e 350, which readily fragments to give a strong $[M-64]^{+\cdot}$ ion, usually associated in similar compounds with the loss of sulphur dioxide, $[M-80]^{+\cdot}$ ion, loss of sulphur trioxide while the rest of the molecule fragments in the same way as the aryl ketone (4-34).

The infrared spectrum showed maxima at ν_{max} (KBr) at 1703, 1360, and 1140 cm^{-1}, which were assigned to the carbonyl group situated next to the aromatic system and to the symmetric and asymmetric stretching frequencies of the sultone function. The 90 MHz ^{1}H n.m.r. spectrum showed the following resonances: τ5.55 (d, 1H, $\underline{J}$ = 14 Hz), 5.95 (m, 1H) which was assigned to the bridgehead proton, 6.55 (d, 1H, $\underline{J}$ = 14 Hz), 6.96-7.2 (m, 2H), assigned to one of the 3a, 9-methano-bridge protons together with one of the protons from the other methylene group, 7.55 (d, 1H, $\underline{J}$ = 14 Hz), 7.85 (d, 1H, $\underline{J}$ = 14 Hz), assigned to the other two methylene protons C-10 and 8.51 (s, 3H). The most obvious feature of this spectrum was the presence of only one methyl group and the presence of the AB system at τ5.55 and 6.55. A 220 MHz ^{1}H n.m.r. spectrum and spin-spin decoupling experiments revealed that the remaining five protons are present as a five-spin proton system with the methine proton at τ5.95 being also spin-spin coupled to ^{19}F.

The ^{13}C n.m.r. spectrum (both ^{1}H noise and off resonance decoupled) showed resonances at 24.5 (-CH$_3$), 33.4 ($>$CH), 42.0 ($>$CH$_2$), 45.5 ($>$CH$_2$), 49.6 ($>$CH$_2$) [the AB system with widely different chemical shifts], 66.5 ($>$C-), 95.0 (-$\overset{|}{\underset{|}{C}}$-), 131.7 and 153.5 (2 x Ar-C-) and 187.5 (C=O) p.p.m. from T.M.S. The ^{19}F decoupled ^{13}C n.m.r. spectrum revealed aromatic carbon resonances at 140.3, 142.9, 144.6 and 148.4 p.p.m. from T.M.S.

These data can be accommodated by the following suggested structures

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(4-41) and (4-42). The construction of a scale molecular model strongly
suggested that the stereochemistry of the sulphur containing ring and the
methyl group was as shown in structure (4-41).
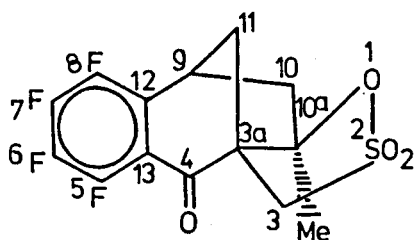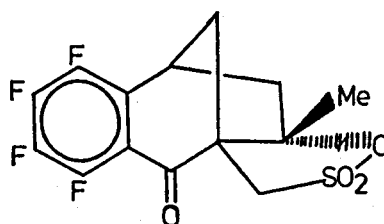
[4 - 41]   [4 - 42]

The full implications of these structures will not be clear until the
studies with the tetrachloro- and dehalogeno-analogues of the compound (2-5)
are considered. We therefore decided to look into the acid-catalysed re-
arrangements of 2,6-dimethyl-1-methoxytetrachlorobenzobarrelene (2-8) and
its dehalogeno-analogue (3-36) as part of the general study.

The reactions of the benzobarrelenes [(2-8) and (3-36)] with trifluoro-
acetic acid gave initial mixtures of the aryl ketones [(4-36) and (4-38)]
and the αβ-unsaturated ketones [(4-37) and (4-39)] [Scheme 4-12].

$X_4 = F_4$ [2 - 5] $X_4 = F_4$ [4- 34] $X_4 = F_4$ [4 - 35]
$X_4 = Cl_4$ [2 - 8] $X_4 = Cl_4$ [4 - 36] $X_4 = Cl_4$ [4 - 37]
$X_4 = H_4$ [3-36] $X_4 = H_4$ [4 - 38] $X_4 = H_4$ [4 - 39]
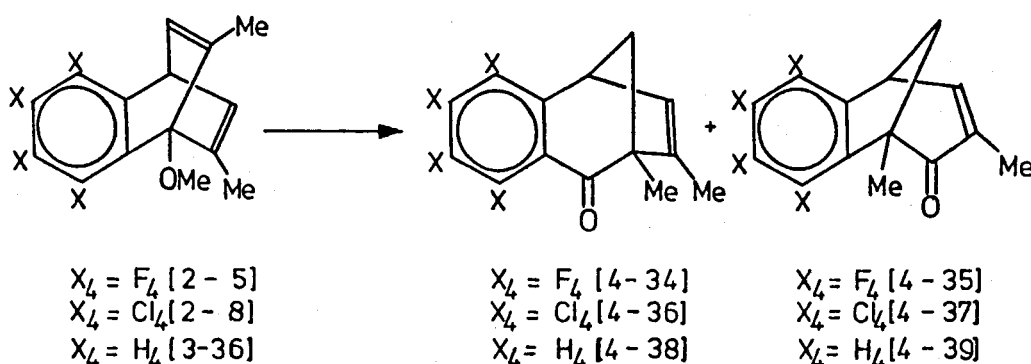
[Scheme 4-12]

In each case the aryl ketones [(4-36) and (4-38)] equilibrate with the exo-cyclic methylene isomers [(4-43) and (4-44)] on prolonged treatment with trifluoroacetic acid [Scheme 4-13].

X_4 = Cl$_4$ [4-36]
X_4 = H$_4$ [4-38]

X_4 = Cl$_4$ [4-43]
X_4 = H$_4$ [4-44]
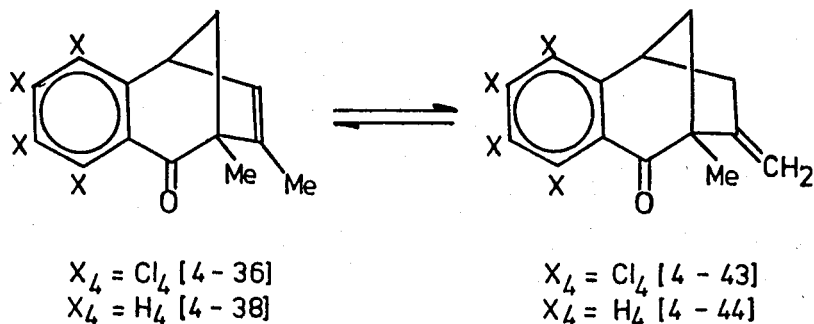
[Scheme 4-13]

However, the reactions differ in the presence of strong acids. For instance, the rearrangement of 2,6-dimethyl-1-methoxytetrachlorobenzo-barrelene (2-8) in concentrated sulphuric acid, at room temperature, surprisingly gave only one product, the αβ-unsaturated ketone (4-37) (66%); in addition to that a brown tar was obtained which could not be purified or identified. No other compound was found even when aqueous sulphuric acid (80%) was used. It could not be explained why we got just one product and what happened to the aryl ketone (4-36). Presumably, the reaction medium was too harsh on an intermediate which via the aryl ketone (4-36) goes to the tar. When the aryl ketone (4-36) was treated with concentrated sulphuric acid at room temperature, a brown tar was also obtained. The reaction was repeated using aqueous sulphuric acid (80%) at 0° + 5°, for a very short time, but without any success. The infrared spectrum of the tar showed the broad maxima v_{max} at 1710 and 1603 cm^{-1}, which were inconclusive. In addition we could not get any good ¹H n.m.r spectra on the product.

In the case of 2,6-dimethyl-1-methoxybenzobarrelene (3-36), the re-arrangement in concentrated sulphuric acid, at room temperature, gave a

complex mixture of products. One of the ketones was characterised as the αβ- unsaturated ketone (4-39) (29 %), but neither of the aryl ketones [(4-38) and 4-44)] could be detected. An examination of ^{1}H n.m.r. spectrum of the crude reaction mixture showed the presence of a number of other products. Thin layer chromatography showed that products which were much more polar than the normal products were present in the mixture. The αβ-unsaturated ketone (4-39) was found to be stable in concentrated sulphuric acid even after 3 h, prolonged treatment gave decomposed products which could not be identified, whereas both the aryl ketones [(4-38) and (4-44)] gave the new polar products. These polar products were later shown on the basis of accumulated chemical and spectral data to be the sultone (4-45), related to that obtained in fluoro-series (4-41) and a diastereomeric mixture of diketones (4-46).
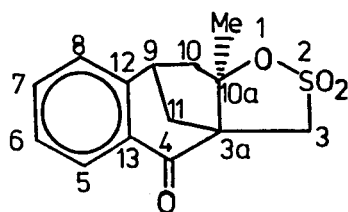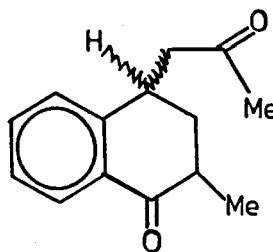
[4 - 45]   [4 - 46]

The structures of the diketones (4-46) were established later by independent synthesis, but it will be helpful to consider the spectral data for the compounds (4-45) and (4-46) at this stage.

The presence of sulphur in the compound (4-45) was established by means of the Lassaigne test. Elemental analysis for carbon and hydrogen and mass spectrometry gave the molecular formula $C_{14}H_{14}SO_4$ which was further confirmed by an accurate mass measurement on the molecular ion.

The molecular ion in the mass spectrum (at m/e 278) fragments to give the $[M-SO_2]^{+\cdot}$ at m/e 214 and $[M-SO_3]^{+\cdot}$(100%) at m/e 198. The infrared spectrum showed maxima at ν_{max} (KBr) 1693, 1328 and 1153 cm^{-1}, which are assigned to the carbonyl group and $-CH_2-SO_2-$stretching. The 90 MHz ^1H n.m.r. spectrum showed a singlet for a methyl group at τ8.6, an AB system for the $-CH_2-SO_2-$ at τ5.52 and 6.56 ($\underline{J}$ = 14 Hz), which corresponds to the values in the other sultone (4-41). The other obvious feature in this spectrum are the presence of four aromatic protons at τ1.94 (dd, 1H, $\underline{J}$ = 2.2 Hz), $\underline{J}$ = 7.2 Hz), 2.25 - 2.74 (m, 3H) bridgehead proton at 6.37 (m, 1H), and the other two methylene groups at 7.08 (m, 2H), 7.48 (m, 1H), and 7.88 (m, 1H). Spin-spin decoupling experiments did not reveal much useful structural information.

The ^{13}C n.m.r. spectrum (both ^1H noise and off resonance decoupled) showed resonances at τ24.4 ($-CH_3$), 41.4 ($>CH$), 43.6 ($>CH_2$), 46.5 ($>CH_2$), 50.1 ($>CH_2$), 66.0 ($-\overset{|}{\underset{|}{C}}-$), 96.2 ($-\overset{|}{\underset{|}{C}}-$), 129.0 and 149.3 (2 x Ar-C-), 126.9, 127.9, 128.1, 135.2 (4 x Ar-C-H) and 192.1 ($>C=O$) p.p.m. from T.M.S. Several structures appear compatible with these spectral characteristics but the most reasonable structure appeared to be (4-45).

[4 - 45]
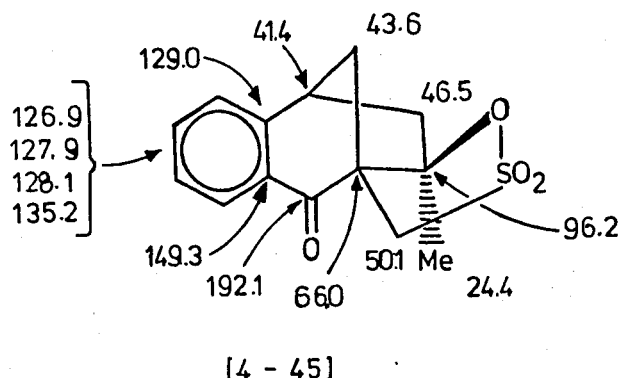
The structures of the sultones (4-41) and (4-45) not only follow from the spectroscopic data, but also the stereochemistry has been confirmed by a single crystal X-ray structure determination on (4-45).[‡]

‡ The crystallographic work was carried out by Drs.D.S.Brown and K.G.Mason of this department. Crystal structure data are deposited with Dr.Brown.
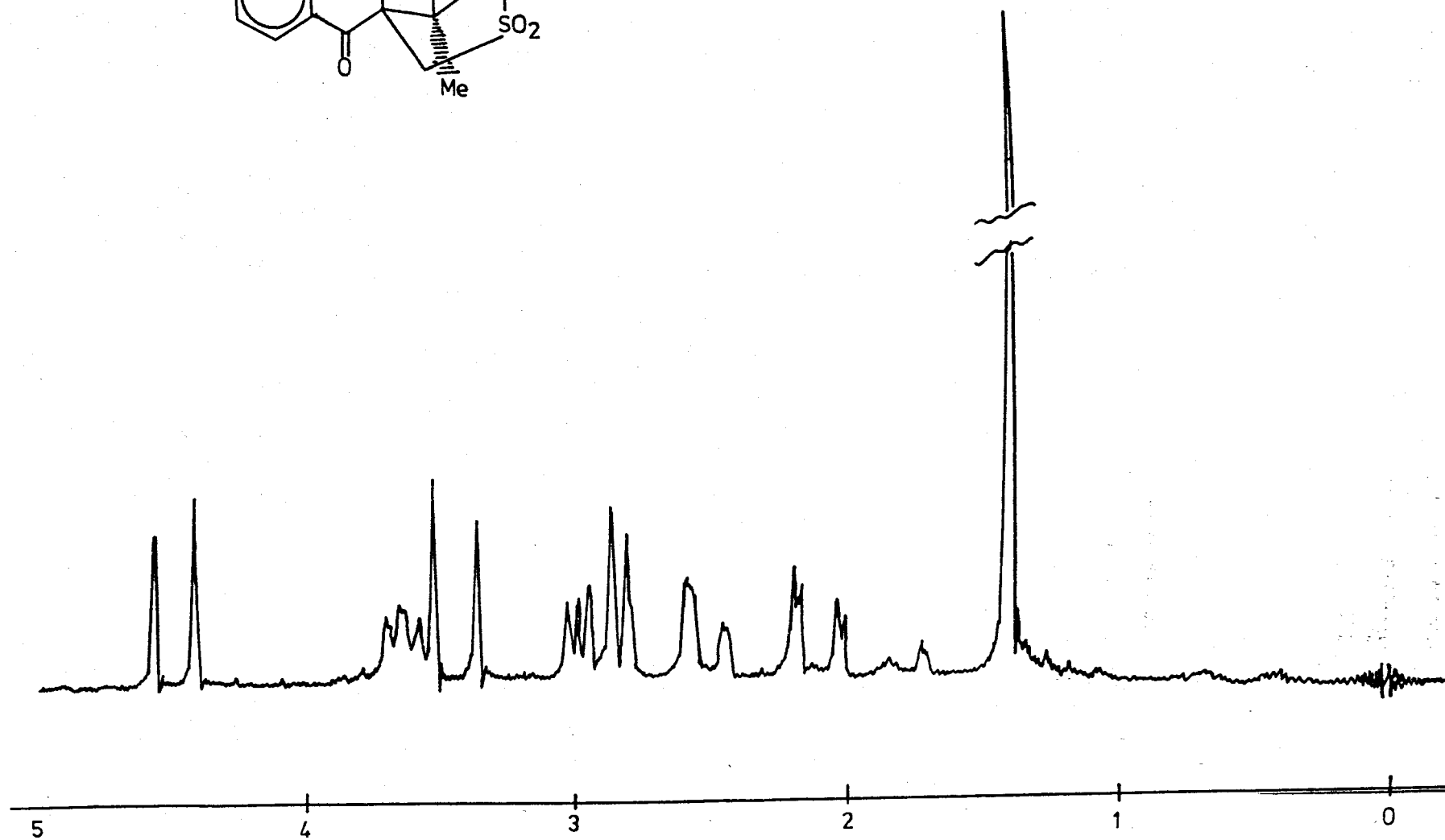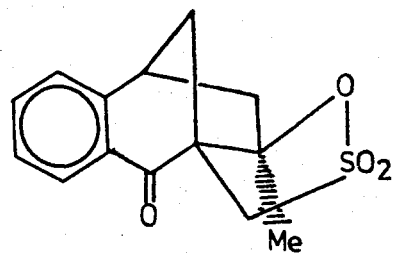
The crystals are monoclinic, a = 11.672 (2), b = 7.717 (1), c = 14.489 (a)
A^O, and p = 101.7^O; space group P2$_1$/c, Z = 4. The data were collected on a
Hilger-Watts Y290 four circle diffractometer with MoK$_\alpha$ radiation, allowing the
measurement of 1467 observed reflexions.

The structure was solved by direct methods using the tangent formula and
refined by full matrix least squares methods to a final conventional R of
0.074. MULTAN was used for the direct methods solution and all other cal-
culations were carried out using X RAY 72.
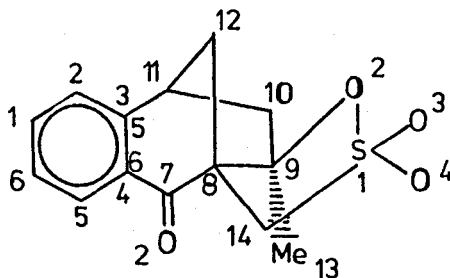
Numbering Schemes used in the presentation of the
X-ray crystallographic data. ‡

From the above discussion it is clear that the sultone (4-45) results
from the sulphonation of a double bond. An earlier publication on this
type of reaction suggests that it has many precedents. The stage at which
the sulphonation occurs is not known but the available data strongly suggests
one of the following mechanistic pathways [Scheme 4-14] entailing sulphonation
of an exo-cyclic methylene group.

The benzobarrelene undergoes vinyl shift to give the double bond isomer,
which is then sulphonated by the reaction medium. Subsequent rearrangement
to the carbocation produced during sulphonation and acid-catalysed cyclization

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‡ The crystallographic work was carried out by Drs.D.S.Brown and K.G.
Mason of this department. Crystal structure data are deposited with Dr.Brown.

of the unsaturated sulphonic acid would give the desired sultone (4-45)
[Scheme 4-14]. The aryl ketones [(4-38) and (4-44)] under similar reaction
conditions produce the sultone (4-45). From these results it is evident that
the reaction proceeds via the aryl ketones [(4-38) and (4-44)] to give the
sultone (4-45). Thus, further studies concerning the mechanistic implications
involved in the formation of the sultone (4-45) have been concentrated on the
aryl ketones [(4-38) and (4-44)].
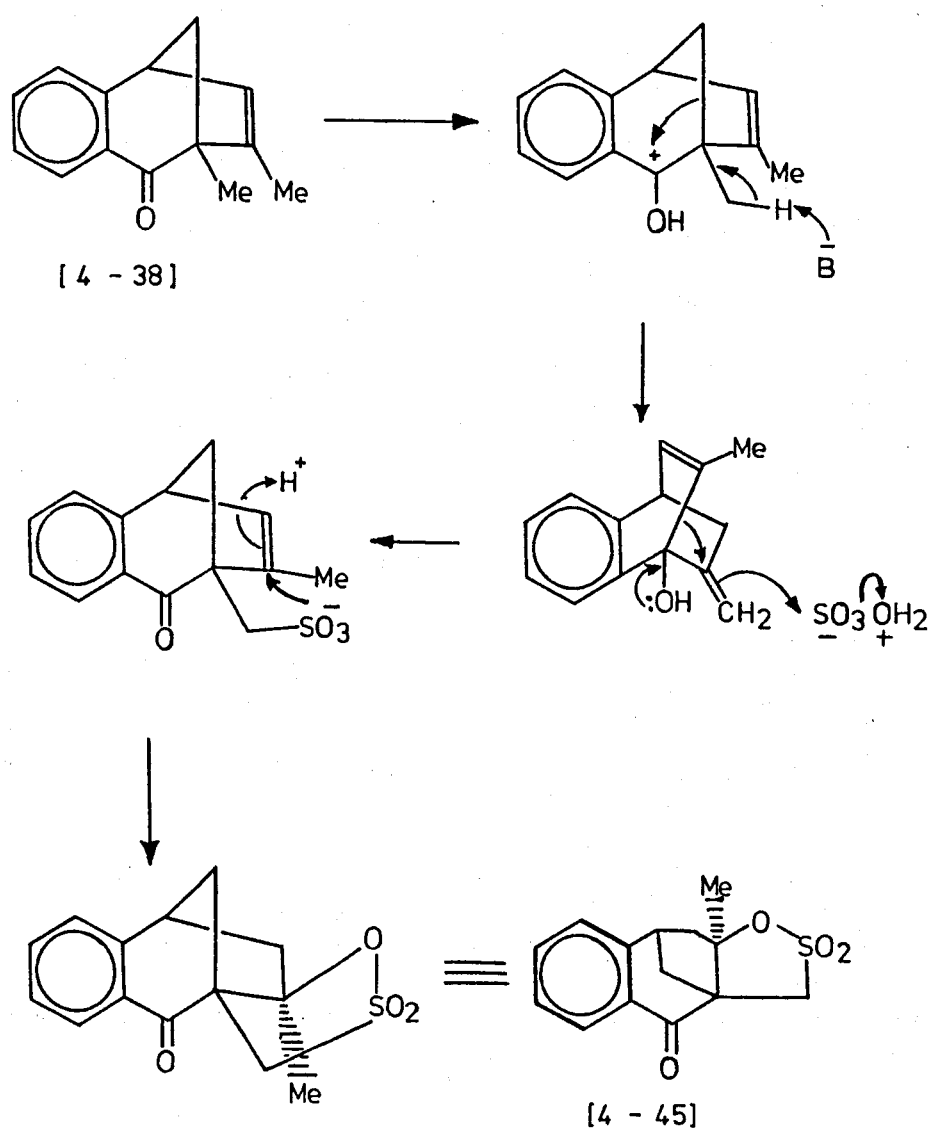
[Scheme 4-14]

The rearrangement of the aryl ketones [(4- 38) and (4- 44)] in concentrated sulphuric acid gives rise not only to the analogous sultone (4-45) but also to the diastereomeric mixture of diketones (4-46) which can be envisaged to arise from the retro-Aldol condensation of the alcohols (4-47).
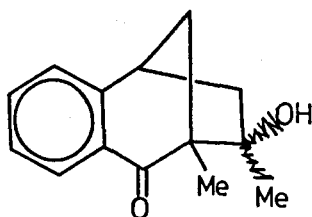
[4 - 47]

The structure of the diastereomeric mixture of diketones (4- 46) was established on the basis of the spectral evidence. Elemental analysis of the ketones (4-46) gave a molecular formula $C_{14}H_{16}O_2$. Mass spectrometry showed the molecular ion $M.^+$ at m/e 216. The molecule undergoes a McLafferty rearrangement, the schematic representation of the fragmentation pattern is as shown in Scheme 4-15.

The various peaks assigned to different structures are as reported in Table 4-1.

Table 4-1

Measured Mass (m/e)	Possible Formula	Calculated Masses (m/e)	Measured Metastable Peak (m/e)	Calculated Metastable Peak (m/e)
216.1148	$C_{14}H_{16}O_2$	216.1150	-	-
173.0967	$C_{12}H_{13}O$	173.0966	138.5	138.5
158.0730	$C_{11}H_{10}O$	158.0732	115.6	115.6
131.0861	$C_{10}H_{11}$	131.0861)	99.2	99.2
131.0497	C_9H_7O	131.0497)	99.2	99.2
103.0550	C_8H_7	103.0548	81.0	81.0
77.1019	C_6H_5	77.1019	57.6	57.6
51.0659	C_4H_3	51.0659	-	-

m/e : 216.1

m/e : 158.0 (100 %)

m* 138.5 − MeĊO

m/e : 173.0

−C₃H₆
m* 99.2

m/e : 131.0

m* 81.0 −CO

m/e : 77.1

−C₂H₂
m* 57.6

m/e : 103.0
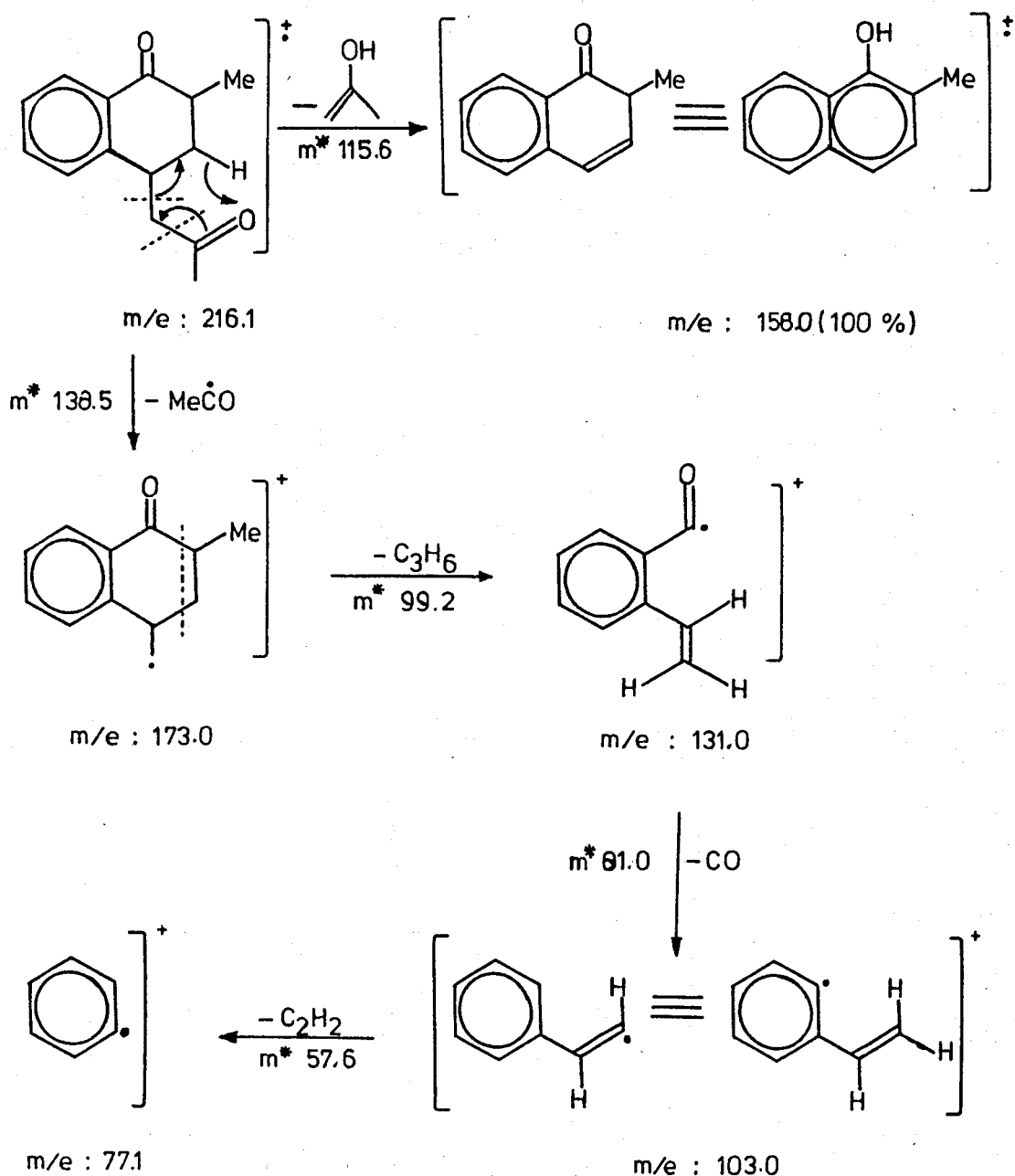
[Scheme 4-15]

The infrared spectrum showed absorption maxima at ν_{max} (KBr) 1708 and 1680 cm^{-1}, one of which was assigned to the saturated ketone and other confirms the presence of an aryl carbonyl group. The 90 MHz ^{1}H n.m.r.

spectrum of the distereoisomeric mixture showed the following resonances: one of the aromatic protons appeared at 1.96 as a double doublet ($\underline{J}$ = 2.2 Hz, $\underline{J}$ = 7.0 Hz) and the other three protons appeared as a multiplet at τ2.4-2.91, the methine protons appeared as multiplets at τ6.33 and 7.40, whereas the two methylene groups also appeared as multiplets at τ7.10 and 7.84-8.5. The most obvious feature of the spectrum is due to the presence of two chiral centres showing one methyl as singlets at τ7.82 and 7.72 (as the two isomers) and the other methyl group appeared as a doublet at τ8.74 ($\underline{J}$ = 14.0 Hz). The two isomers can be separated by preparative thin layer chromatography by multiple elutions. Since the R_f value of these two isomers is very close, their separation was tedious and only one of the isomers could be purified up to 85% purity. The spin-spin decoupling experiments further revealed the position of the rest of the protons and helped in establishing the structure. The stereochemistry of the molecule is not fully understood although the structure has been confirmed on the basis of its synthesis by an alternative route, which will be discussed later. Deuterium labelling work was also done to pin-point exactly the various positions of protonation.

From the experimental evidence it was clear that the aryl ketones [(4-38) and (4-44)] give rise to the distereoisomeric diketones (4-46) and the sultone (4-45); in/none of the reactions was the αβ-unsaturated ketone (4-39) detected. These facts allow us to exclude mechanisms involving the return to compounds related to the starting material. Also that the distereoisomeric diketones (4-46) give rise to the sultone (4-45) over a longer period of time suggests that an acid-catalysed aldol condensation can give the aryl ketones [(4-38) and (4-44)], which in fact are then sulphonated to give the sultone (4-45). The sultone (4-45) could not be
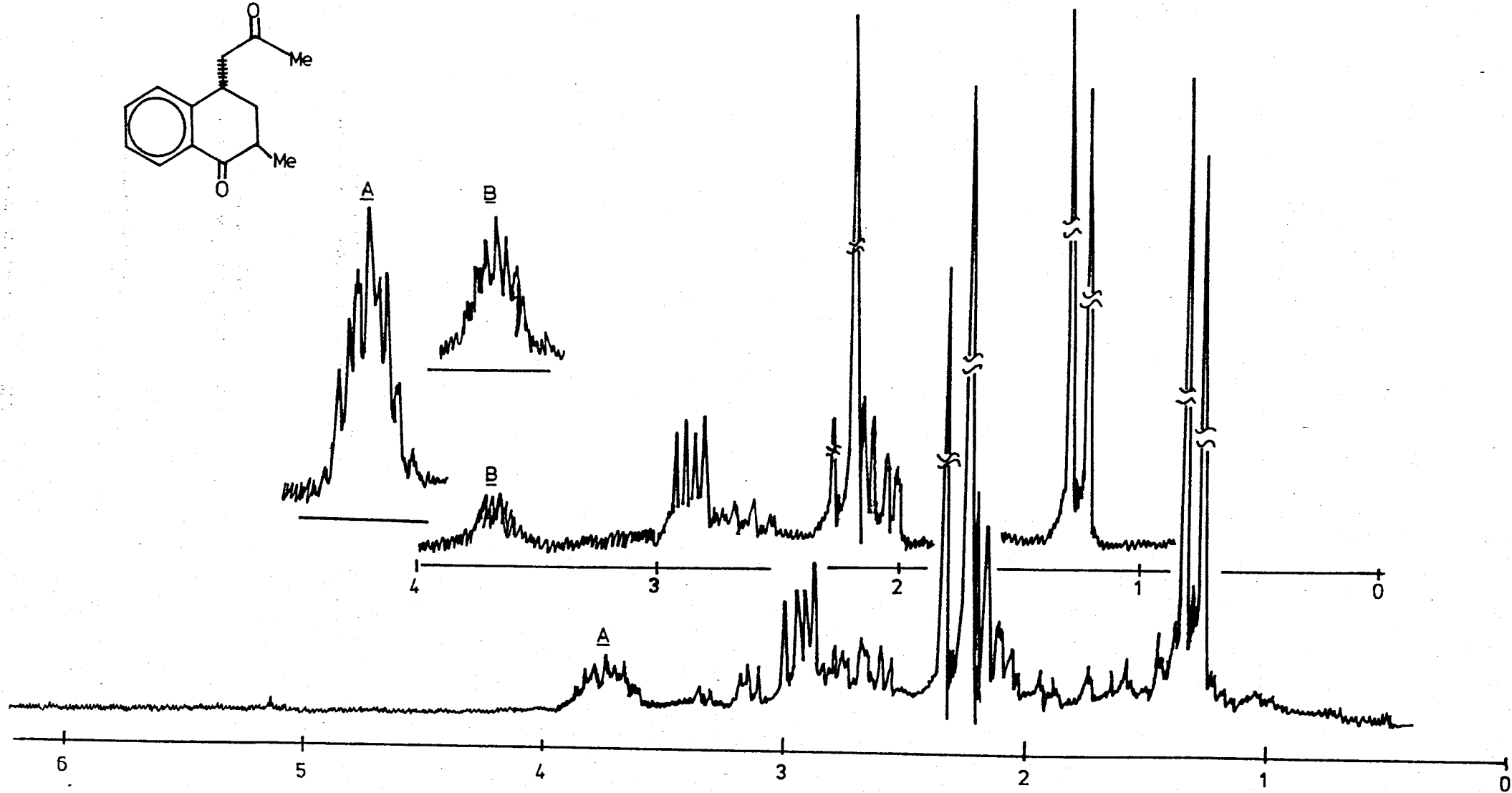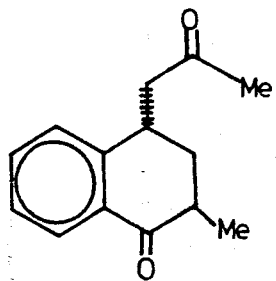
desulphonated to afford either of the ketones [(4-38) and (4-44)] shows that the process is irreversible. The formation of the intermediate aryl ketones [(4-38) and (4-44)] from the distereoisomeric diketones (4-46) is summarized in Scheme 4-16.

[4 - 46]

[4 - 38]   [4 - 44]
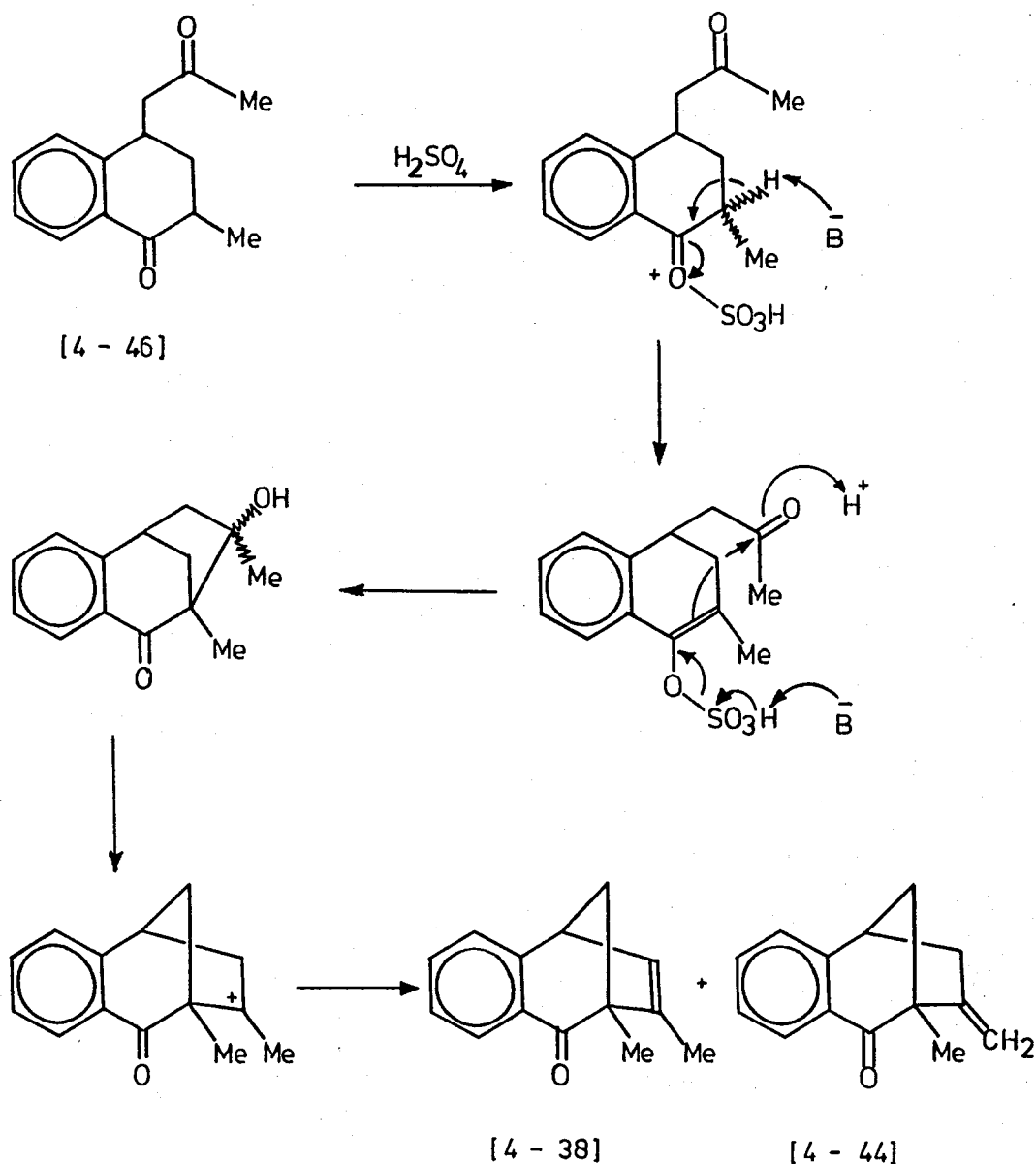
[Scheme 4-16]

None of these intermediate stages could be detected under the experimental conditions. Presumably the rest of the sulphonation proceeds as explained earlier in the case of aryl ketones [(4-38) and (4-44)] [Scheme 4-14].

167.

While working on the structure of the sultone (4-45), we read a number
of papers published by Wolinsky and his co-workers [18] in which they showed
that the sultones may be formed by sulphonation of olefins or conjugated
dienes with the dioxan-sulphur trioxide complex. In the recent years improved
methods for the preparation of primary and secondary sultones have been
reported and a number of reviews have been published.

We decided to treat the aryl ketones [(4-38) and (4-44)] with the sulphur
trioxide-dioxan complex. These compounds [(4-38) and (4-44)] gave the sultone
(4-45) in ca. 40% yield on treatment with the sulphur trioxide-dioxan complex
in methylene chloride at -70° along with a new sultone (4-48) also in ca.
40% yield. Remarkably the new sultone (4-48) was produced in 84% yield from
the αβ-unsaturated ketone (4-39) under identical conditions.[Scheme 4-17].

[4 - 48]
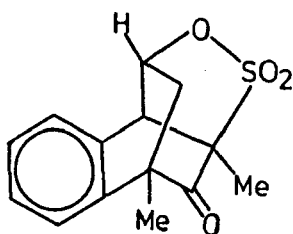
The αβ-unsaturated ketone (4-39) is relatively stable in concentrated
sulphuric acid but did afford the new sultone (4-48) in 2% yield in the
presence of oleum (40% free SO_3). The spectral data and mechanistic
arguments suggested that the structure of the new sultone might be as shown
above [Scheme 4-18].
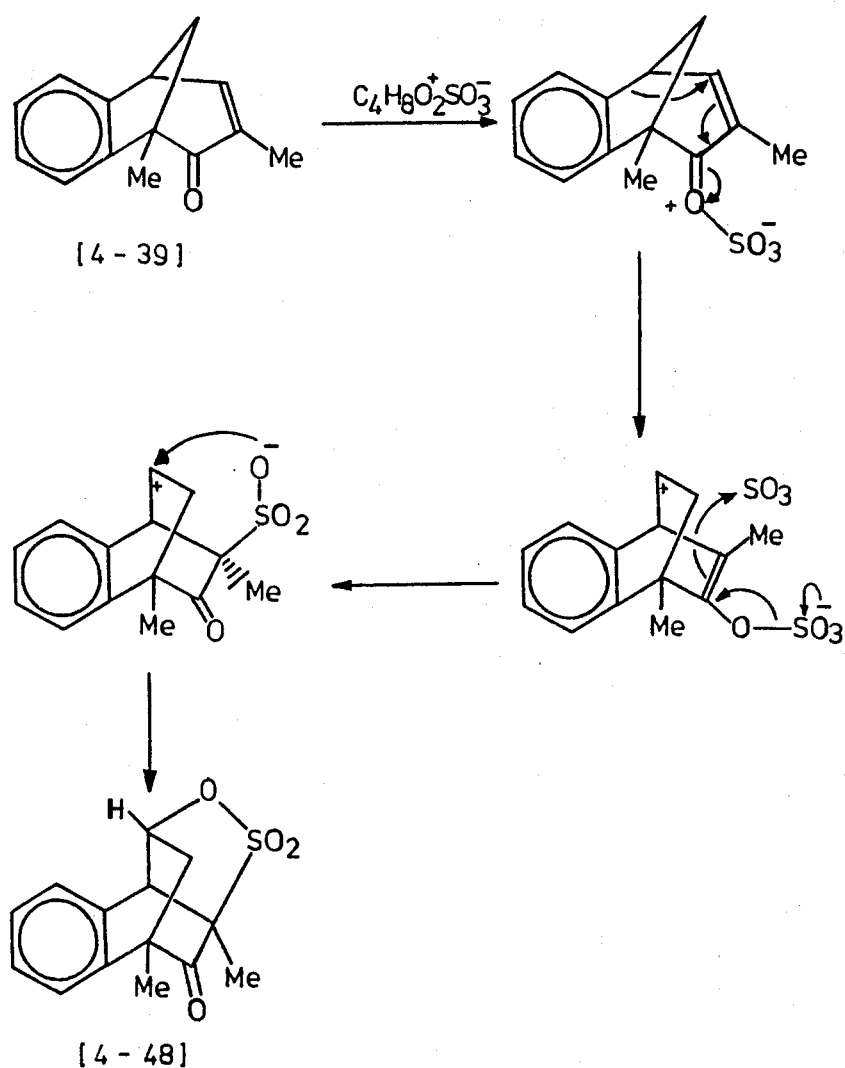
[Scheme 4-17]

A Lassaigne test established the presence of sulphur. Elemental analysis and mass spectrometry gave a molecular formula $C_{14}H_{14}SO_4$. The infrared spectrum showed maxima at ν_{max} (KBr) at 1735, 1350 and 1145 cm^{-1}, which were assigned to the carbonyl group and the $-CH_2-SO_2-$ group. The 90 MHz ^1H n.m.r. spectrum showed the following resonances: the four aromatic protons appeared as a multiplet at $\tau 2.3-2.8$, the bridgehead proton also showed as a multiplet at $\tau 4.62-4.88$, the proton which was present next to the $-SO_3-$ bridge appeared as multiplet at $\tau 5.54-5.78$ whereas the

[4 - 38]

a

b

[4 - 48]

[Scheme   4-18]

[4 - 45]

170.
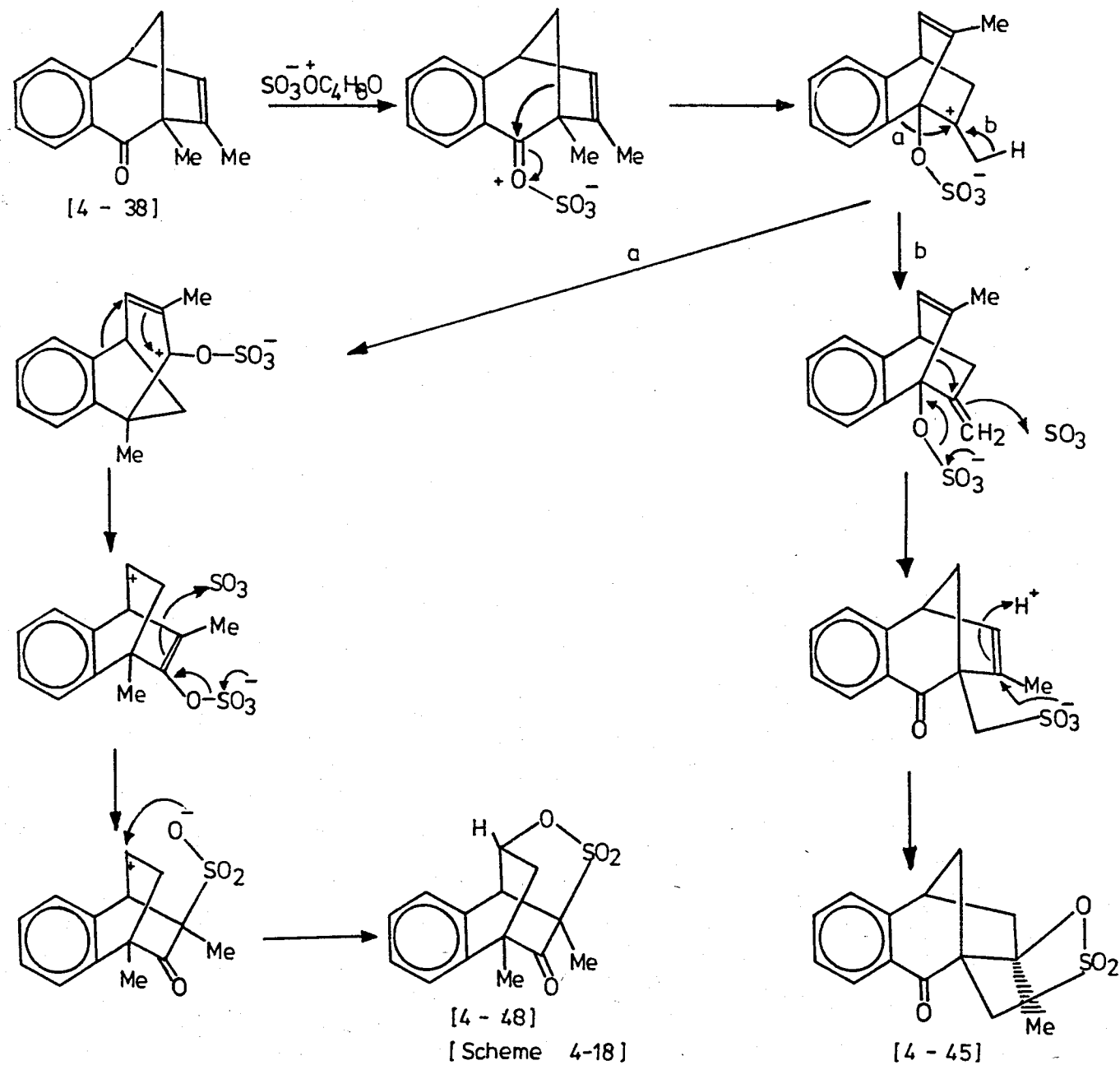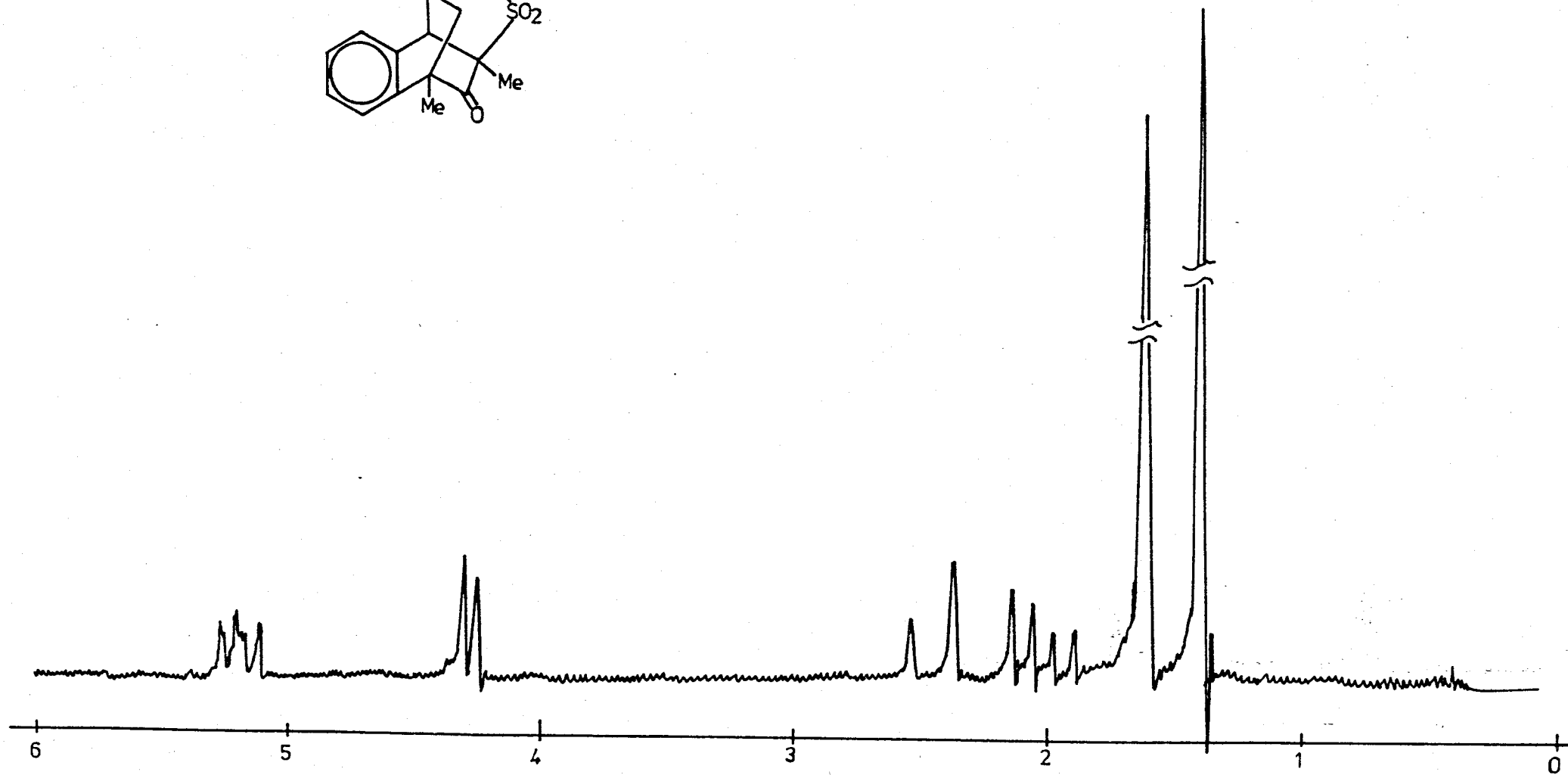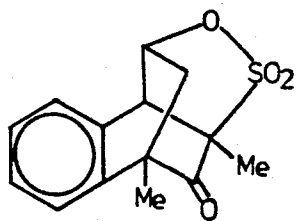
methylene group appeared as two doublets at τ7.54 and 8.02 ($\underline{J}$ = 15 Hz).
The most significant feature of the spectrum was the appearance of two
methyl groups as singlets at τ8.37 and 8.58. Spin-spin decoupling experiments
established certain assignments.

The ^{13}C n.m.r. spectrum (both ^1H noise and off resonance decoupled)
showed resonances at δ14.26 (-CH$_3$), 14.38 (-CH$_3$), 40.93 (>CH$_2$), 51.11 (≩CH),
51.28 (≩CH), 63.74 (-C-), 79.41 (-C-), 122.86 and 139.82 (2 x Ar-C-) and 199.82
(>C=O) p.p.m. from T.M.S. The off resonance decoupled ^{13}C n.m.r. spectrum
revealed the four aromatic carbon resonances at δ127.71, 128.53, 129.82 and
131.45 p.p.m. from T.M.S. The ^{13}C n.m.r. data are summarised below.
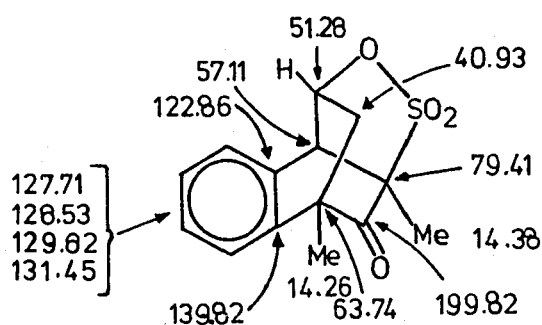
[4 - 48]

A single crystal X-ray structure determination confirmed the proposed
structure.‡ The crystal structure data on the molecule were collected on a
Stöe automatic Weissenberg diffractometer,[graphite monochromated, ω Scan,
θ max = 25° reflexions] allowing the measurement of 1101 above 3σ back-
ground. The crystals are monoclinic, a = 7.45 (10), b = 25.246 (10), c =
6.980 (5), β= 104.6° and U = 1270.7Å, space group C2/c, Z=4, D$_c$ = 1.455 g cm.$^{-3}$

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‡ As before.

$\lambda(MOK\alpha) = 0.7107$ and $\mu(MO) = 2.50$ cm^{-1}. Crystal size 1.0 x 0.1 x 0.2 mm. The structure is shown below.
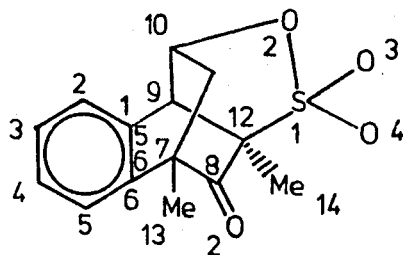
Numbering Schemes used in the presentation of

the X-ray crystallographic data.

The reaction of 2,6-dimethyl-1-methoxybenzobarrelene (3-36) with sulphur trioxide-dioxan complex gave unchanged starting material (94%). It is clear from these results that the sulphonation proceeds through the double bond, maybe with the help of a carbonyl group. Since the sulphonation occurs even with the distereoisomeric diketones (4-46) (in 2%), this very strongly suggests that under the influence of reaction medium, the distereoisomeric diketones (4-46) go back to an earlier intermediate stage.

In order to establish various pathways we decided to use deuteriated solvents for the equilibration studies. This was because from the earlier work[2,3] it was clear that the formation of the aryl ketones or the αβ-unsaturated ketone or the distereoisomeric diketones, or the sultones from 2,6-dimethyl-1-methoxybenzobarrelene (3-36) arise as a result of Wagner-Meerwein rearrangements.

The rearrangement of 2,6-dimethyl-1-methoxybenzobarrelene (3-36) in deuteriosulphuric acid followed by quenching with deuterium oxide gave a mixture of all the three ketones [(4-39), (4-45) and (4-46)]. Mass

spectrometry and [1]H n.m.r. studies revealed that deuterium was present in the whole of the molecule except for the four aromatic protons and the bridgehead proton. Similar results were obtained when the aryl ketones [(4-38) and (4-44)] were used as the starting material. Even when deuteriated tri-fluoroacetic acid was used for the equilibration of the aryl ketones [(4-38) and (4-44)], we observed extensive incorporation of deuterium.[19]

On the basis of the proposed mechanism we had expected to find only four deuterium atoms in the rearranged products. However, it seems that the exchange mechanism involves a complex process, in which the molecule ultimately contains up to nine deuterium atoms. Mass spectrometric analysis of the $\alpha\beta$-unsaturated ketone showed that it contained four deuterium atoms, the positions of which were shown by [1]H n.m.r. spectroscopy. The positions of the deuterium atoms in the $\alpha\beta$-unsaturated ketone were as shown below.
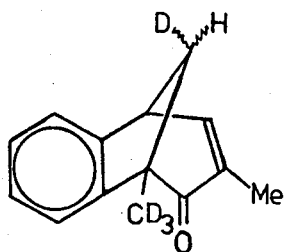
[4 - 49]

When the $\alpha\beta$-unsaturated ketone (4-39) was treated under the same reaction conditions, no exchange of deuterium was observed. A mechanism which explains why four deuterium atoms are incorporated into the $\alpha\beta$-unsaturated ketone (4-49) is shown in Scheme 4-19.

174.
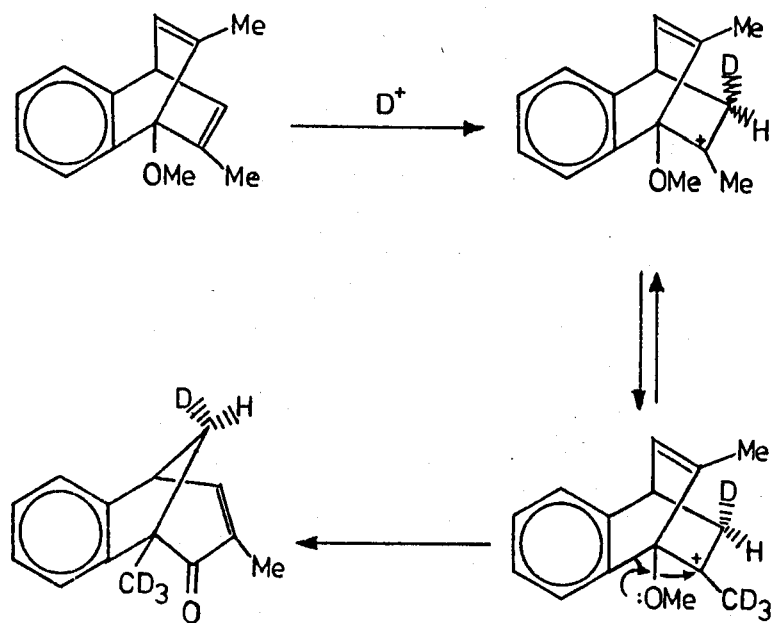
[4 - 49]

Solvents : 98.5% D_2SO_4/D_2O.

[Scheme 4-19]

When the aryl ketones [(4-38) and (4-44)] were treated with deuteriated sulphuric acid (98.5%) and quenched with deuterium oxide, we obtained similar products to those reported earlier. In an attempt to prepare specifically deuteriated intermediates which would be useful, we carried out reactions of the aryl ketones [(4-38) and (4-44)] under less vigorous conditions. Heating the compound (4-38) with deuteriated trifluoroacetic acid allowed us to obtain the expected equilibrium mixture which had been deuteriated. Interestingly, mass spectrometry showed that both products [(4-50) and (4-51)] contained up to nine deuterium atoms. Evidently a return to a symmetrical intermediate must be involved [Scheme 4-20].

175.

(Scheme 4-20)
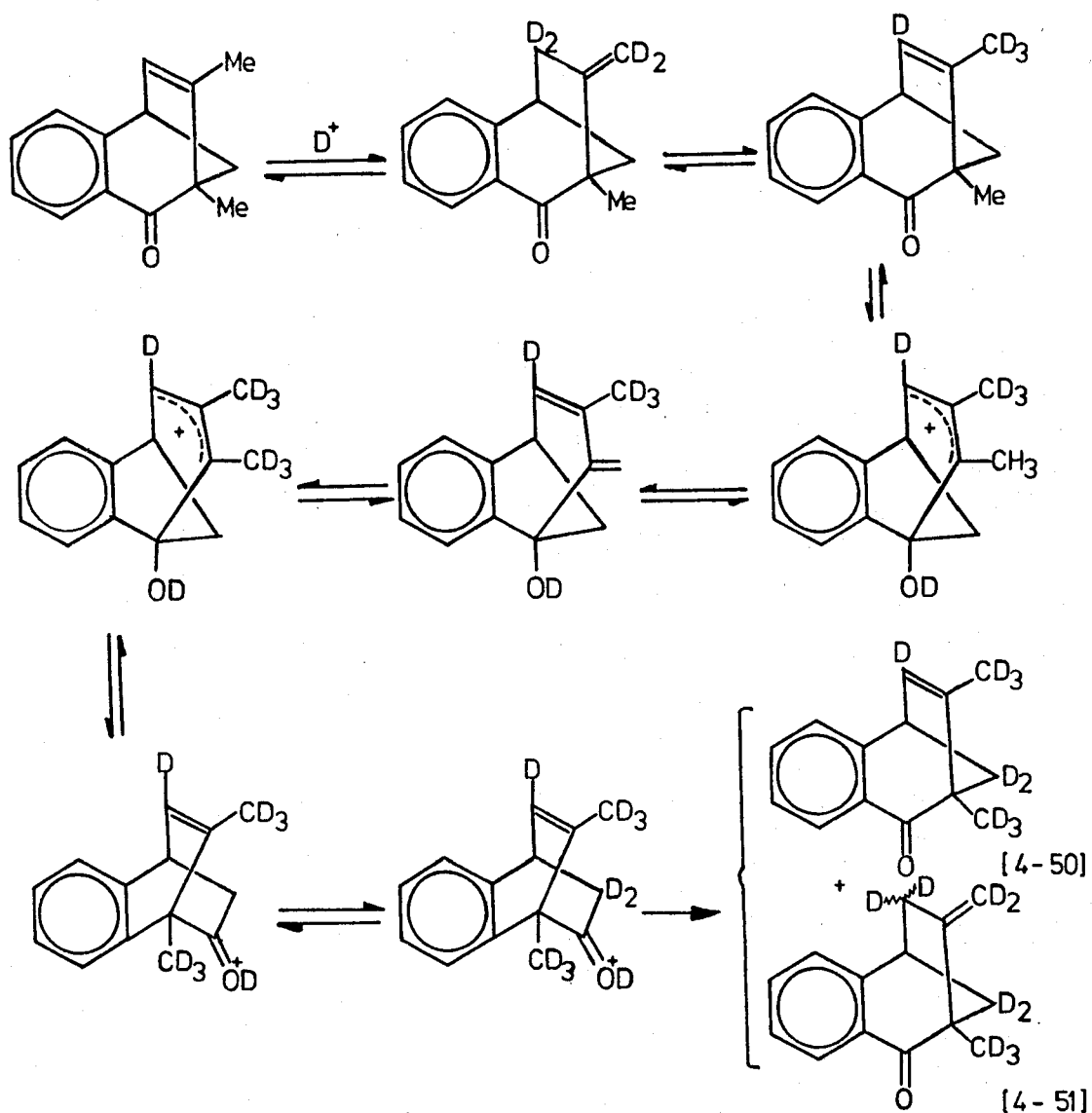
Mass spectrometry of diastereoisomeric diketones (4-52) showed that they contained up to nine deuterium atoms, similarly sultone (4-53) incorporated up to nine deuterium atoms. The possible structures of these compounds can be shown as:

(4-52)

(4-53)

176.
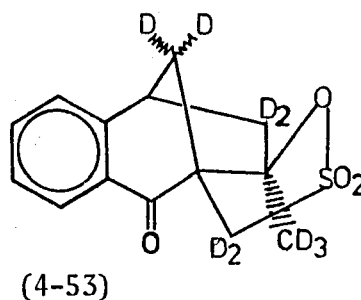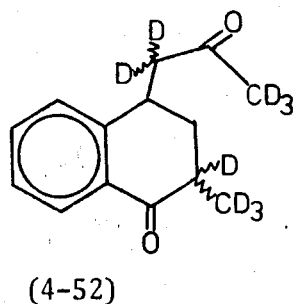
These deuterium exchange experiments did not provide the information which had been hoped for. These systems need further detailed examination in order to fully understand the reaction pathways involved.

In view of the fact that we were unable to completely separate the mixture of diastereoisomeric diketones, it was decided that they should be prepared by an alternative route. An attempt was made to effect the synthesis from α-tetralone as outlined in Scheme 4-21.
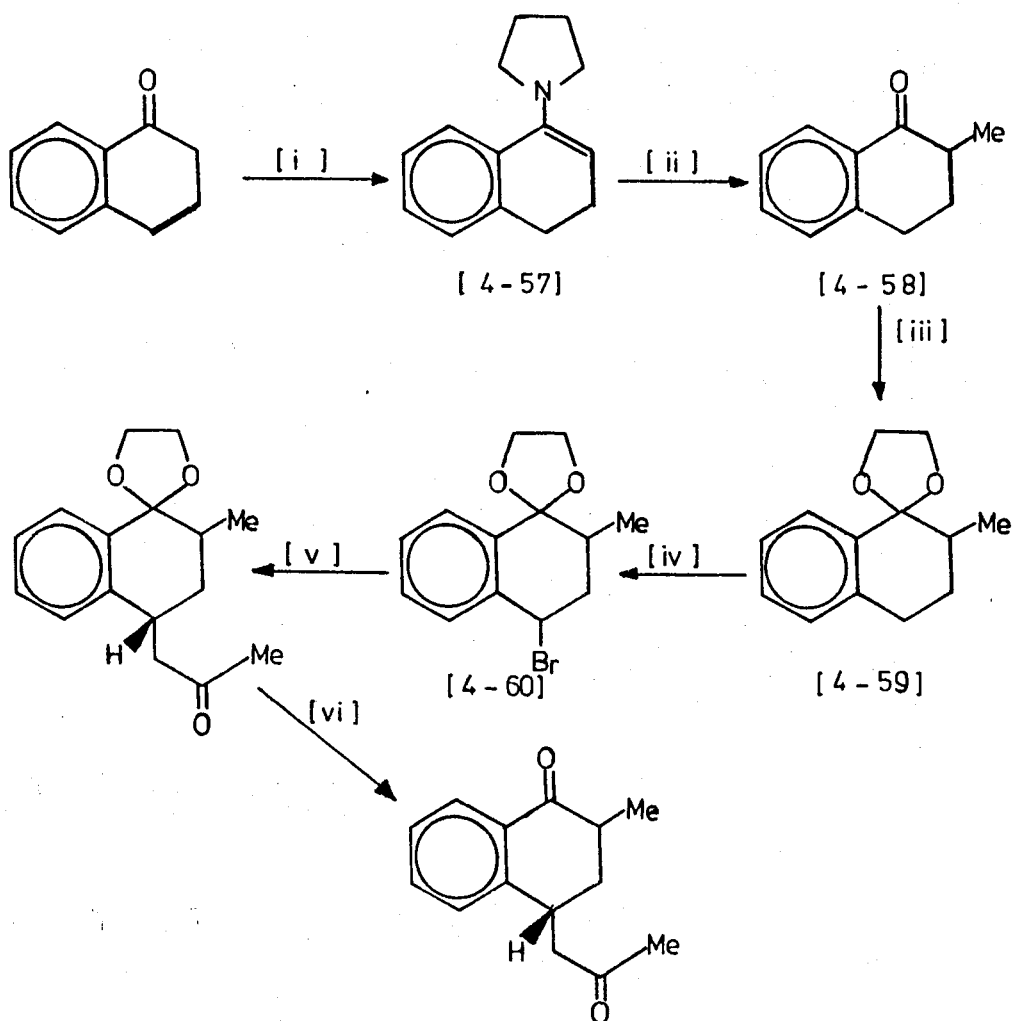
Solvents: (i) C_4H_9N-$TiCl_4$-C_6H_6; (ii) MeI (iii) $(CH_2OH)_2$-p.t.s.a - C_6H_6; (iv) N.B.S. - $CaCO_3$-CCl_4 (v) $K^+\bar{C}H_2COCH_3$; (vi) 3N HCl.

[Scheme 4-21]

177.

Alkylation of the enolate from α-tetralone is known to afford a mixture of mono- and dialkylation products. We therefore decided to investigate the methylation of enamines derived from α-tetralone. The general method for converting carbonyl compounds into enamines using titanium tetrachloride and free amine was employed. A mixture of α-tetralone, dimethylamine or pyrrolidine and titanium tetrachloride was allowed to stir in benzene or ether (in the ratio 1:1.3:0.75:20) at room temperature for several hours. The progress of the reaction was followed by ^{1}H n.m.r. analysis of aliquots.

When 1-N,N-dimethylamino-3,4-dihydronaphthalene (4-55) was heated with methyl iodide (1 mol) in freshly distilled chloroform, a white crystalline material separated out and was shown to be tetramethylammonium iodide (4-56) (50% based on the enamine). The soluble material was shown to be α-tetralone [Scheme 4-22].

[4 - 55]   [4 - 56]
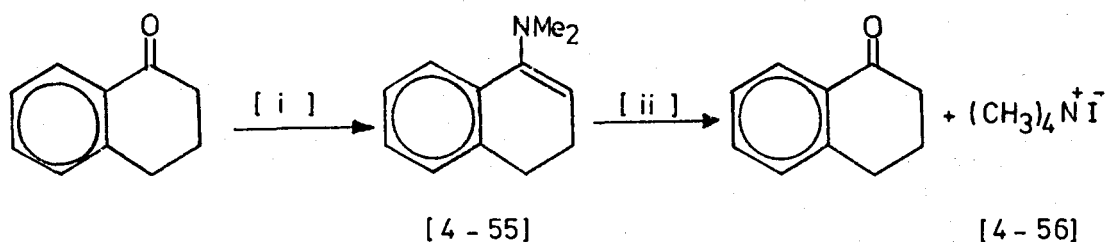
Solvents: (i) $(CH_3)_2NH$ - $TiCl_4$ - C_6H_6

(ii) MeI - $CHCl_3$

[Scheme 4-22]

We assume that the explanation of this rather surprising result is connected with the failure of the N-alkylated enamine to rearrange.

On the other hand, when 1-pyrrolidino-3,4-dihydronaphthalene (4-57) was heated with methyl iodide in dry benzene, we obtained 2-methyl-α-tetralone (4-58) in 80% yield. No N-alkylation was observed in this case.

178.

[4 - 57]   [4 - 58]

Solvents: (i) MeI - C_6H_6
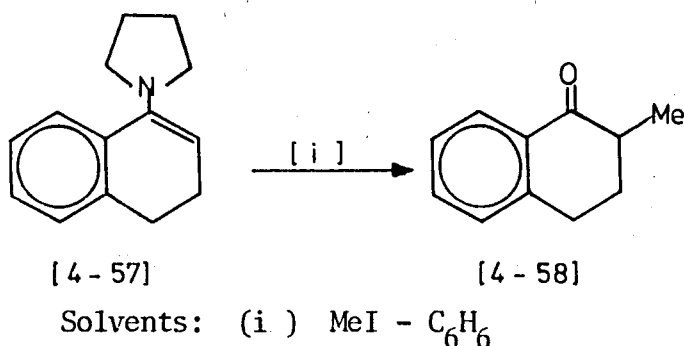
Scheme 4-23

For the acetonylation we required 4-bromo-2-methyl-α-tetralone (4-60).
However, all the attempts to prepare this compound were unsuccessful.   The
carbonyl group of the compound (4-58) was protected as the ethylenedioxy
derivative (4-59), which was then mixed with equimolar amounts of N-bromo-
succinimide and calcium carbonate in carbon tetrachloride and heated under
reflux with illumination (tungsten lamp 200 W).   The solid succinimide formed
was filtered off and the residual oil on purification showed that bromine was
also present at C-2.   So the reaction scheme was abandoned half way through
because of the lack of pure compound (4-60).

While working on this project we read a number of papers published by
Heiba and his co-workers.[20]   They showed that acetophenone reacts with olefins
(e.g. butene-1, butene-2 etc.) in the presence of manganic acetate (MnIII),
which led to the formation of four products, the substituted α-tetralone
being the predominant product.   Several experiments using olefins and
acetophenone in the presence of hydrated or anhydrous manganic acetate were
carried out.   Examination of the crude products by [1]H n.m.r. spectroscopy
showed that cyclization had occurred to give α-tetralone derivatives, as one
of the major products, in each case.   We therefore decided to carry out model
reactions using propiophenone and octene-1 in the presence of manganic acetate.
Four major products were isolated : the saturated ketone (4-61), the
unsaturated ketone (4-62), the keto-acetate (4-63), and the α-tetralone (4-64).

179.

From these model reactions it was observed that the ratio of these products could be changed by modifying the reaction conditions [Scheme 4-24].

$$CH_2=CH(CH_2)_5CH_3 \xrightarrow{Mn(III)}$$

[4 - 61]

$$C_6H_5\overset{O}{\overset{\|}{C}}\underset{CH_3}{\overset{|}{C}}H CH=CH(CH_2)_5CH_3$$

[4 - 62]

$$C_6H_5\overset{O}{\overset{\|}{C}}\underset{CH_3}{\overset{|}{C}}HCH_2\underset{OAc}{\overset{|}{C}}H (CH_2)_5CH_3$$

[4 - 63]

[4 - 64]
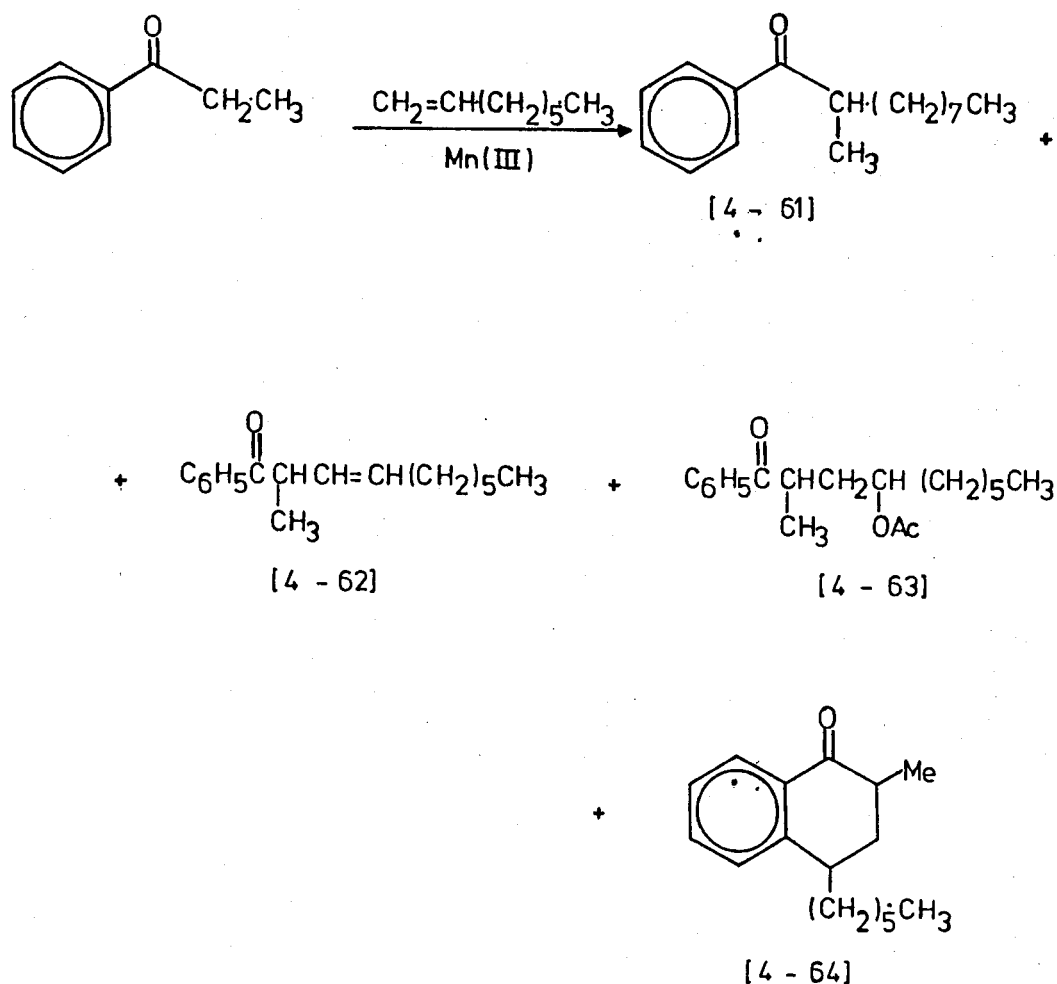
[Scheme 4-24]

In our case we wanted an olefin which could ultimately give us 4-acetonyl-2-methyl-1-tetralone (4-46). Since pent-1-en-4-one (4-67) is not commercially available, it was prepared in 80% yield by the oxidation of pent-1-en-4-ol (4-65) with pyridinium chlorochromate (4-66) (Scheme 4-25).

[4-65] [4-66] [4-67]

HCrO₃Cl

[Scheme 4-25]
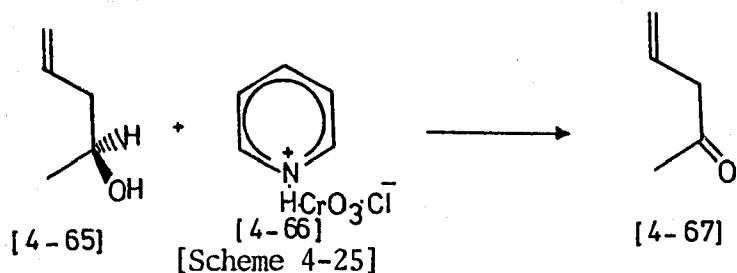
The reaction of propiophenone with pent-1-en-4-one (4-67) in the presence of anhydrous manganic acetate gave along with the other products 5.6% of the desired diastereoisomeric diketones (4-46). The reaction was repeated by varying the reaction conditions but the yield could not be improved. When pent-1-en-4-ol was used as the olefin, the yield of the diketones (4-46) was 6.2%. However, the reaction of propiophenone with 4-acetoxy-pentene-1 (4-68) in the presence of manganic acetate gave 9.2% of the 4-acetonyl-2-methyl-α-tetralone (4-46), along with a large number of other products.

The formation of these cyclic ketones together with the three or more noncyclic products can be best explained by the mechanism as shown in Scheme 4-26. It appears that the radical intermediate (4-69) undergoes three competing reactions: (i) hydrogen abstraction from the solvent to give saturated ketone (4-70); (ii) oxidation by the metal ion to give a carbocation, which then either looses a proton to give unsaturated ketone (4-71) or abstracts an acetate ion to give stable keto-acetate (4-72); (iii) the molecule undergoes an internal cyclization to give the α-tetralone (4-46). Similar results were also obtained when copper(II) acetate was used for the oxidation. These observations are all consistent with the proposed Scheme (4-26) in which products (4-46) and (4-72) are produced via afree radical pathway [Scheme 4-26].

181.

[4 - 68]

[4 - 69]
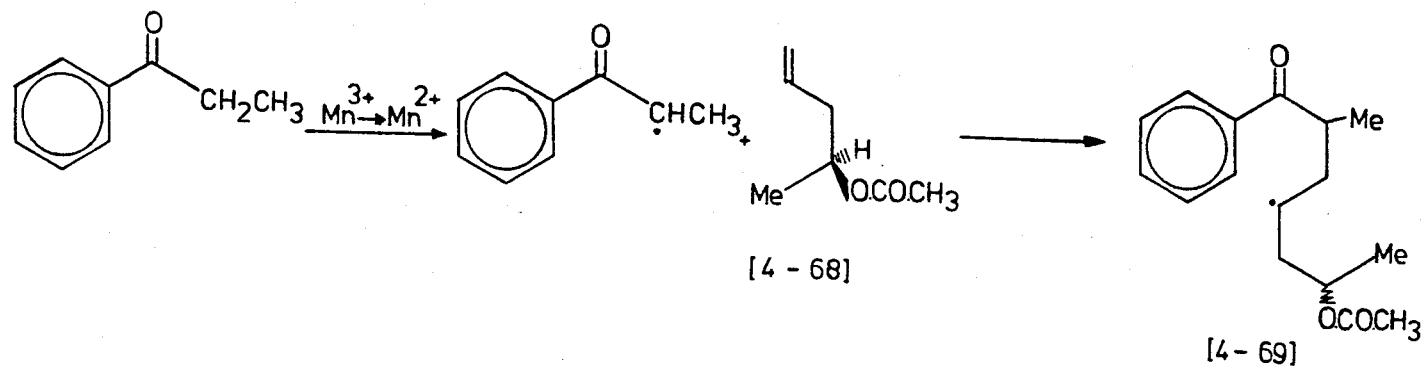
Various possibilities :

(i) hydrogen abstraction :

$$[4 - 69] \xrightarrow{C_6H_5COC_2H_5/CH_3COOH} $$

[4 - 70]
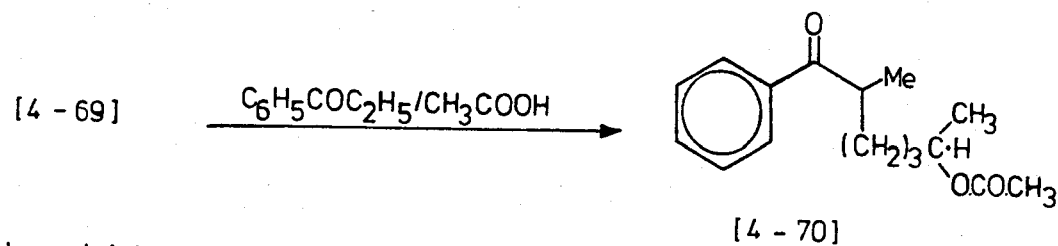
(ii) oxidation by metal ion :

$$[4 - 69] \xrightarrow{Mn^{3+} \rightarrow Mn^{2+}} $$

a   b

$^-$OAc

[4 - 69A]

[4 - 69A] →ᵃ   →

[4 - 71]

[4 - 72]
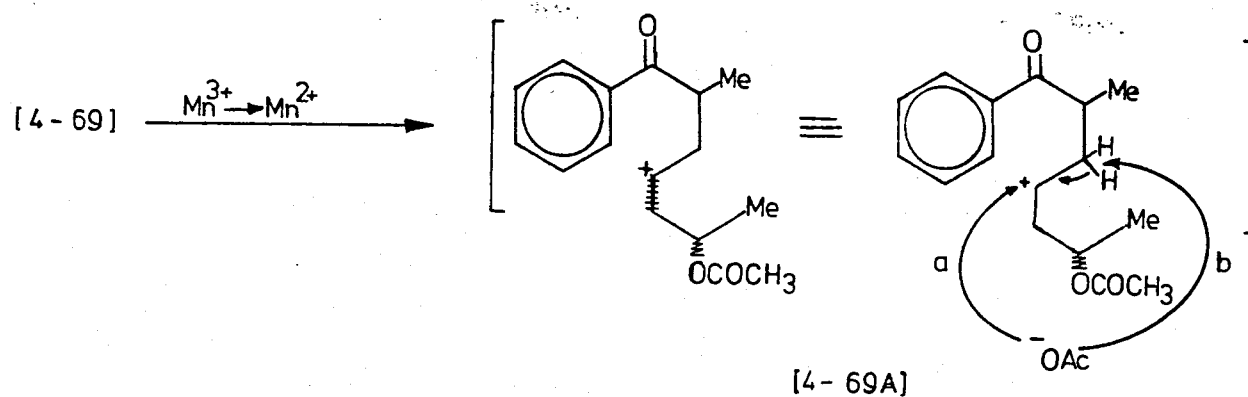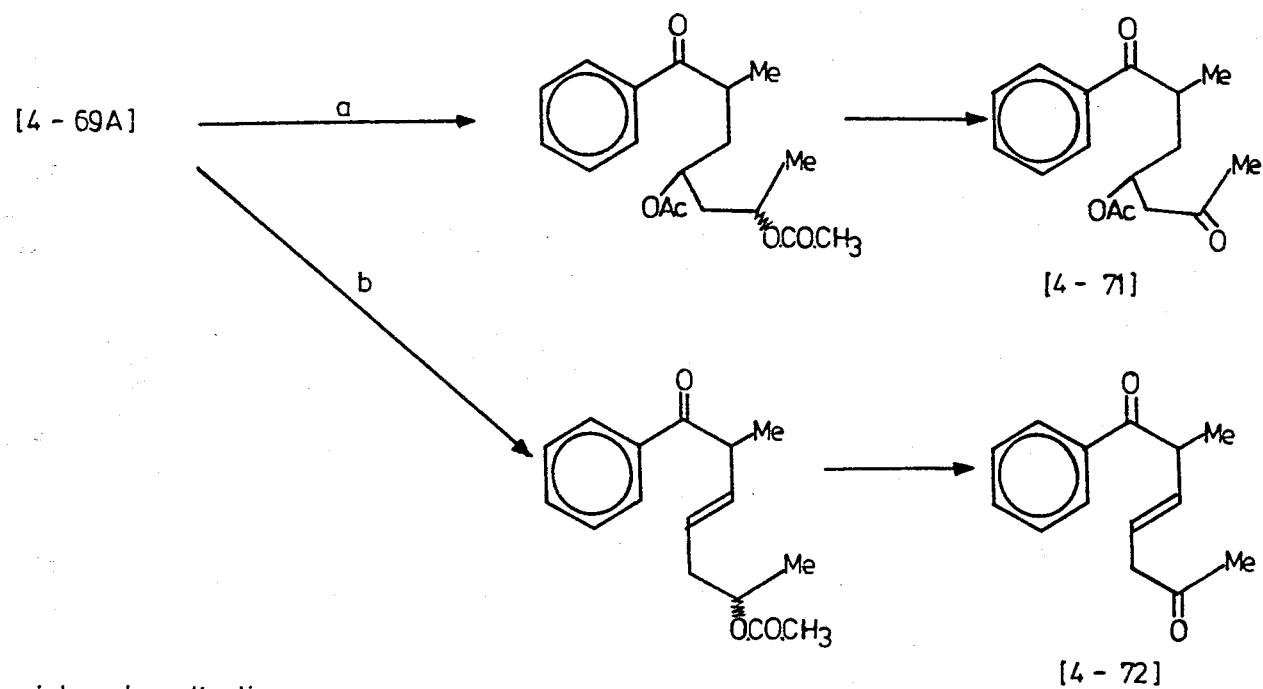
(iii)   internal cyclization :

[4 - 69]

[4 - 46]
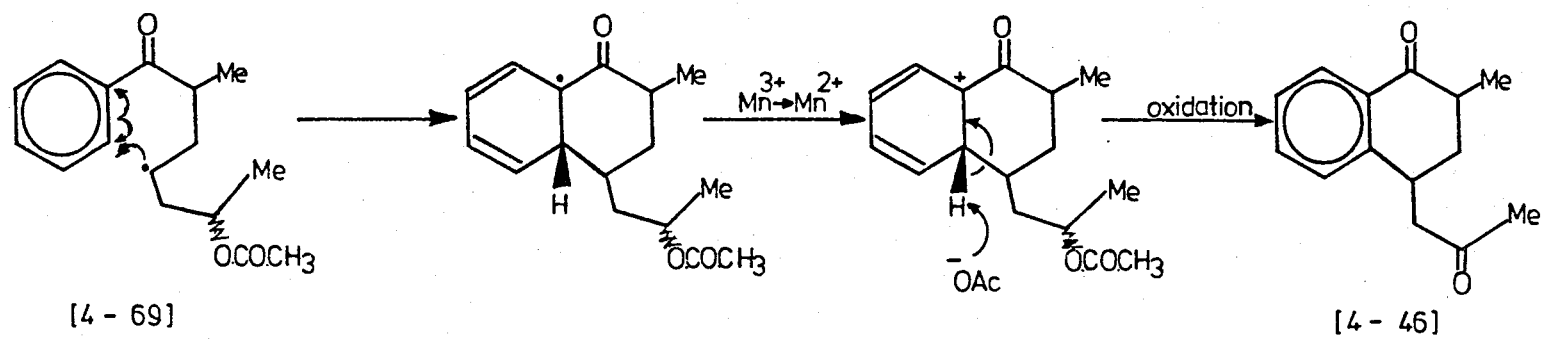
[Scheme 4-26]

Success of the reaction was attributed to the very selective oxidation of the intermediate radicals by the metal salt, the initial α-keto-radical ($C_6H_5CO.\overset{\bullet}{C}HCH_3$) is not easily oxidized, whereas the secondary alkyl radical formed by addition to the olefin is readily oxidized by the metal ion, as suggested by the earlier workers.

The alternative route did not help us in building up the stock, which we required for further chemistry on the molecule. However, it did help in establishing the structure of the diastereoisomeric diketones(4-46) on the basis of their alternative origin.

Identical results were obtained when 2,6-dimethyl-1-hydroxybenzobarrelene (3-39) was used for the acid-catalysed rearrangements. It is clear from the above discussion that the presence of halogen atoms do not alter the reaction pathway noticeably and the primary protonation proceeds in a similar fashion in all cases. Presumably, the initial protonation is guided by the presence of alkyl groups on the olefinic double bond, giving rise to various products after rearranging. However, the presence of alkyl groups in those products facilitate the secondary rearrangements. The halogen atoms do not seriously affect the reactions, but their presence may create solubility problems, particularly in the cases involving the tetrachloro-compounds, and this can then influence the extent to which secondary rearrangements occur.

2,5-Dimethyl-1-methoxybenzobarrelene:

The rearrangement of 2,5-dimethyl-1-methoxytetrachlorobenzobarrelene (2-4) in strong acidic medium was studied, in detail, by N.J. Hales[3] in this laboratory. Since the tetrachlorobenzobarrelene (2-4) showed complex behaviour in acidic media, giving rise to a number of unexpected products, this led us to examine the 2,5-dimethyl-1-methoxybenzobarrelene (3-34) more closely under the similar conditions.

2,5-Dimethyl-1-methoxybenzobarrelene (3-34) incorporates the more obvious structural features of 2-methyl and 3-methyl-1-methoxybenzobarrelene [(3-32) and (3-33)] within one molecule, and offers a more significant competition between the two types of rearrangements. The system illustrates the competitive behaviour of the carbocations which can localize at either of the carbon atoms at position C-2 or C-3, carrying methyl groups. The results reported now provide further evidence on the effect of the halogens on the reaction pathways taken.

The rearrangement of 2,5-dimethyl-1-methoxybenzobarrelene (3-34) in trifluoroacetic acid, at room temperature, gave the aryl ketone (4-73) (9%), a mixture of the benzobarrelenones [(4-74) and (4-75)] (total yield 41%), and the αβ-unsaturated ketone (4-76) (48%) [Scheme 4-27]. All the four products formed were in accord with expectation. The ratio of the benzobarrelenones [(4-74) and (4-75)] to the other reaction products did not change significantly on addition of water to the reaction medium. These findings differ from the results obtained in the case of the tetrachloro-benzobarrelene (2-4) rearrangements, when a small change in the reaction conditions resulted in significant changes to the product ratios.

Treatment of 2,5-dimethyl-1-methoxybenzobarrelene (3-34) with fluorosulphuric acid at -78° for 5 minutes, gave mixture of the same four products, along with the traces of another compound (0.3%) which could not be identified because of the very small quantity isolated. The [1]H n.m.r. spectrum of the crude product did not show the presence of any benzosemibullvalenone (4-77) or the dihydro-benzopentalenone (4-78), which were present in the chloro-series.[3]

[4 - 77]   [4 - 78]
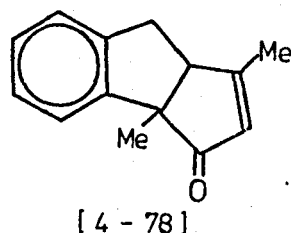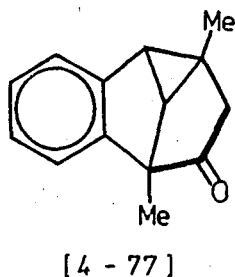
When 2,5-dimethyl-1-methoxybenzobarrelene (3-34) was treated with concentrated sulphuric acid (98%), at room temperature, the usual mixture of the aryl ketone (4-73), the benzobarrelenones [(4-74) and (4-75)] and the αβ-unsaturated ketone (4-76) were obtained, along with a new compound which was later shown, on the basis of accumulated chemical and spectral data, to be the sultone (4-79) (16% yield) (Scheme 4-27).

The isomerization of the αβ-unsaturated ketone (4-76) and the rapid degradation of both the aryl ketone (4-73) and the 1,5-dimethylbenzobarrelenone (4-75) to uncharacterized products in the strong acidic medium, over a longer period, led us to the conclusion that 1,4-dimethylbenzobarrelenone (4-74) may be the intermediate involved in the formation of the sultone (4-79).

Treatment of the 1,4-dimethylbenzobarrelenone (4-74) with concentrated sulphuric acid (98%), at room temperature for 3 minutes, gave the sultone (4-79) (Scheme 4-27).

No trace of the benzosemibullvalenone (4-77) or the dihydro-benzo-pentalenone (4-78) was found in either of the reactions. The formation of sultone (4-79) could not be rationalized within the accepted mechanisms as a primary rearrangement product, and its generation from 1,4-dimethylbenzo-barrelenone (4-74) further verifies this argument.

The correct assignment of the structure of the sultone (4-79) is of fundamental importance, in order to justify this molecule as a member of the bicyclooctane family. The spectral data agree closely with those for the sultones [(4-41) and (4-45)] obtained in the case of 2,6-dimethyl-1-methoxy-benzobarrelene (3-38) rearrangements.

Mass spectrometry and combustion analysis established the molecular formula as $C_{14}H_{14}SO_4$. The sultone (4-79) fragments readily in the mass spectrometer to give strong $[M-64]^{+\cdot}$ and $[M-80]^{+\cdot}$ ions, associated with the loss of SO_2 and SO_3. The infrared spectrum of the compound showed absorption at
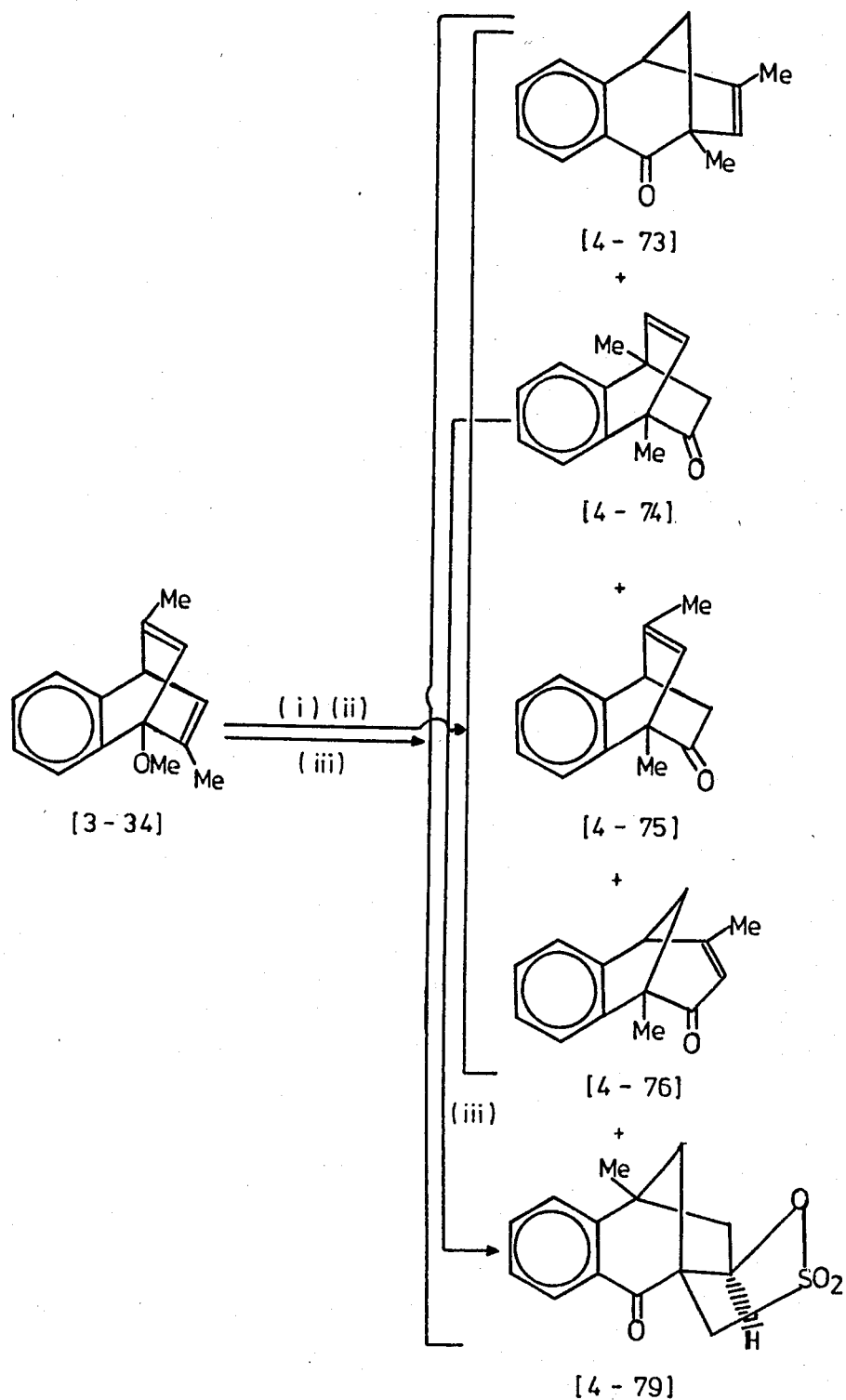
Solvents: (i) CF$_3$COOH; (ii) FSO$_3$H at -78°;

(iii) Conc. H$_2$SO$_4$ (98%).

[Scheme 4-27]

187.

ν_{max} (KBr) 1692, 1355, and 1180 cm^{-1} indicating that the compound is an aryl ketone containing a -CH$_2$-SO$_2$-O- group.

A ^{1}H n.m.r. spectrum showed a methyl singlet at τ 8.53, an AB quartet for the -CH$_2$-SO$_2$-, one doublet at τ 5.75 ($\underline{J}$ = 14 Hz) and the other at τ 6.47 ($\underline{J}$ = 14 Hz) and the remaining ring protons were spread between 7.42 and 7.85. The four aromatic protons, showed as multiplet, three of which were located between τ 2.20 and 2.82, whereas the fourth proton, next to the carbonyl group, appeared as double doublet at 1.83 ($\underline{J}$ = 2.2 Hz, $\underline{J}$ = 7.2 Hz). The remaining proton was a multiplet at τ 5.37.

The ^{13}C n.m.r. spectrum (^{1}H noise and off resonance decoupled) showed resonances at δ 20.23 (-CH$_3$), 39.53(>CH$_2$), 50.05(>CH$_2$), 56.60(>CH$_2$), 63.79(-$\overset{|}{\underset{|}{C}}$-), 70.05(>C-H), 98.76(-C-), 123.73 and 146.89(2xAr-C-), 128.94, 129.41, 130.17, 132.27 (4xAr-CH) and 193.03 (>C=O) p.p.m. from T.M.S. These data strongly support the formulation of the sultone as (4-79):
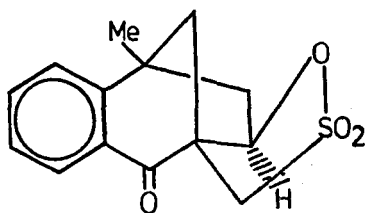
[4 - 79]

It is evident from the available data that the sultone (4-79) clearly results from the sulphonation of a double bond. As discussed earlier in case of the sultone (4-45) from 2,6-dimethyl-1-methoxybenzobarrelene rearrangement that the stage at which the sulphonation occurs is not known. However, it is clear that the formation of the sultone (4-79) is the result of secondary rearrangement.

From the above discussion it is clear that the benzobarrelene (3-31) gives sultone (4-79) via the benzobarrelenone (4-74), which has been further confirmed by the isolation of the latter. Since the benzobarrelenone (4-74)

188.
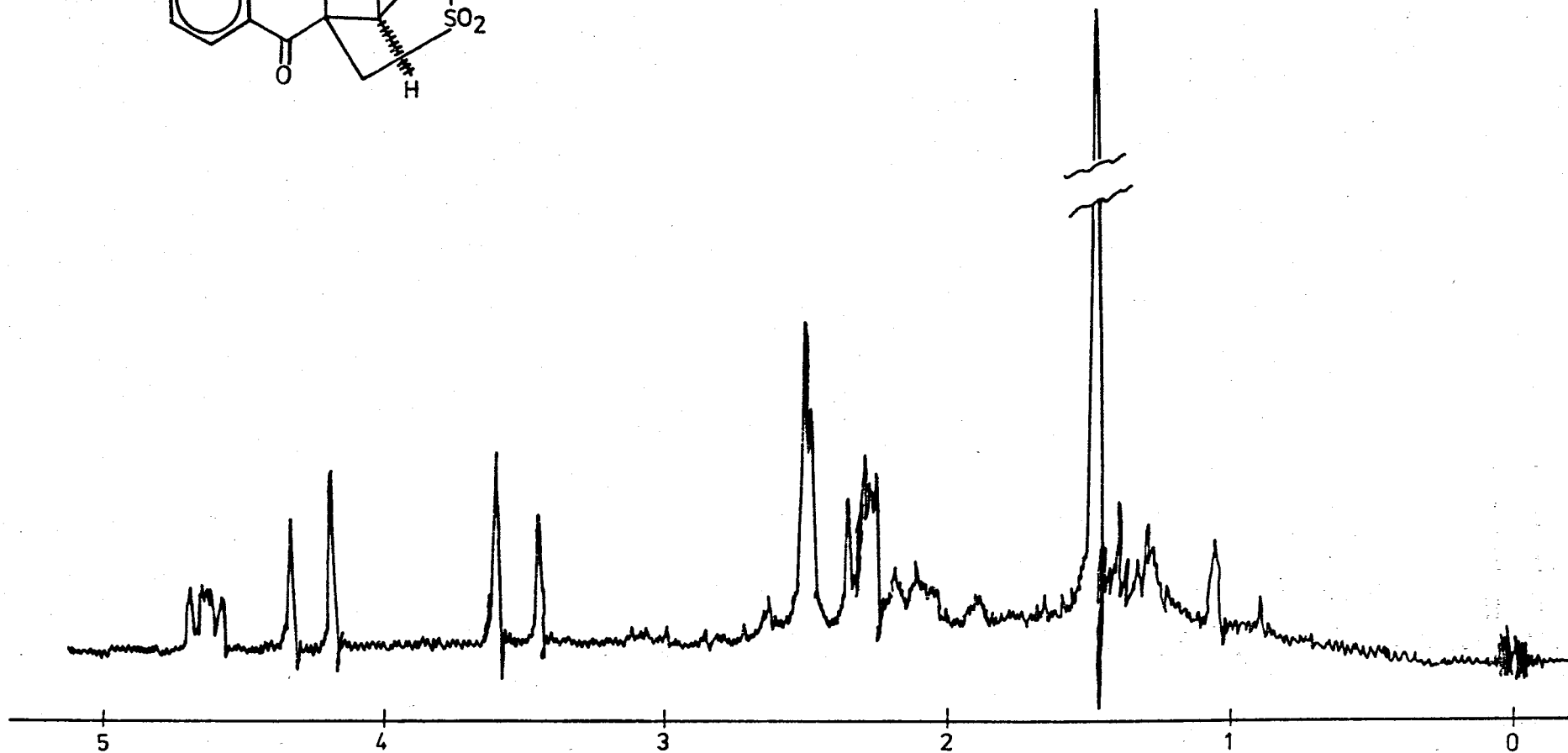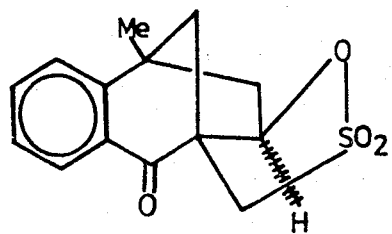
cannot be sulphonated directly, it is most likely that the protonation of the carbonyl group and the rearrangement gives another stable species, the aryl ketone (4-80) as an intermediate. The aryl ketone (4-80) could not be isolated, maybe because of its unstable nature. It subsequently undergoes further rearrangement in the strong acidic medium. The cation produced by the sulphonation presumably results in the intramolecular cyclization to give the sultone (4-79) [Scheme 4-28].

[Scheme 4-28]

189.
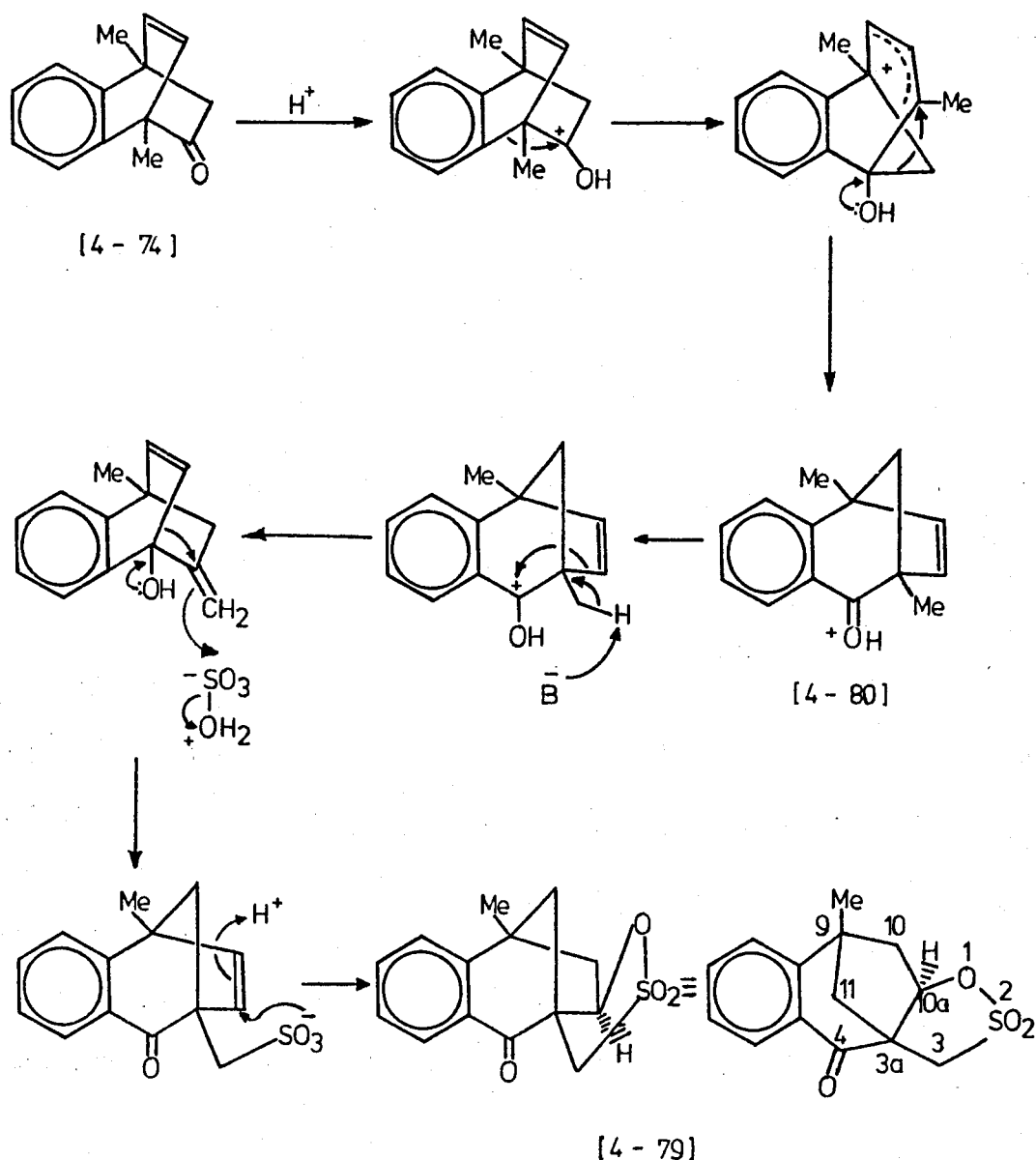
There is another possibility, the reaction may not be proceeding through the unstable intermediate, the aryl ketone (4-80). It may proceed through a more reactive intermediate giving rise to a bridgehead methylene group (4-81), followed by the alkyl migration and the ring closure to the carbocation produced from the sulphonic acid, which would give the sultone (4-79) [Scheme 4-29]. Although it is most unlikely that the reaction will follow such a pathway because of steric problems, the intervention of the sulphonate intermediate (4-81) might stabilize the equilibrium between the two reactive intermediates, thus allowing such migration.

[Scheme 4-29]

190.
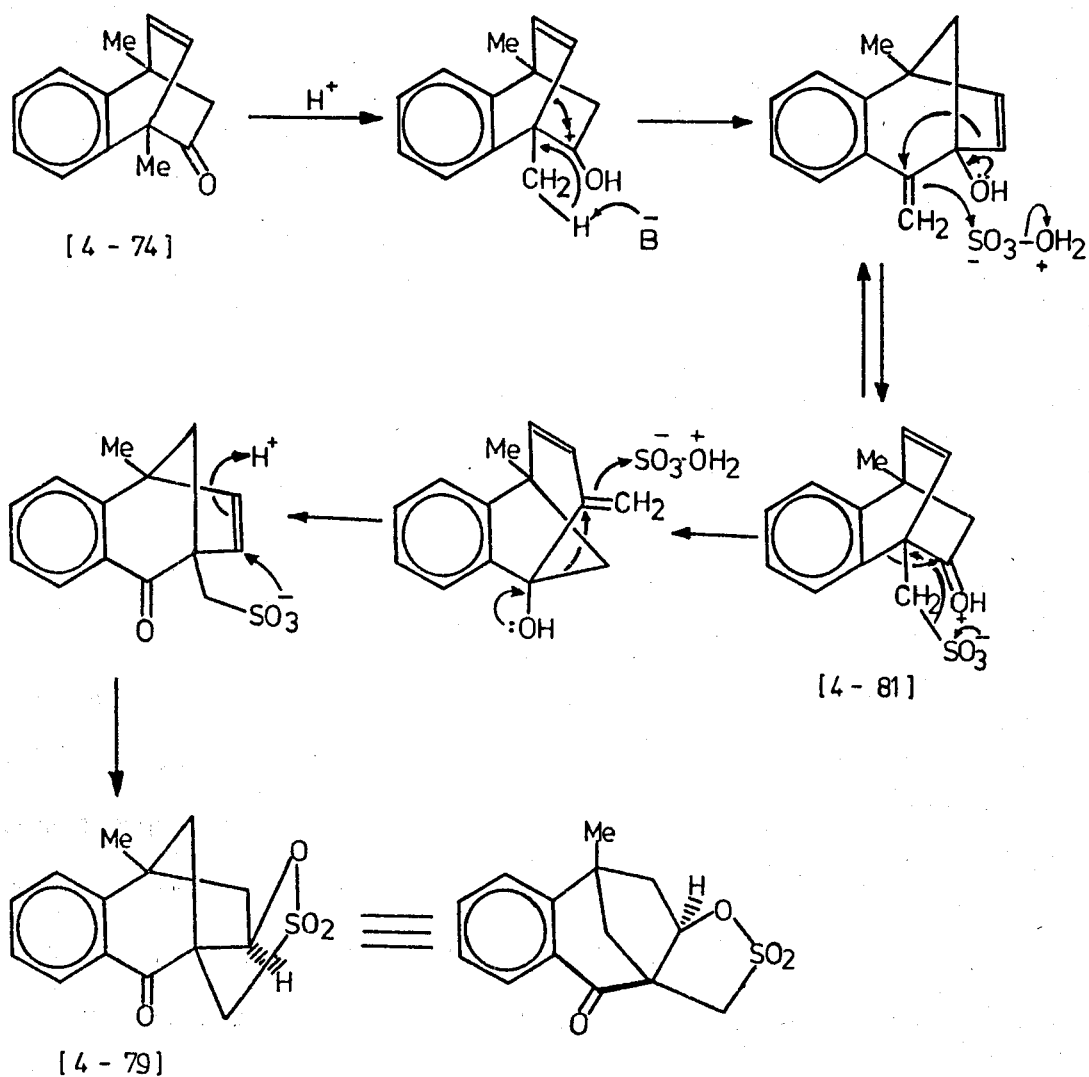
On the basis of previous studies and the spectral evidence, the stereochemistry of the sultone can easily be suggested.

From the above discussion and results one can easily show that two different modes of reaction operate within one molecule. Protonation at C-3 followed by rearrangement at C-2 gave the aryl ketone (4-73) and the α,β-unsaturated ketone (4-76) [Scheme 4-30], whereas protonation at C-2(6) resulted in the rearrangement at C-3(5), led to the formation of two benzo-barrelenones [(4-74) and (4-75)] [Scheme 4-30a]. These products were obtained in either trifluoroacetic acid or the fluorosulphuric acid. These results suggest that in the former case [Scheme 4-30] rearrangement to a C-2 rather than a C-3 carbocation is favoured, whereas in the later case [Scheme 4-30b] the rearrangement to a C-3 is favoured over that at C-2.

[Scheme 4-30a]

191.

[4 - 74]

[3 - 34B]

[4 - 75]

- Me⁺

- Me⁺

a

b

a

b

Me

OMe Me

Me

:OMe Me

Me

Me

Me

Me

Me

:OMe Me

Me

OMe Me

Me

Me
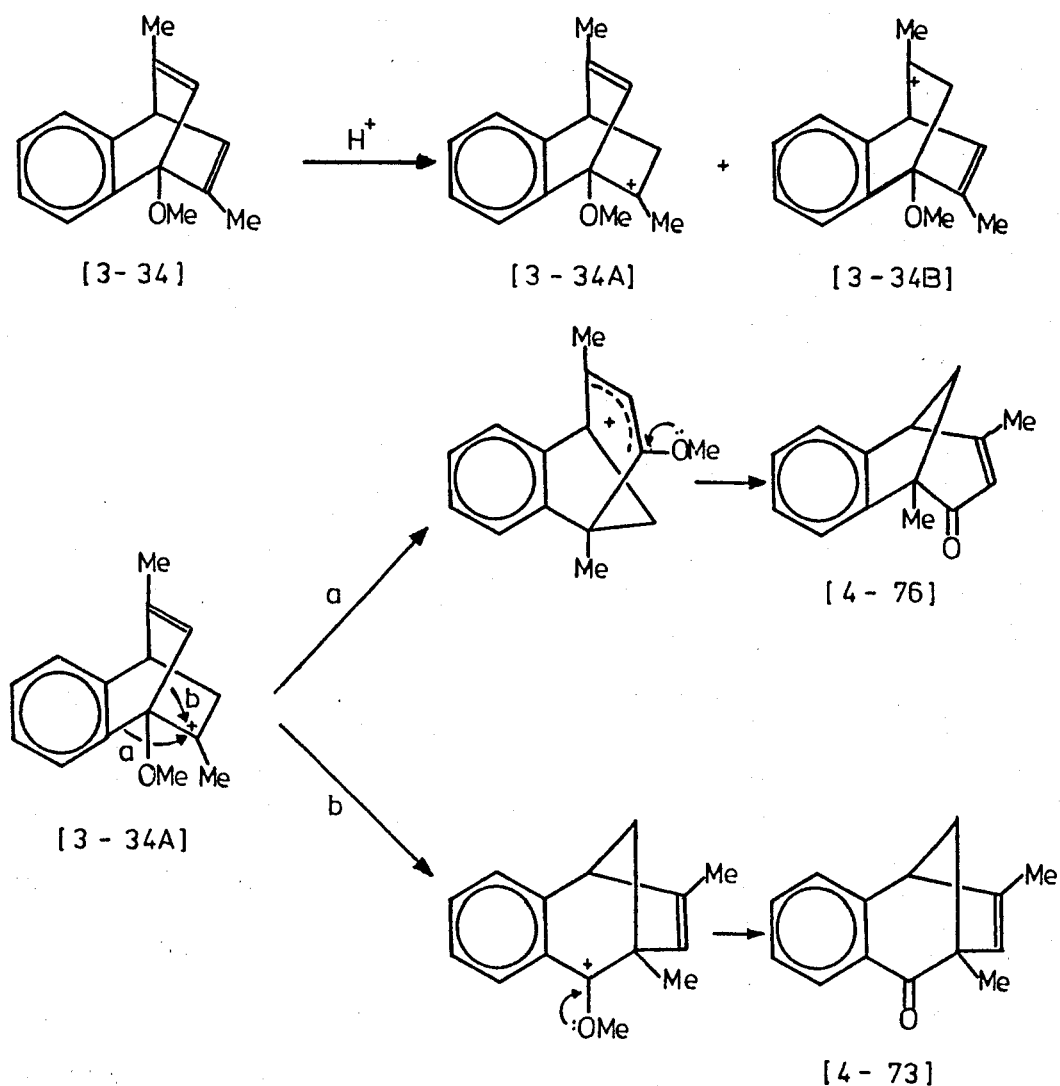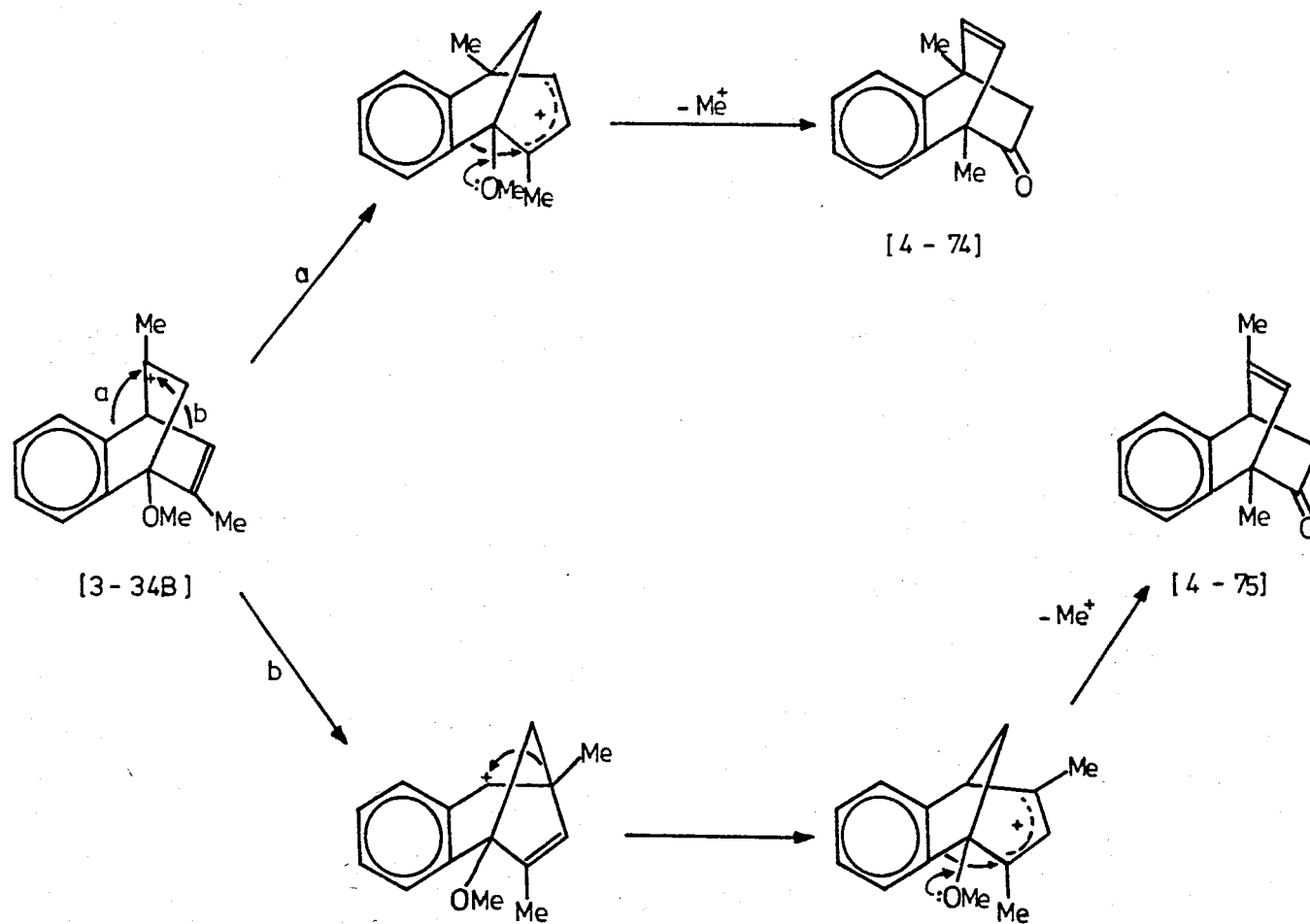
[Scheme 4 - 30b]

The rearrangement in strong acids implicate 1,4-dimethylbenzo-
barrelenone (4-74) a s the important intermediate, again impressively
showing that rearrangement to a C-3(5) carbocation is much more important
than rearrangement to a C-2(6) carbocation.   A [1,2] bridge shift is
required in ion (3-34B$_b$) to account for the formation of 1,5-dimethyl-
benzobarrelenone (4-7⁵). The stability of this intermediate is probably
due to the presence of methyl group at position C-5.   Furthermore the
factors which make [1,2]-bridge shift competitive with circumambulation
probably, suggests the greater ease of such intermediate ion (3-34Bb$_i$)
formation than the other (3-34Bb$_{ii}$).

[3- 34Bb$_i$]   [3-34Bb$_{ii}$]

[1,2] shift

circumambulation

[4 - 75]
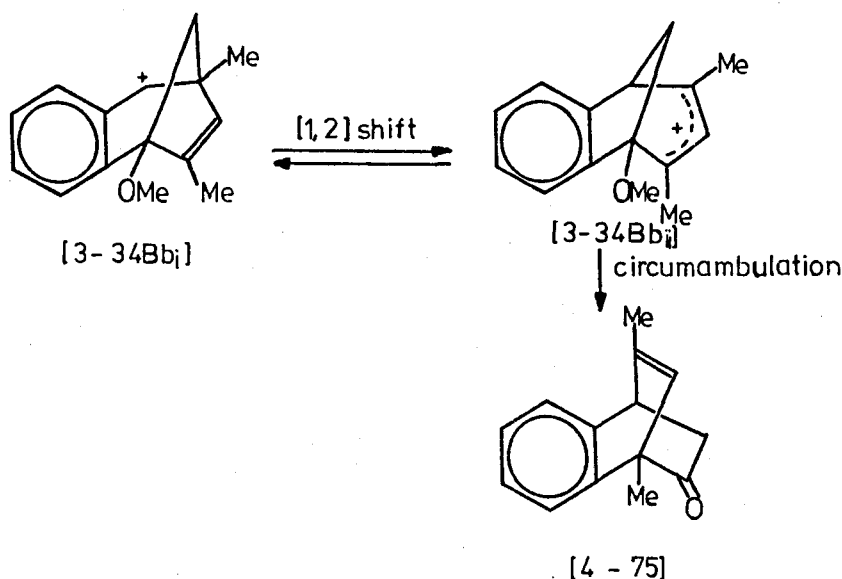
This concept of circumambulation and [1,2] bridge shift has been
suggested by Hart and co-workers,[6] during the acid-catalysed rearrangement
of benzobarrelenes and related compounds.

The formation of the sultone (4-79) as a result of secondary
rearrangement, strongly suggests that the protonation on the carbonyl-group

193.

to give an intermediate carbocation, which results in the rapidly
equilibrating Wagner-Meerwein rearrangements, trapping sulphur trioxide in
the process of equilibration.   From the structural elucidation it seems
clear that the rearrangement of the carbocation (4-81) proceeds via [1,2]
aryl shift and results in the formation of another intermediate which in
turn is stabilized by the HSO_3^+ ion.   Finally the desulphurization and the
attack of the sulphuric acid on the exo-cyclic methylene group, thus
attaining the original aryl carbon skeleton, followed by the ring closure
results in the formation of the sultone (4-79).   The mechanistic approach
seems quite logical.   However, in the absence of the relevant information
regarding intermediate stages along with the specifically labelled studies,
no further comments can be made.

3,5-Dimethyl-1-methoxybenzobarrelene:

The acid-catalysed studies of 3,5-dimethyl-1-methoxytetrachloro-
benzobarrelene (2-10) and its dechlorinated analogue (3-35) in strong acid
medium did not give any α,β-unsaturated ketones or aryl ketones.   However,
the products obtained in the present study are analogous to those obtained
by S.V. Ley[2] using 3,5-dimethyl-1-methoxytetrafluorobenzobarrelene.   The
protonation of the olefinic double bond was directed by the presence of
methyl groups to give initially a cation at C-3 ($\equiv$C-5), as predicted earlier.

Because of solubility problems 3,5-dimethyl-1-methoxytetrachloro-
benzobarrelene (2-10) was heated under reflux in trifluoroacetic acid for
12 h.   Two products were obtained, which, on the basis of accumulated
chemical and spectral data were identified as the tetrachlorobenzobarrelenone
(4-82) and the lactone (4-83).   When the compound (2-10) was dissolved in
concentrated sulphuric acid and then immediately quenched with an excess

of ice, a quantitative yield of a single product was obtained and which was characterized as the lactone (4-83). In order to verify whether the 4,6-dimethyltetrachlorobenzobarrelenone (4-82) was the key intermediate for the formation of the lactone, it was dissolved in concentrated sulphuric acid and after workup gave a 95% yield of the lactone (4-83). The structure of the benzobarrelenone (4-82) was established by comparison with the ketone (2-11) obtained as a minor product from the reaction of tetrachlorobenzyne with 3,5-dimethylanisole. Similar results were obtained in reactions using 3,5-dimethyl-1-methoxybenzobarrelene (3-35). (Scheme 4-31).

$X_4 = Cl_4$ [4 - 82]
$X_4 = H_4$ [4 - 84]

$X_4 = Cl_4$ [2 - 10]
$X_4 = H_4$ [3 - 35]

$X_4 = Cl_4$ [4 - 83]
$X_4 = H_4$ [4 - 85]
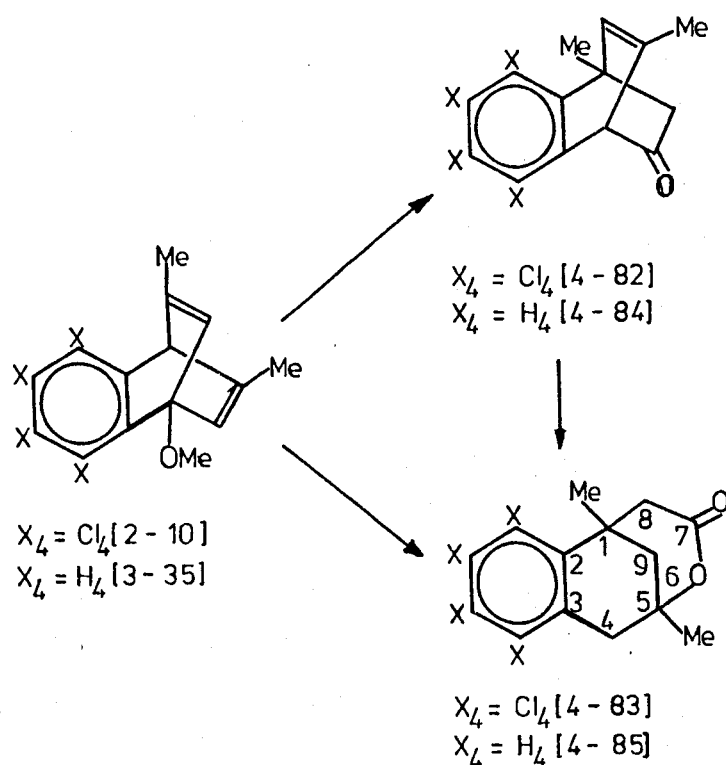
[Scheme 4-31]

The correct structures of the benzobarrelenones [(4-82) and (4-84)] and the lactones [(4-83) and (4-85)] were assigned on the basis of elemental analytical and spectral data. Mechanistically, the formation of the

195.

lactones [(4-83) and (4-85)] from the benzobarrelenones [(4-82) and (4-84)] could be explained as shown in Scheme 4-32.

$X_4 = Cl_4$ [4 - 82]
$X_4 = H_4$ [4 - 84]

$X_4 = Cl_4$ [4 - 83]
$X_4 = H_4$ [4 - 85]
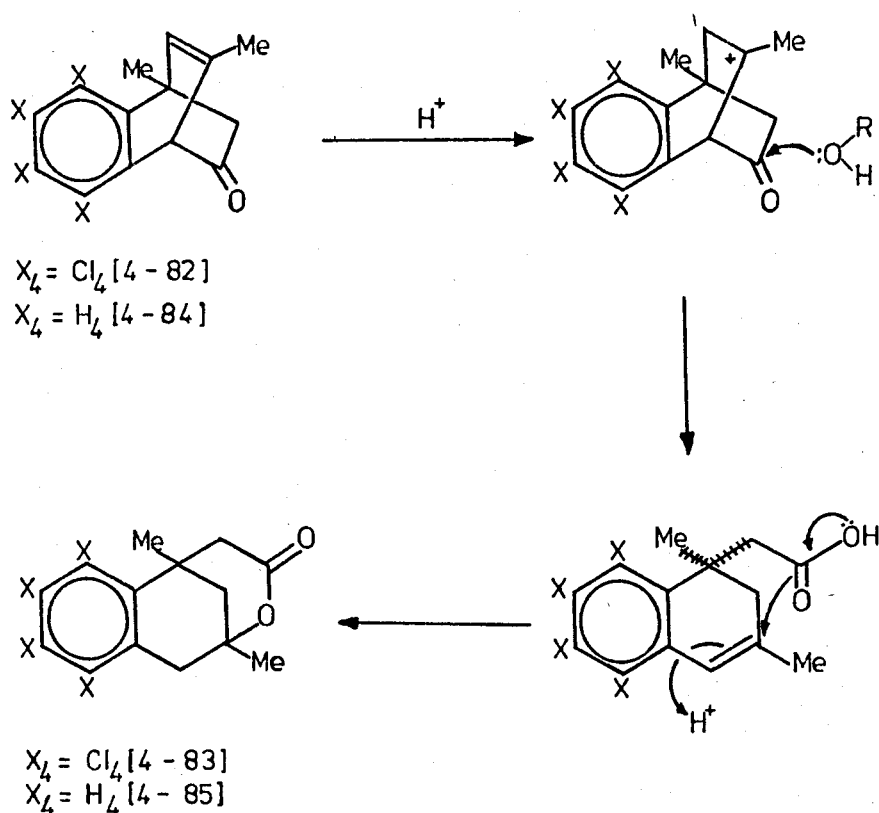
[Scheme 4-32]

Having verified that the ketones [(4-82) and (4-84)] could be converted into the lactones [(4-83) and (4-85)], a number of other chemical transformations were carried out to confirm the structures of the lactones [(4-83) and (4-85)]. Reduction with lithium aluminium hydride gave the diols [(4-87) and (4-88)] which were converted back into the lactones [(4-83) and (4-85)] on oxidation with pyridinium chlorochromate or Jones' reagent.

196.

$X_4 = Cl_4 [4-83]$
$X_4 = H_4 [4-85]$

$X_4 = Cl_4 [4-87]$
$X_4 = H_4 [4-88]$
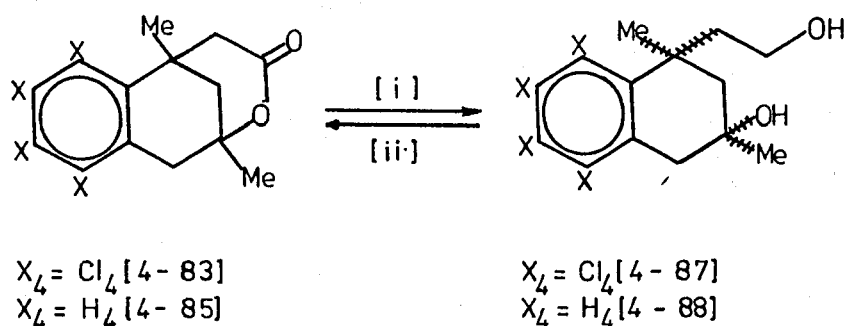
Reagents: (i) $LiAlH_4$; (ii) Pyridinium chlorochromate or Jones' reagent

[Scheme 4-33]

Barkhash and his co-workers[7] have studied the ring opening reactions of the tetrafluorobenzobarrelenones with base. So on the established lines, we hydrolysed the ketones [(4-82) and (4-84)] with aqueous sodium hydroxide in tetrahydrofuran. In each case we obtained an acid [(4-89), (4-90)]. These were characterized as their methyl esters [(4-91), (4-92)]. The acids [(4-89), (4-90)] were readily cyclized to the lactones [(4-83), (4-85)] in the presence of concentrated sulphuric acid. These reactions are summarized in Scheme 4-34.

$X_4 = Cl_4 [4-82]$
$X_4 = H_4 [4-84]$

$X_4 = Cl_4 [4-89]$
$X_4 = H_4 [4-90]$

$X_4 = Cl_4 [4-91]$
$X_4 = H_4 [4-92]$

$X_4 = Cl_4 [4-83]$
$X_4 = H_4 [4-85]$

[Scheme 4-34]

197.
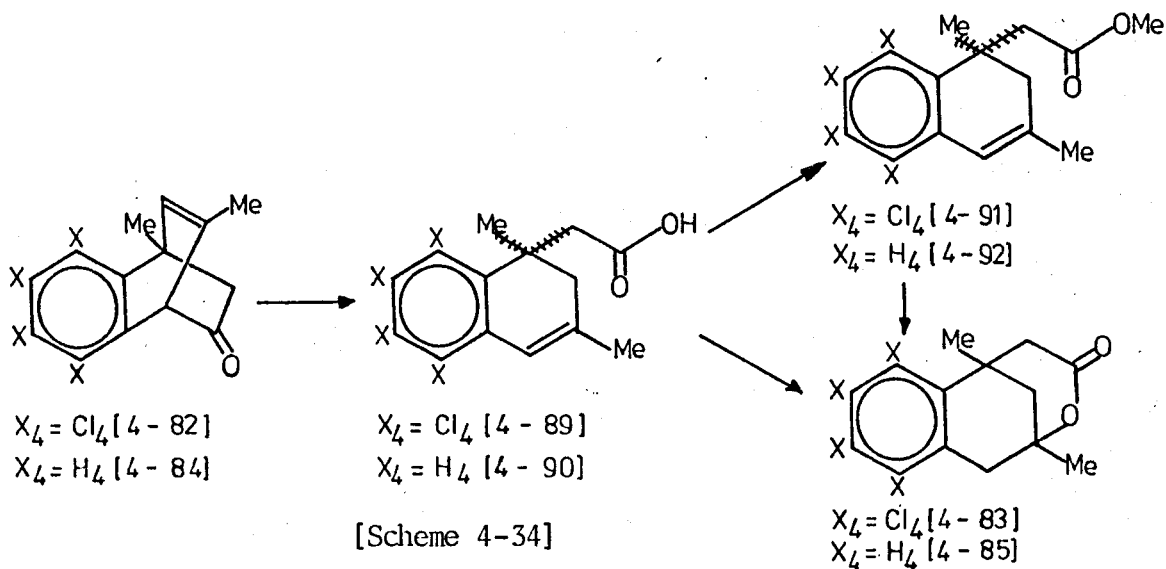
On the basis of the above discussion it is clear that the rearrangement of 3,5-dimethyl-1-methoxytetrachlorobenzobarrelene (2-10) and its dechlorinated analogue (3-35) is dominated by the protonation at C-2 ($\equiv$C-6) followed by the rearrangement at C-3 ($\equiv$C-5) to give 4,6-dimethyl-benzobarrelenones [(4-82) and (4-84)] [Scheme 4-31]. The results suggest that the directing effect of the methyl groups substitution at positions C-3 and C-5 are completely controlling the reactions and thus restrict the direction of protonation to initially afford the benzobarrelenones [(4-82) and (4-84)] only.

2,3,5-Trimethyl-1-methoxybenzobarrelene:

In a preceding section, we discussed the acid-catalysed rearrangements of 2,5-dimethyl-1-methoxybenzobarrelene (3-34). The four major ketonic products were shown to be produced in a non-equilibrating system. Hart and his co-workers[66] showed that the hexamethylbenzobarrelenone (4-1) rearranges in an acidic medium to afford an equilibrium mixture of four ketones. In the rearrangements of 7,8,9,10-tetrachloro- and 2,5-dimethyl-1-methoxybenzo-barrelene [(2-4) and (3-34)], the two compounds behave differently in strong acidic media. We decided therefore to extend the study to 2,3,5-trimethyl-1-methoxytetrachlorobenzobarrelene (2-12) [see Chapter 2] and 2,3,5-trimethyl-1-methoxybenzobarrelene (3-37) [see Chapter 3].

When 2,3,5-trimethyl-1-methoxytetrachlorobenzobarrelene (2-12) was dissolved in concentrated sulphuric acid (98%) and then quickly quenched with ice, three isomeric ketones were obtained in the ratio 1:3:1. The products were eventually identified by chemical and spectroscopic methods as the α,β-unsaturated ketone (4-93), the benzobarrelenone (4-94), and the lactone (4-95), along with some minor products which could not be identified [Scheme 4-35].

198.

In an attempt to isolate intermediates we decided to carry out the reactions under less vigorous conditions. Thus, heating the compound (2-12) under reflux in trifluoroacetic acid gave two major products, the α,β-unsaturated ketone (4-93) (17%) and the benzobarrelenone (4-94) (55%). The lactone (4-95) was obtained in quantitative yield when the benzobarrelenone (4-94) was dissolved in concentrated sulphuric acid and quenched with ice cold water. The rearrangement of compound (2-12) was also studied in aqueous sulphuric acid (80%) in the hope that the cations produced might be trapped, but in this case some of the unchanged starting material (7%) was recovered in addition to the above three compounds.

Similar results were obtained when 2,3,5-trimethyl-1-methoxybenzobarrelene (3-37) was treated with either trifluoroacetic acid at room temperature or with concentrated sulphuric acid (98%). In refluxing trifluoroacetic acid the major product was the lactone (4-98) (80%) whereas at room temperature the benzobarrelenone (4-97) (78%) was obtained as the major product [Scheme 4-35]. No additional product could be trapped at any intermediate stage. From these results it appears that the carbocation is being generated predominantly at C-3, which very rapidly undergoes rearrangement to give the benzobarrelenones [(4-94) and (4-97)], which in the presence of strong acid undergo fragmentation and cyclization to give the lactones [(4-95) and (4-98)].

The exact nature of the reaction pathway is not completely clear and requires further investigation.

Although no aryl-ketones have been isolated from the above reactions they may have been formed in low yields. We must ask why they are not formed in amounts similar to those of the α,β-unsaturated ketones. One

199.

$X_4 = Cl_4$ [4- 93]
$X_4 = H_4$ [4- 96]

+

$X_4 = Cl_4$ [4 - 94]
$X_4 = H_4$ [4 - 97]

[ii][iii].   +

$X_4 = Cl_4$ [2-12]
$X_4 = H_4$ [3-37]

$X_4 = Cl_4$ [4- 95]
$X_4 = H_4$ [4 - 98]
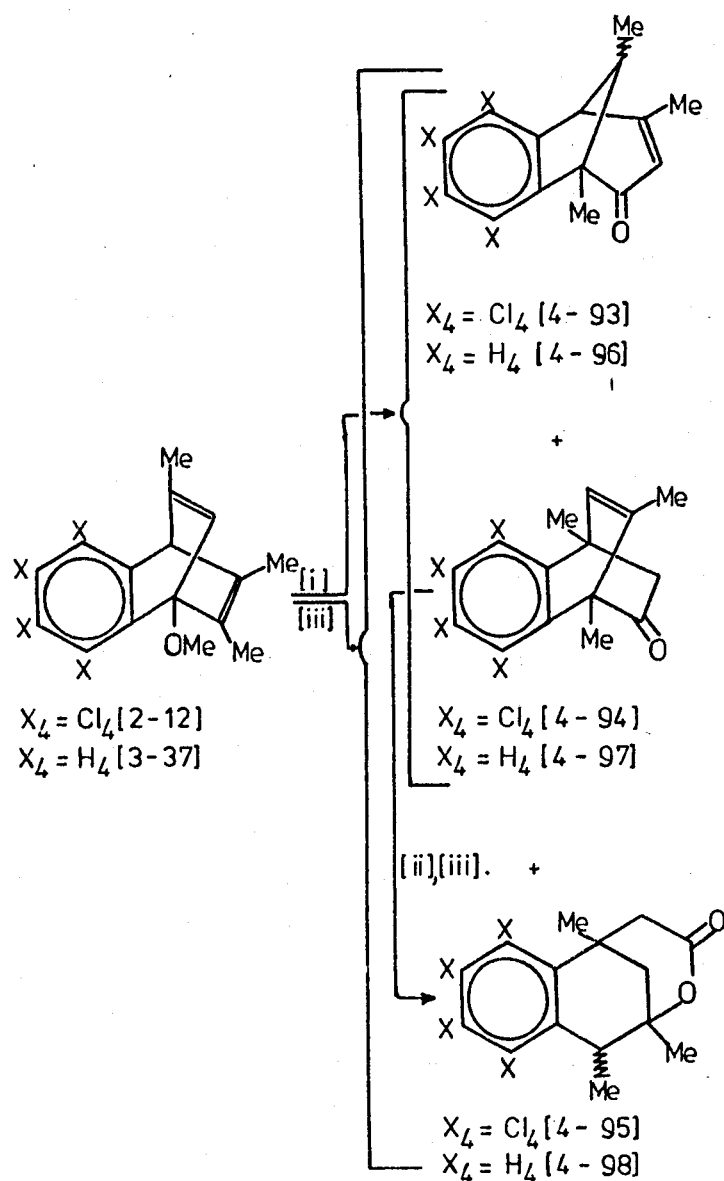
Solvents: (i) CF_3COOH (ii) boiling CF_3COOH (iii) conc. H_2SO_4.

[Scheme 4-35]

possible explanation is that a tight-ion pair involving the bisulphate ion
is involved in the reactions in sulphuric acid.   This could, of course,
collapse to a half-sulphate ester.   The subsequent rearrangement would
be directed by the stereochemistry of such a tight-ion pair, or ester.

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It would be predicted that approach of the bisulphate ion to the exo-face of the initial carbocation would be preferred. A similar argument would apply to those reactions involving trifluoroacetic acid. The charge delocalization around the olefinic double bond on protonation could be shown as:

$$X_4 = Cl_4$$
$$X_4 = H_4$$

$$X_4 = Cl_4$$
$$X_4 = H_4$$
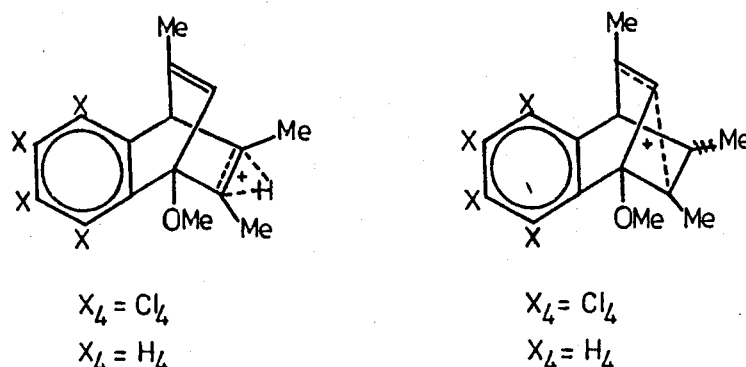
Interconversions of the lactones [(4-95) and (4-98)] of the type discussed earlier were carried out and are as summarized in Scheme 4-36.

$$X_4 = Cl_4 \, [4 - 94]$$
$$X_4 = H_4 \, [4 - 97]$$

$$X_4 = Cl_4 \, [4 - 99]$$
$$X_4 = H_4 \, [4 - 100]$$

[i]

[ii]

$$X_4 = Cl_4 \, [4 - 101]$$
$$X_4 = H_4 \, [4 - 102]$$

[iii]

[iv]

$$X_4 = Cl_4 \, [4 - 95]$$
$$X_4 = H_4 \, [4 - 98]$$
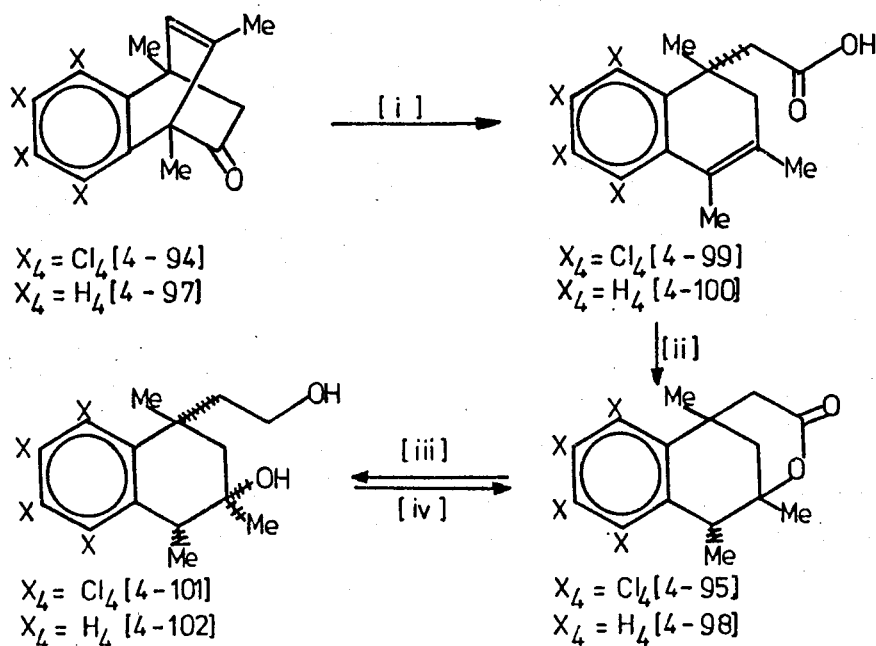
Reagents: (i) Aq. NaOH-T.H.F. ; (ii) Conc. H_2SO_4; (iii) $LiAlH_4$;
(iv) $C_5H_5\overset{+}{N}H.CrO_3Cl^-$ or Jones' reagent.

[Scheme 4-36]

201.

The results obtained support the view that the α,β-unsaturated ketones [(4-93) and (4-96)] and the benzobarrelenones [(4-94) and (4-97)] are formed by the mechanisms outlined in Schemes [4-37] and [4-38].

$X_4 = Cl_4 [2-12]$
$X_4 = H_4 [3-37]$

$X_4 = Cl_4 [4-93]$
$X_4 = H_4 [4-96]$

[Scheme 4-37]

202.

$X_4 = Cl_4 [2-12]$
$X_4 = H_4 [3-37]$

$X_4 = Cl_4 [4-94]$
$X_4 = H_4 [4-97]$

$X_4 = Cl_4 [4-103]$
$X_4 = H_4 [4-104]$

[Scheme 4-38]

203.
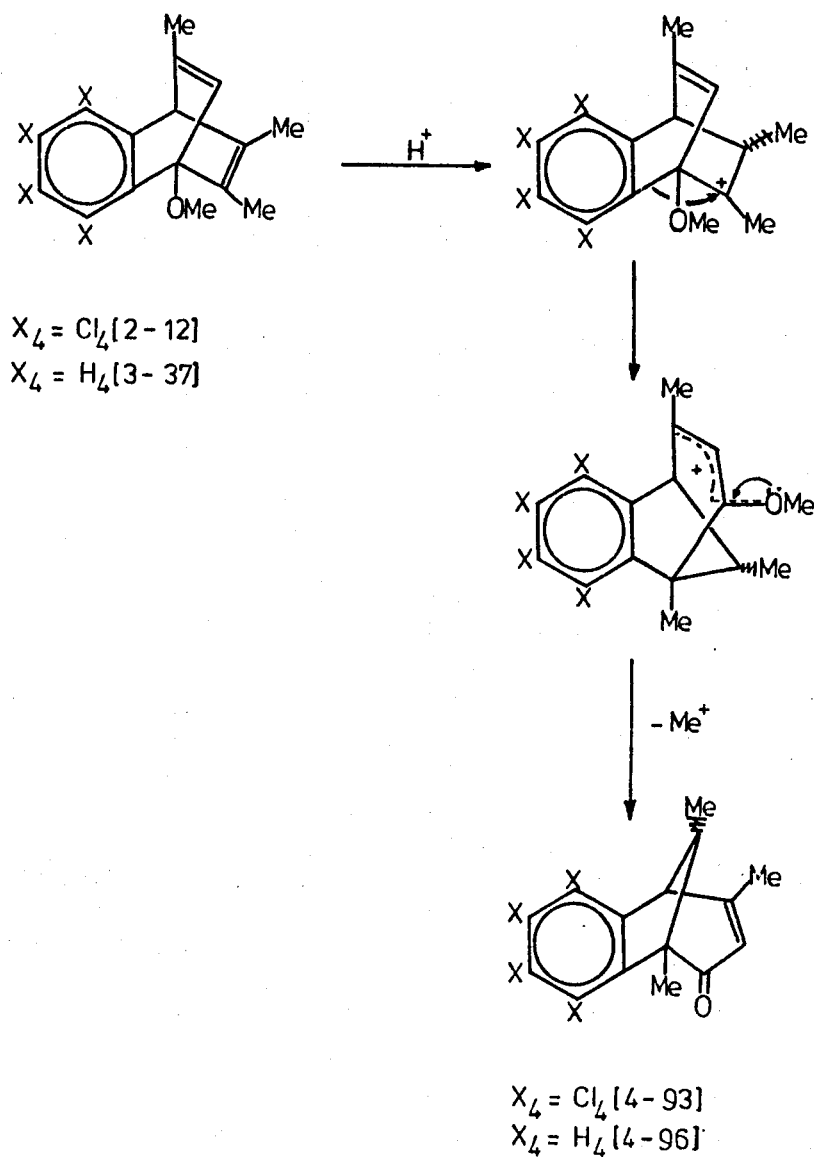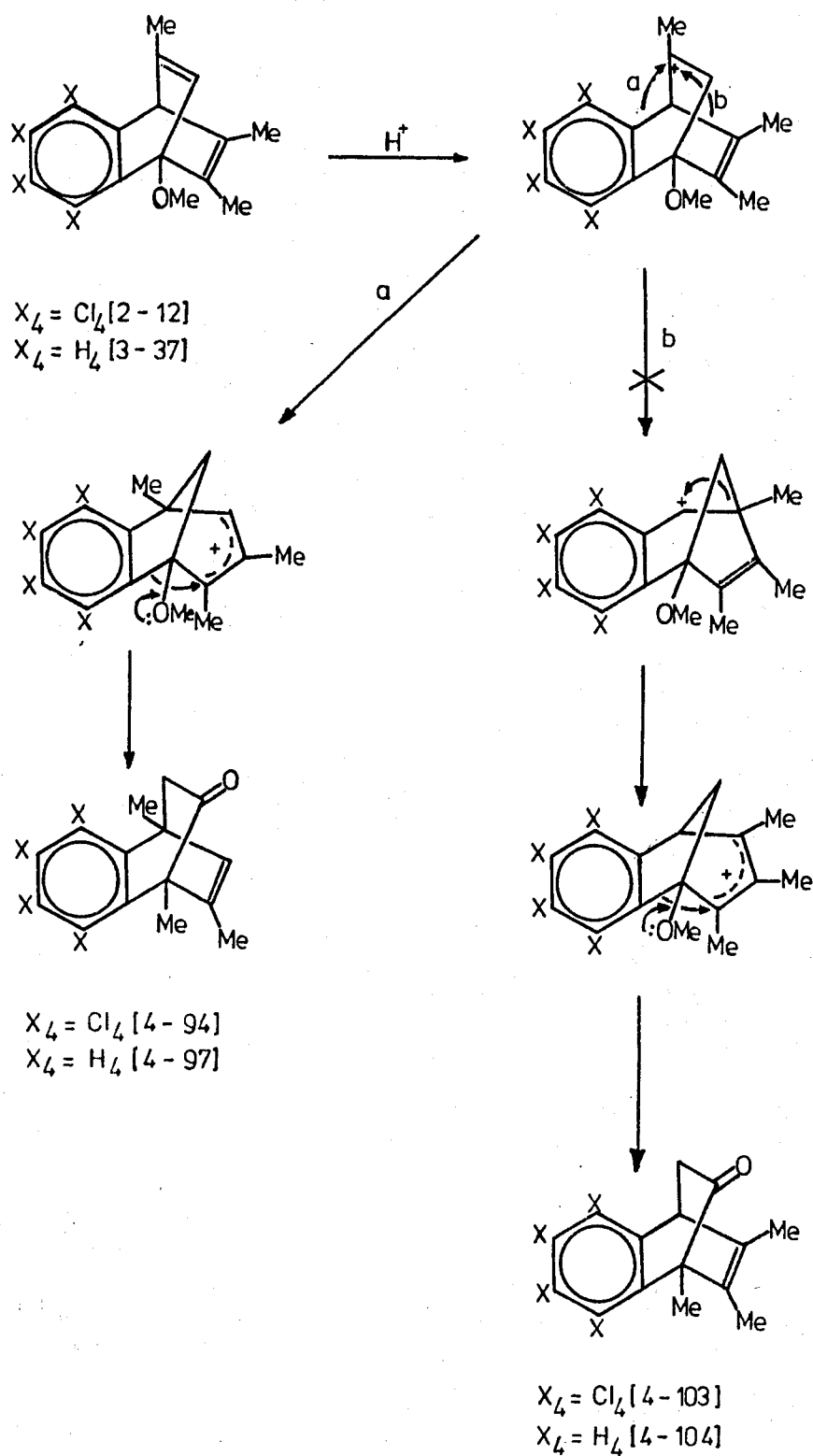
From the above discussion it is clear that two different reaction pathways are encountered, in which protonation at position C-3 followed by the rearrangement at C-2 gave only the α,β-unsaturated ketones [(4-98) and (4-96)] [Scheme 4-37], whereas protonation at position C-2 followed by rearrangement at C-3 resulted in the formation of the benzobarrelenones [(4-94) and (4-97)] [Scheme 4-38]. These results suggest that in the first case rearrangement to a C-2 rather than a C-3 carbocation is favoured, however, because of steric hindrance only one product was formed. Similarly, when rearrangement occurs at C-3 carbocation gives rise to only one of the benzobarrelenone types [(4-94) or (4-97)] instead of two benzobarrelenones; the absence of the additional ones [(4-103) or (4-107)] again strongly suggests that steric problems allow the reaction to proceed in one direction only. The absence of the aryl ketones or the benzobarrelenones [(4-103) or (4-104)] could be explained by simply saying that they do form in the reaction mixture in very minute quantities which could not be isolated, on the basis of the discussion presented in the preceding sections.

2,3,5,6-Tetramethyl-1-methoxybenzobarrelene:

2,3,5,6-Tetramethyl-1-methoxytetrachlorobenzobarrelene (2-14) and its dehalogenated analogue (3-38) incorporate a number of obvious structural features present in the more simple systems [(2-5) and (2-10)]. They provide an interesting opportunity for competition between the various rearrangements already discussed. The results were unexpected, the reaction products were complex mixtures, the compositions of which varied with the acid strength and reaction time.

The reaction of 2,3,5,6-tetramethyl-1-methoxytetrachlorobenzobarrelene (2-14) with trifluoroacetic acid at room temperature gave the aryl ketone

(4-105) (6%), a mixture of the benzobarrelenones [(4-106) and (4-107)] (total yield 22%), the α,β-unsaturated ketone (4-108) and traces of a new ketone, later shown on the basis of accumulated chemical and spectral evidence to be the tetramethyltetrachlorobenzosemibullvalenone (4-109) [Scheme 4-39].   All the four major products formed were those expected according to previously suggested mechanistic pathways. The formation of the semibullvalenone (4-109) must result from secondary rearrangement. The ratio of the benzobarrelenones [(4-106) and (4-107)] to the other products varied considerably from reaction to reaction and appeared to depend upon the precise reaction conditions [Scheme 4-39].

When the rearrangement was conducted in boiling trifluoroacetic acid, the benzobarrelenones [(4-106) and (4-107)] were obtained as the major products along with the aryl ketone (4-105), the α,β-unsaturated ketone (4-108), and the benzosemibullvalenone (4-109) in low yield. An additional unknown product was also formed as shown by an analysis of the olefinic region of the ^{1}H n.m.r. spectrum.

Treatment of 2,3,5,6-tetramethyl-1-methoxytetrachlorobenzobarrelene (2-14) with fluorosulphuric acid in dichloromethane at -0$^{\text{o}}$ gave a mixture of traces of the aryl ketone (4-105), the α,β-unsaturated ketone (4-108), the benzobarrelenones [(4-106) and (4-107)], but the major product was the tetrachlorobenzosemibullvalenone (4-109) which was isolated in 80% yield. The four products of the rearrangement were the same as those obtained from the trifluoroacetic acid rearrangements at room temperature.   The formation of the benzosemibullvalenone (4-109) could not be rationalized within the usual mechanistic Scheme as the product of a primary rearrangement. Presumably the key intermediate for its generation was the benzobarrelenones [(4-106) and (4-107)], since from the above experiments it was very clear that the

yield of the benzobarrelenones had gone down remarkably, whereas the amounts of the other two ketones (4-105) and (4-108) remained almost unchanged.

Thus treatment of the benzobarrelenones [(4-106) and (4-107)]with fluorosulphuric acid gave exclusively the tetrachlorobenzosemibullvalenone (4-109) in 70% yield. Interestingly when the tetrachlorobenzosemibullvalenone (4-109) was heated with trifluoroacetic acid it gave a new compound in 72% yield which was later shown, on the basis of accumulated chemical and spectral data, to be the dihydro-tetra-chlorobenzopentalenone (4-110). These results led us to the conclusion that either of the benzobarrelenones [(4-106) or (4-107)] give rise to the benzosemibullvalenone (4-109) which in turn give the other new product, the dihydro-benzopentalenone (4-110).

The rearrangement of 2,3,5,6-tetramethyl-1-methoxytetrachlorobenzo-barrelene (2-14) in concentrated sulphuric acid at room temperature gave a complex mixture of the products. Surprisingly neither of the above benzobarrelenones [(4-106) and (4-107)] were found in the reaction mixture but a new ketone was obtained in 45% yield, along with the traces of the aryl ketone (4-105), the α,β-unsaturated ketone (4-108), the benzosemibullvalenone (4-109) and the dihydro-benzopentalenone (4-110). Lastly 0.5% of the lactone (4-111) was also recovered.

Not surprisingly, treatment of either of the benzobarrelenones [(4-106) and (4-107)] or the benzosemibullvalenone (4-109) with concentrated sulphuric acid (ca. 98%) at room temperature, on quenching with ice cooled water gave a mixture of two products, the new unknown ketone (42%), and the dihydro-benzopentalenone (4-110) (27%).

A significant product, formed in very low yield in the latter reaction, was the α,β-unsaturated ketone (4-108) which, although not isolated, was detected by means of analytical t.l.c. It is clear that the dihydro-

207.

[4 – 105]

+

[4 – 112]

+

[4 – 108]

+

[4 – 110]

+

[4 – 111]

[iv]

[2 – 14]

[i]

[ii],[iii]

[4 – 105]

+

[4 – 106]

+

[4 – 107]

+

[4 – 108]

+

[4 – 109]

[4 – 110]

Solvents: (i) CF$_3$ COOH at room temperature
(ii) CF$_3$ COOH at B.T.
(iii) F.SO$_3$H.
(iv) conc. H$_2$SO$_4$.

[Scheme 4-39]
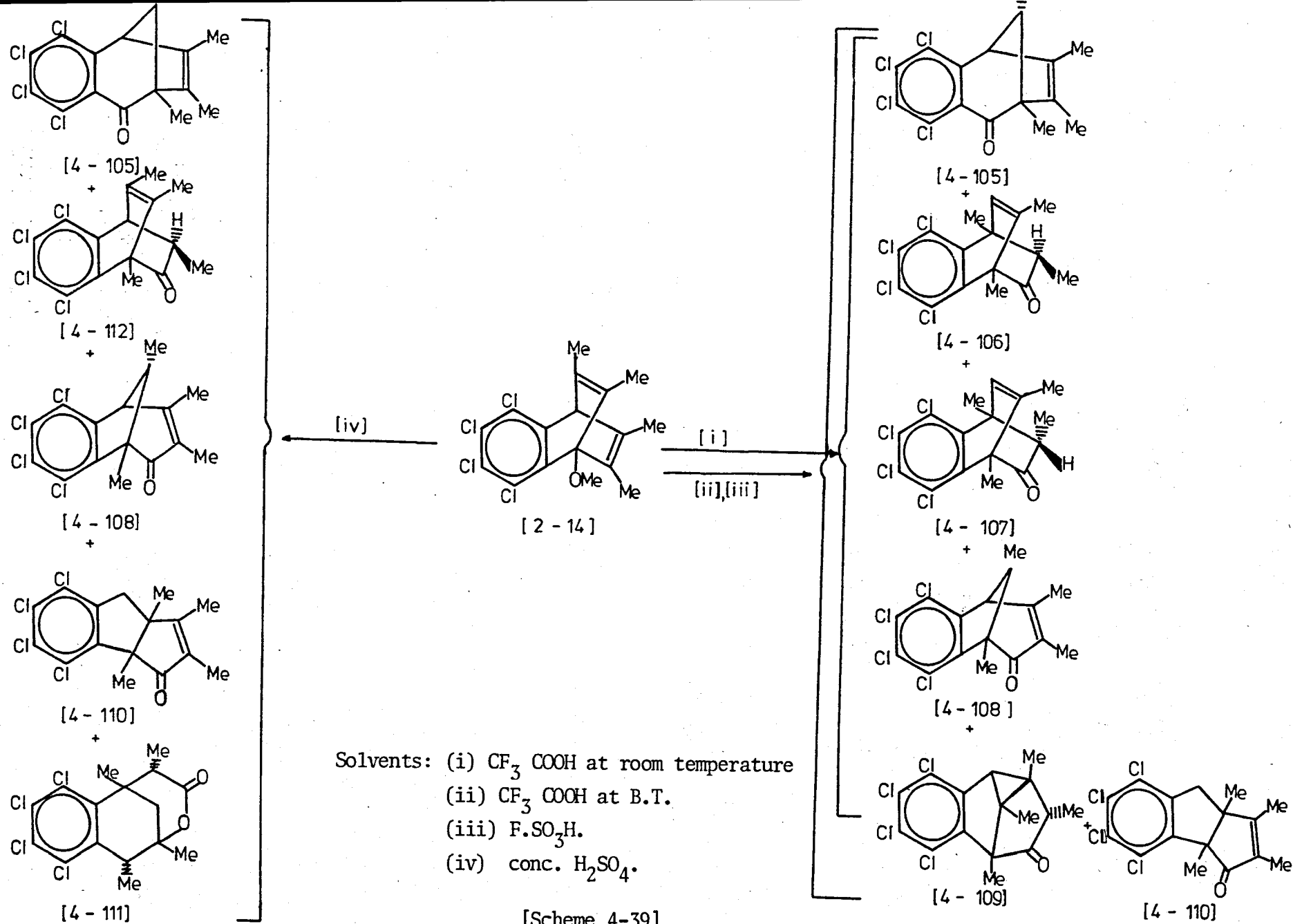
benzopentalenone (4-110) could have been formed from the tetrachlorobenzo-barrelenones [(4-106) or (4-107)] by way of the benzosemibullvalenone (4-109) and this is the most reasonable explanation. The available chemical and spectral data on the new ketone showed that it was another member of the benzobarrelenone family, the tetramethyltetrachlorobenzobarrelenone (4-112) [Scheme 4-39].

The assignment of the correct structures of these ketones (4-109), (4-110) and (4-112) is of prime importance to any discussion of the place which these molecules occupy in the bicyclooctane systems. Spectral data helped in establishing their structures.

Elemental analysis of the benzosemibullvalenone (4-109) showed the molecular formula to be $C_{16}H_{14}Cl_4O$. The infrared spectrum confirmed that the ketone is not conjugated and probably it is in a five membered ring (ν_{max} KBr 1750 cm^{-1}). The dihydro-benzopentalenone (4-110) exhibits ν_{max} KBr 1720 and 1610 cm^{-1}. The latter band is strong and suggests the presence of a conjugated double bond; the former as usual indicates the ketone, but if the compound is an α,β-unsaturated ketone the position of the band indicates a five-membered ring as a structural sub-unit. The 90 MHz ^{1}H n.m.r. spectrum showed the following resonances; methyl at C-1 appeared as a singlet at τ 8.29, the other two methyls appeared as singlets at τ 8.56 and 8.58, whereas the fourth methyl which was present next to the carbonyl group appeared as a doublet at τ 9.24. The bridgehead proton did not seem to couple with any other position and appeared at τ 7.62. The other proton which was present at position C-3 appeared as a quartet at τ 7.43. The other relevant information about the structure of the molecule was obtained by comparison with the 2,5-dimethyltetrachlorobenzo[6,7]tricyclo[3.2.1.0^{2,8}]oct-6-ene-4-one, which appeared in the 2,5-dimethyl-1-methoxytetrachlorobenzobarrelene (2-4) acid-catalysed rearrangements.

The 90 MHz ^{1}H n.m.r. spectrum of the dihydro-tetrachlorobenzopentalenone (4-110) was much simpler, the four methyls appeared at τ 7.98, 8.33, 8.47, and 8.71 as sharp singlets whereas the methylene group appeared as an AB quartet at τ 6.69 and 7.16. The magnitude of the coupling constant ($|\underline{J}|$ = 18.0 Hz) is in the range characterizing a diastereotopic methylene group. Further, comparative studies with the benzosemibullvalenone (4-109) suggest that the immediate environments of all of these methyl groups are similar.

The ^{13}C n.m.r. spectrum (both ^{1}H noise and off resonance decoupled) showed resonances at δ 8.57 (-CH$_3$), 12.45 (-CH$_3$), 15.07 (-CH$_3$), 21.89 (-CH$_3$), 41.77 (>CH$_2$), 55.69 (-Ċ-), 65.47 (-Ċ-), 134.65 (>C=), 141.04 and 143.06 (2 x Ar-C-), 169.49 (>C=) and 204.92 (>C=O); the remaining four aromatic carbons showed resonances at δ 128.81, 130.52, 131.71 and 132.60 p.p.m. from T.M.S.
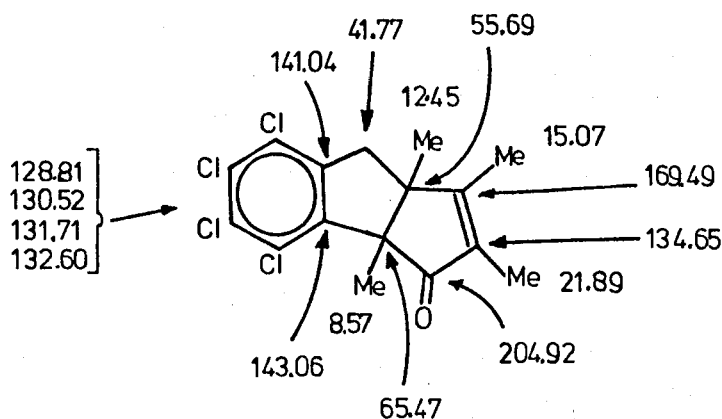
[4 - 110]

From comparative studies of the ^{1}H n.m.r. spectra of the three ketones, the α,β-unsaturated ketone (4-108), the benzosemibullvalenone (4-109), and the dihydro-benzopentalenone (4-110), it is clear that the immediate environments of all of these methyl groups are similar.

Fig. 4-1.

Chemical shift in p.p.m.

Moles [Eu(dpm)$_3$] / Mole [Ketone 4-110]

Fig. 4-2.
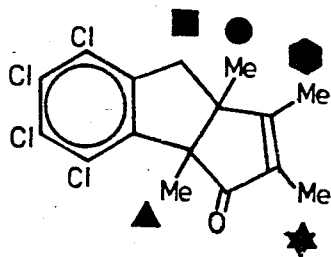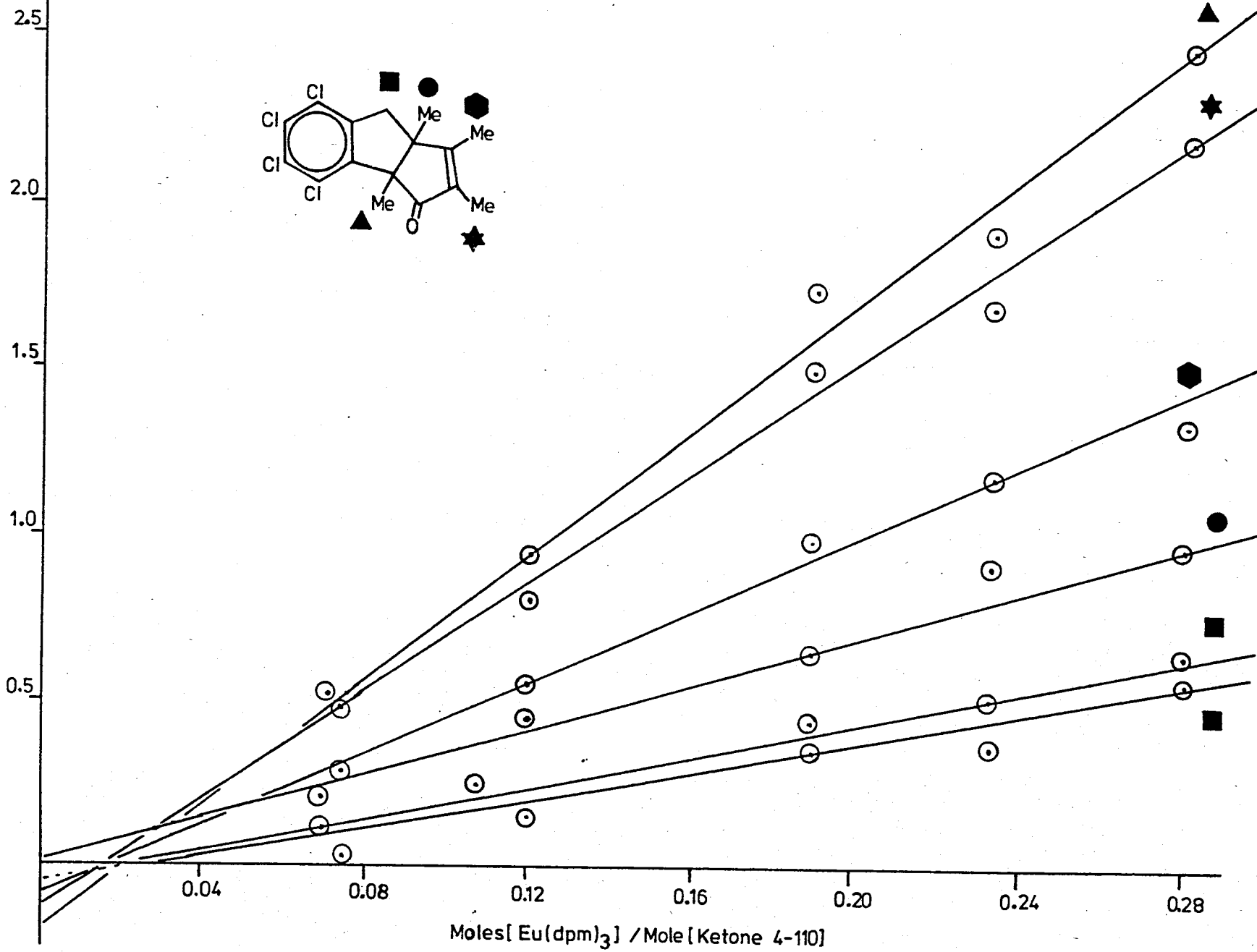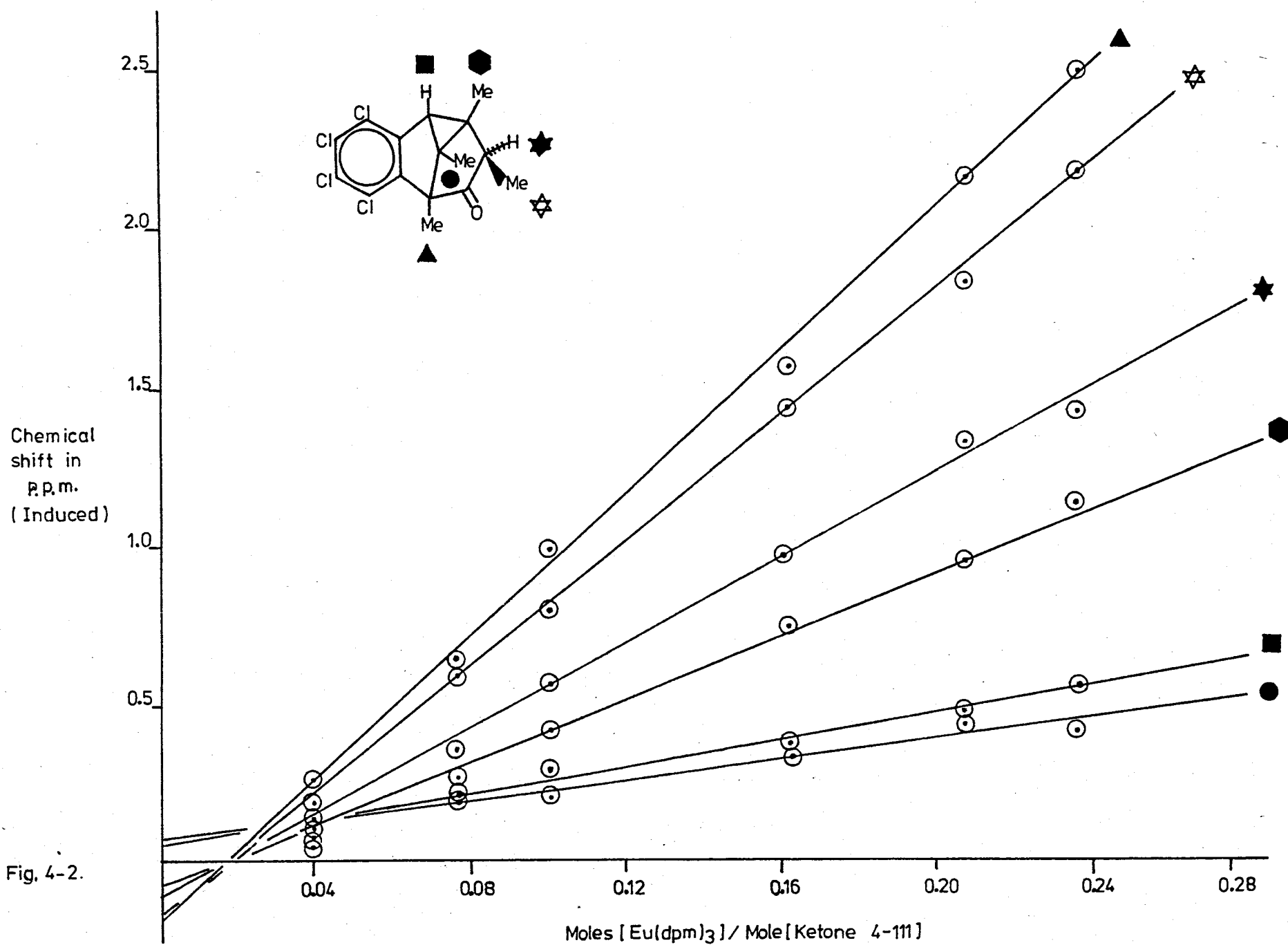
In the presence of tris[dipinaloylmethanato-]europium (III)

[Eu(dpm)$_3$][9] the methyl groups near to the carbonyl group produces changes in the ^{1}H n.m.r. spectrum of the dihydro-benzopentalenone (4-110) which bear a remarkable similarity to those produced in similar experiments with the benzosemibullvalenone (4-109). The sharp methyl group resonances at τ 7.98 and 8.71 respectively were shifted at similar rates to lower field (3.8 p.p.m./mole/mole, and 3.52 p.p.m./mole/mole respectively), whereas the methyl groups resonances at τ 8.33 and 8.47 respectively were shifted to lower field at a much smaller rate (ca. 0.92 p.p.m./mole/mole and ca. 1.2 p.p.m./mole/mole respectively) (fig. 1 and 2).

The significant difference between the results obtained were the overall larger magnitude of the shifts induced in the spectrum of the dihydro-benzopentalenone (4-110) by comparison to those observed with the benzo-semibullvalenone (4-109). The observed difference was not due to the concentration effect and is in accord with the Lewis acid complexation effect (similar effects have been observed in related saturated compounds). These results further confirm the presence of the structural units shown in fig. 1.

Further, the dihydro-benzopentalenone (4-110) is derived chemically from the benzosemibullvalenone (4-109) and more remotely from the benzo-barrelenones [(4-106) and (4-107)]. A possible mechanistic pathway has been suggested which accounts for the formation of all of the intermediates [Scheme 4-40]. The olefinic double bond of the dihydro-benzopentalenone (4-110) could not be catalytically reduced either by using palladium on carbon or platinum oxide under one atmosphere of hydrogen. Scale molecular models revealed that the methyl on the endo-face of the folded bicyclo[3.3.0]octadiene part of the molecule restricts the approach to the β-carbon of the α,β-unsaturated system, whereas the presence of the other methyl group also

210.

obstructs the approach from the _exo_-face thus creating a steric compression in the reduction transition state.

The formation of the third benzobarrelenone (4-112) in the concentrated sulphuric acid reaction is peculiar and needs careful consideration. Before we go any further, let us discuss the correct assignment of the structure of this new molecule.

Elemental analysis showed the molecular formula to be $C_{16}H_{14}Cl_4O$. The infrared spectrum confirmed the presence of the carbonyl group (ν_{max} KBr 1730 cm^{-1}) which was in the same region as those of the other similar systems. The 90 MHz ^{1}H n.m.r. spectrum showed the following resonances: the bridgehead proton appeared as a tight doublet at τ 6.91 and the other proton appeared as a multiplet at τ 7.36, whereas out of the four methyl groups three showed up as singlets at τ 8.36, 8.47, and 8.62 and the fourth methyl group appeared as a doublet at τ 8.63. Spin-spin decoupling experiments helped in assigning their correct positions. The 220 MHz ^{1}H n.m.r. did not reveal any further details.

Treatment of 2,3,5,6-tetramethyl-1-methoxytetrachlorobenzobarrelene (2-14) with concentrated sulphuric acid gave the new benzobarrelenone (4-112) along with the other products as reported earlier [Scheme 4-41]. However, none of the benzobarrelenones [(4-106) and (4-107)] was found in the reaction mixture. Interestingly, when the other benzobarrelenones [(4-106) and (4-107)] were treated with concentrated sulphuric acid and quenched with ice cooled water, the products obtained were the new benzobarrelenone (4-110) and the dihydro-benzopentalenone (4-110) [Scheme 4-42]. Whereas the new benzobarrelenone (4-112) and the dihydro-benzopentalenone (4-110) remained unchanged in the presence of strong acid, only the decomposed products were obtained at much longer treatment.

It is clear from the above discussion that the formation of the new benzobarrelenone (4-112) from the other benzobarrelenones [(4-106) and (4-107)] resulted from the common carbocation. From the earlier studies of Hart and Cristol and their co-workers[6,17] on the circumambulation process of acid-catalysed rearrangements of the benzobarrelenone systems, the initial protonation in strong acidic media should be relatively more common than those products which require a 1,2-bridge shift before their formation. The observations of these authors have also shown that intramolecular equilibration of the highly alkylated benzobarrelenone systems can occur in acidic media. On the basis of Hart's study[6] one can envisage the charge distribution effect among the olefinic double bonds thus restricting or guiding the various protonation patterns.

The results obtained support the view that the various products are formed as outlined in Schemes [4-40] to [4-42].

The acid-catalysed rearrangements of the dechlorinated analogue (3-38) did not create any problems. Thus, treatment of 2,3,5,6-tetramethyl-1-methoxybenzobarrelene (3-38) with trifluoroacetic acid at room temperature gave the aryl ketone (4-113), a mixture of the benzobarrelenones [(4-114) and (4-115)] and the α,β-unsaturated ketone (4-116) in the ratio 1:4:1. No additional product was detected. The reaction proceeded in agreement with the suggested mechanistic pathway. Presumably the protonation was directed by the symmetrically substituted methyl groups to form the carbocations [(2-14A) and (2-14B)].

When the reaction was repeated by heating the compound (3-38) under reflux in trifluoroacetic acid, an additional product appeared along with the above four ketones. This additional product was shown on the basis of

212.

[Scheme 4-40]

213.

[2 - 14]

[2 - 14A]

[4 - 105]

[4 - 108]

[2 - 14B]

[4 - 106]

[4 - 107]

[4 - 112]
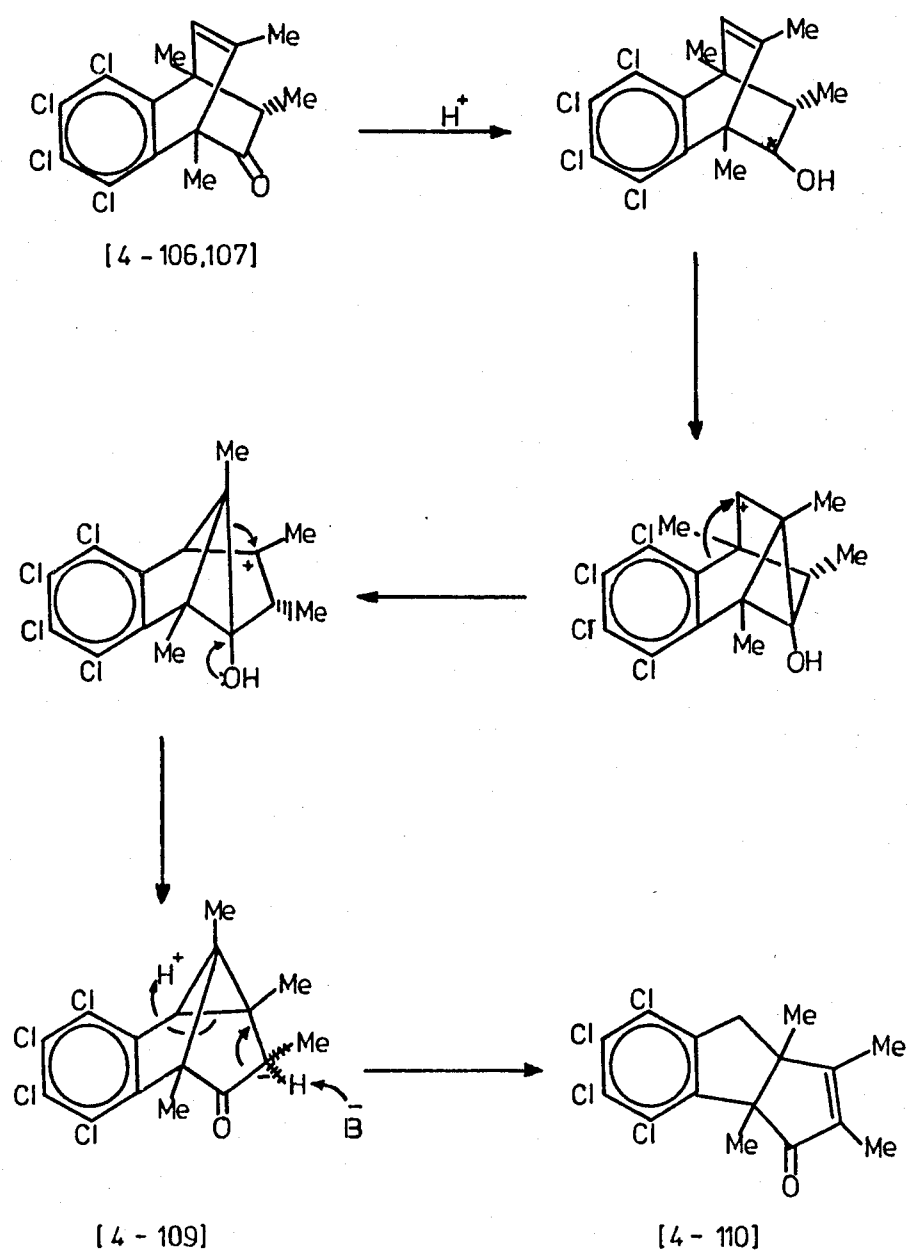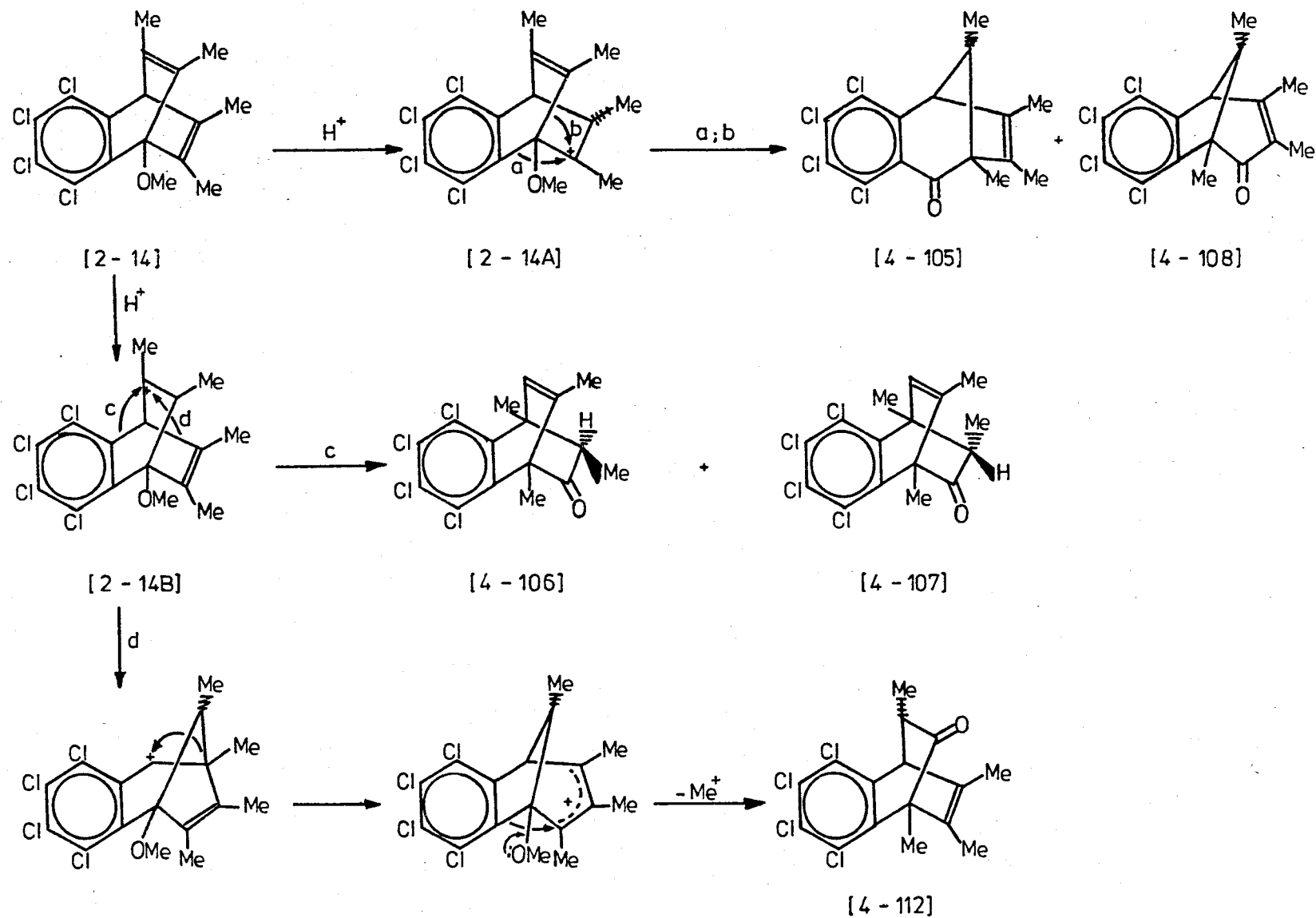
[Scheme 4-41]

[Scheme 4-42]

215.
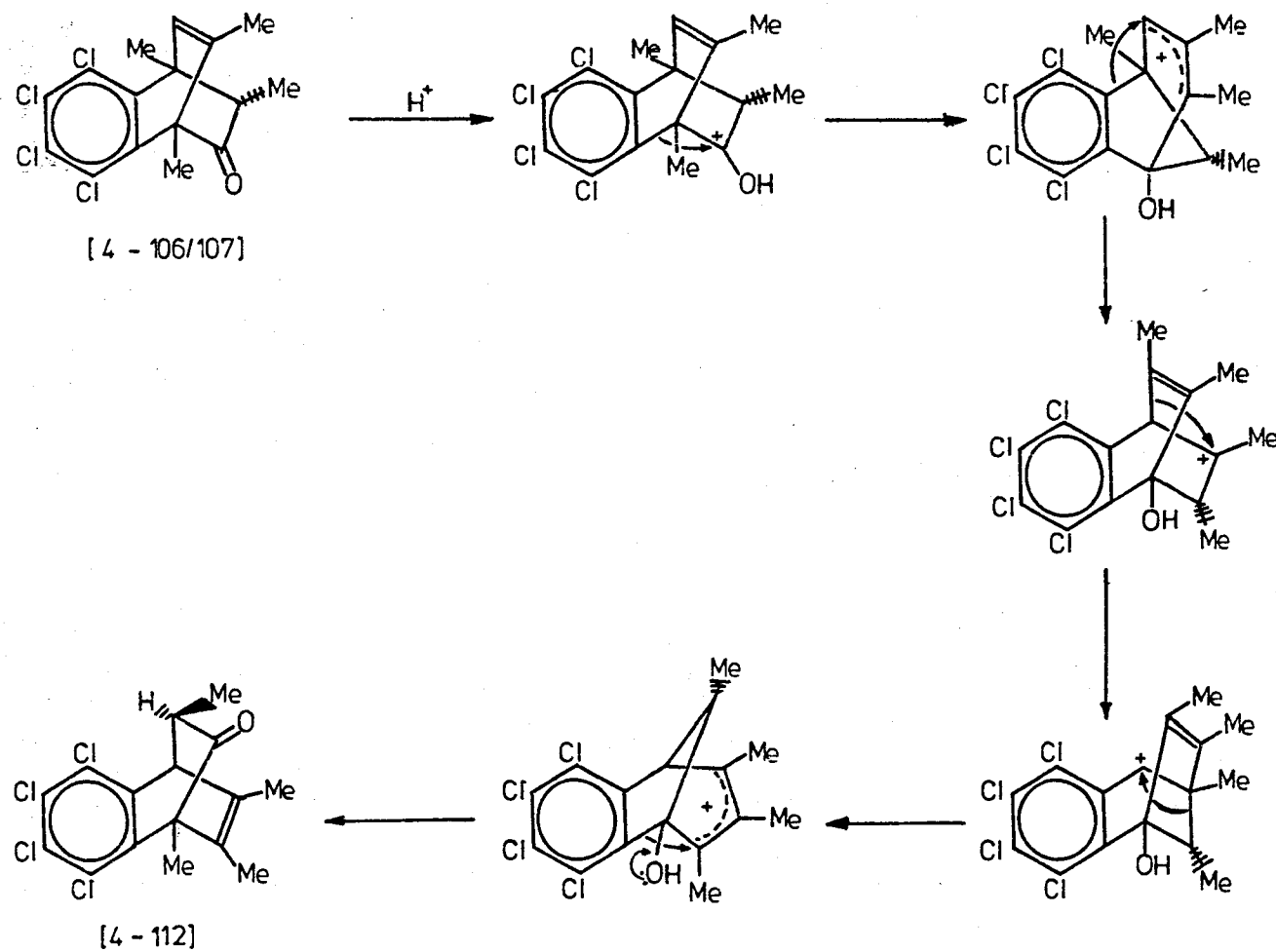
accumulated chemical and spectral data to be the lactone (4-117). However, it was also observed that the yields of the benzobarrelenones [(4-114) and (4-115)] had gone down, presumably these were the source of the lactone.

Treatment of 2,3,5,6-tetramethyl-1-methoxybenzobarrelene (3-38) with concentrated sulphuric acid gave the same five products as in the case of boiling trifluoroacetic acid. Only trace amounts of the benzobarrelenones [(4-114) and (4-115)] were obtained, the major product in this case was the lactone (4-117). The stability of the α,β-unsaturated ketone (4-116) and the rapid degradation of the aryl ketone (4-113) to multitudinous uncharacterised products under conditions which favoured formation of the lactone (4-117), led to the conclusion that the benzobarrelenones [(4-114) and (4-115)] were the only possible source of the lactone. The reaction of tetramethylbenzo-barrelenones [(4-114) and (4-115)] with concentrated sulphuric acid gave the lactone (4-117) in 92% yield [Scheme 4-43].

The formation of the various products can be explained as shown in Scheme 4-41. The formation of the lactone (4-117) from the benzobarrelenones [(4-114) or (4-115)] could be shown as follows:

[4 - 114 / 115]

[4 - 117]
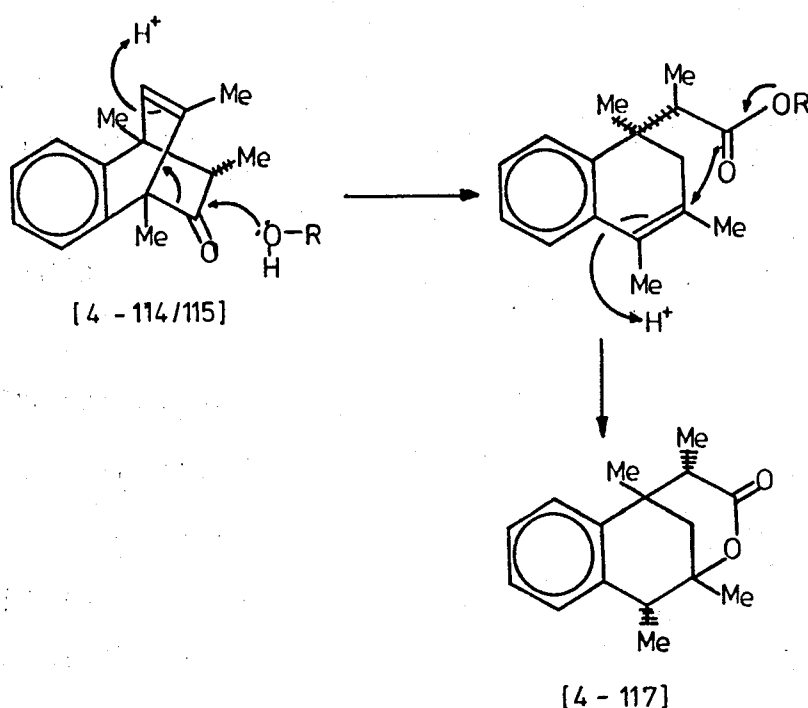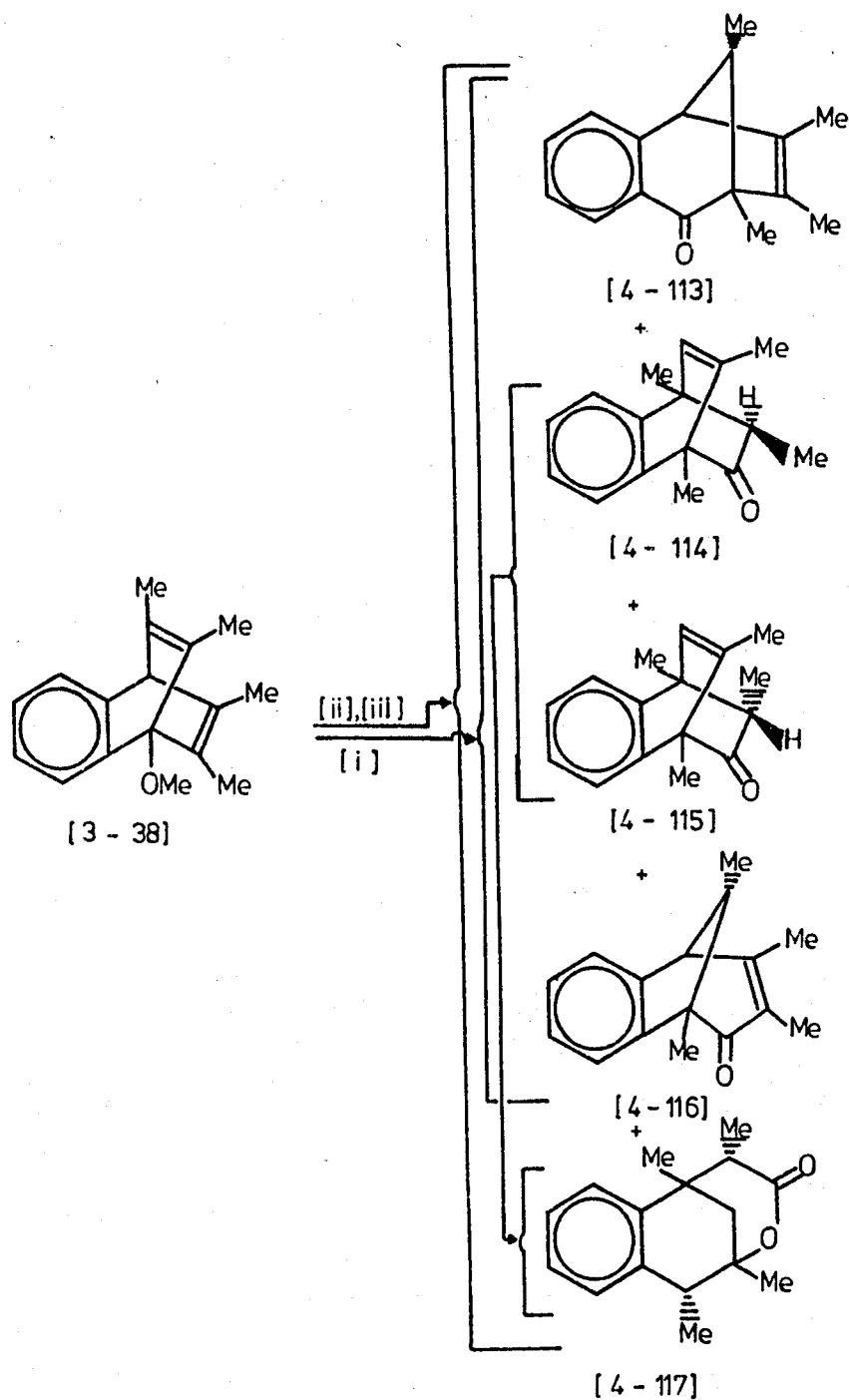
[Scheme 4-43]

Solvents: (i)   CF$_3$COOH at R.T.

(ii) Refluxing CF$_3$COOH.

(iii) Conc. H$_2$SO$_4$.

[Scheme 4-43]

From the above discussion, we have seen that a number of different
reaction pathway operates, which result in different products.

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General Conclusions:

It has been shown that the rearrangements of the substituted 1-methoxybenzobarrelenes in acid led to a number of interesting products. A comparative study has been made between the halogenated and the non-halogenated compounds of the substituted 1-methoxybenzobarrelenes under the solvolytic conditions and it was observed that the presence of halogen atoms do not significantly alter the reaction pathway in the acidic medium. However, the presence of chlorine atoms create solubility problems, which in return offers crystallinity to the molecules.

Some attempts have been made to establish the mechanistic pathways for the rearrangements on the basis of the available data. The acid-catalysed rearrangements of compounds with symmetrically and non-symmetrically placed methyl groups in the 1-methoxybenzobarrelene, discussed in this chapter, have produced interesting answers to some of the questions. The rearrangements are governed by the regioselective protonation of the olefinic double bonds. The initial protonation is dominated by the influence of the methyl-substituents, but as the acidity of the reaction medium increases, the tendency to form a cation remote from the methoxy group becomes important, thus resulting in the other products. The presence of extra methyl-group promotes further rearrangements by stabilising the carbocations formed by secondary rearrangements.

The various explanations advanced in this chapter are based on the earlier work published by Heaney and his coworkers[1,2,3,21] in this laboratory. The relative importance of each of the intermediates must be assessed according to the ease with which it is interconverted with the other intermediates. The nature of the olefinic-substituents and the rate of protonation are clearly important factors in controlling the product ratio and the secondary rearrangements, however, more work needs to be done on these systems.

EXPERIMENTAL

EXPERIMENTAL SECTION

General Procedures:

    The general procedures are as described in
previous chapters.

    The following reagents were prepared according to
the established methods and were used for the purposes required:

    Pyridinium chlorochromate;[22] pent-1-en-4-one;[22]
β-benzoylpropionic acid;[23] γ-phenylbutyric acid;[23] α-tetralone;[24]
manganic acetate;[20] manganic acetate dihydrate.[20]

1. <u>Acid Catalysed Rearrangements of 2-Methyl-1-methoxybenzobarrelene</u> (3-32).

    A.   <u>In Trifluoroacetic Acid</u>:

    A solution of 2-methyl-1-methoxybenzobarrelene (3-32) (1.0 g, 5.05 mmole) in trifluoroacetic acid (15 ml) was vigorously stirred at room temperature for 10 minutes. The solvent was removed under reduced pressure and the residual oil was purified by preparative t.l.c.[silica, 20% ether in light petroleum] to give:

    i)   <u>1-Methylbenzo[3,4]bicyclo[3.2.1]octa-3,6-dien-2-one[5,8-dihydro-8-methyl-5,8-methanobenzocyclohepten-9-one</u>] (4-19):(406 mg, 44%), m.p. 95-96° (from ethanol). (Found: C, 84.55; H, 6.8%; $C_{13}H_{12}O$ requires C, 84.80; H, 6.50% . M^{+} (Mass spectrometry): 184. ^{1}H n.m.r. τ (CDCl$_3$): 1.9 7-2.19 (m, 1H); 2.56-3.02 (m, 3H); 3.36 (dd, 1H, $\underline{J}$ = 5 Hz; $\underline{J}$ = 3.8 Hz); 4.24 (d, 1H, $\underline{J}$ = 6.2 Hz); 6.33 (m, 1H); 7.52 (d, 2H, $\underline{J}$ = 3.3 Hz); and 8.62 (s, 3H). ν_{max} KBr: 3065, 3030, 2970, 2930, 2870, 1710, 1603, 1455, 1375, 1335, 1320, 1280, 1260, 1220, 1185, 1155, 995, 955, 905, 850, 810, 760, 740, 730, and 695 cm^{-1}.

    ii) <u>1-Methylbenzobarrelen-2-one[3,4-dihydro-1-methyl-1,4-etheno</u>naphthalen-2(1<u>H</u>)-one] (4-21):   (75 mg, 8%). (Found: C, 84.6; H, 6.5%; $C_{13}H_{12}O$ requires C, 84.8; H, 6.5%). (M^{+} - 42) (Mass spectrometry); 142. ^{1}H n.m.r. τ (CDCl$_3$): 2.62-3.04 (m, 6H); 6.16 (m, 1H); 7.78 (m, 2H); and 8.58 (s, 3H). ν_{max} KBr: 3070, 3040, 3020, 2970, 2935, 2875, 1735. 1470, 1455, 1400, 1380, 1340, 1255, 1230, 1155, 1120, 1090, 1060, 1020, 990, 940, 825, and 755 cm^{-1}.

    iii) <u>1-Methylbenzo[6,7]bicyclo[3.2.1]octa-3,6-dien-2-one[5,9-dihydro-5-methyl-5,9-methanobenzocyclohepten-6-one</u>] (4-20):   (236 mg, 26%) m.p. 101-102° (from ethanol).   (Found: C, 84.7; H, 6.6%; $C_{13}H_{12}O$ requires C, 84.8;

6, 5.6%). M^{+} (Mass spectrometry); 184. ^{1}H n.m.r. τ (CDCl$_3$): 2.58-3.01 (m, 5H); 4.55 (m, 1H); 7.36 (d, 1H, $\underline{J}$ = 15.0 Hz); 8.06 (s, 2H); and 8.63 (s, 3H). ν_{max} KBr 3040, 3020, 2930, 2890, 1680, 1470, 1458, 1365, 1345, 1290, 1232, 1205, 1155, 1105, 980, 935, 890, 805, 765, and 725 cm^{-1}.

B. In Boiling Trifluoroacetic Acid:

A solution of 2-methyl-1-methoxybenzobarrelene (3-32) (1.0 g, 5.05 mmole) in trifluoroacetic acid (15 ml) was heated under reflux for 10 minutes. The solvent was removed under reduced pressure and the crude product on purification, as explained above, gave:

i) 1-Methylbenzo[3,4]bicyclo[3.2.1]octa-3,6-dien-2-one (4-19): (42 mg, 4.6%), characterized by comparison with authentic sample.

ii) 1-Methylbenzobarrelen-2-one (4-21): (238 mg, 26%), characterized by comparison with authentic sample.

iii) 1-Methylbenzo[6,7]bicyclo[3.2.1]octa-3,6-dien-2-one (4-20): (284 mg, 31%), characterized by comparison with authentic sample.

C. In Concentrated Sulphuric Acid:

A suspension of 2-methyl-1-methoxybenzobarrelene (3-32) (0.5 g, 2.525 mmole) in concentrated sulphuric acid (98%, 5 ml) was shaken at room temperature until dissolution was complete. The reaction mixture was quenched with ice (ca. 100 g) and the resultant suspension was extracted with ether (3 x 25 ml). The combined extracts were dried (MgSO$_4$) and evaporated under reduced pressure. The residual oil was purified by preparative t.l.c. [silica, 20% ether in light petroleum] to give:

i) 1-Methylbenzo[3,4]bicyclo[3.2.1]octa-3,6-dien-2-one (4-19): (20 mg, 4.3%), characterized by comparison with authentic sample.

ii)   1-Methylbenzobarrelen-2-one (4-21): (116 mg, 25%), characterized by comparison with authentic sample.

iii)   1-Methylbenzo[6,7]bicyclo[3.2.1]octa-3,6-dien-2-one (4-20): (148 mg, 32%), characterized by comparison with authentic sample.

iv)   An unidentified product (30 mg).

D.   In Fluorosulphuric Acid:

A stirred solution of 2-methyl-1-methoxybenzobarrelene (3.32) (0.5 g, 2.525 mmole) in fluorosulphuric acid (3 ml) in dichloromethane (3 ml) was maintained at -78° for 5 minutes.   The reaction mixture was quenched with ice (ca. 30 g) and the resultant solution was extracted with ether (3 x 25 ml). The combined extracts were dried ($MgSO_4$) and evaporated under reduced pressure. The residual oil on purification gave:

i)   1-Methylbenzo[3,4]bicyclo[3.2.1]octa-3,6-dien-2-one (4-19): (60 mg, 13%), characterized by comparison with authentic sample.

ii)   1-Methylbenzobarrelen-2-one (4-21): (155 mg, 34%), characterized by comparison with authentic sample.

iii)   1-Methylbenzo[6,7]bicyclo[3.2.1]octa-3,6-dien-2-one (4-20): (58 mg, 12.7%), characterized by comparison with authentic sample.

2.   Isomerization of 1-Methylbenzo[3,4]bicyclo[3.2.1]octa-3,6-dien-2-one (4-19).

A.   In Trifluoroacetic Acid:

A solution of the compound (4-19) (50 mg, 0.271 mmole) in trifluoro-acetic acid (3 ml) was maintained at room temperature for 24 h.   The solvent was removed under reduced pressure and the residual oil on purification gave

unchanged starting material (45 mg, 90%). The ketone (4-19) was again

dissolved in trifluoroacetic acid (3 ml) and heated under reflux for 24 h.

The solvent was removed under reduced pressure and the residue was purified

by preparative t.l.c. to give unidentifiable tar along with unchanged

starting material (25 mg), characterized by comparison with authentic sample.

B.   In Concentrated Sulphuric Acid:

A solution of the compound (4-19) (0.05 g, 0.271 mmole) in concentrated

sulphuric acid (5 ml) was vigorously shaken and quenched with ice (ca. 50 g).

The aqueous phase was extracted with ether (3 x 25 ml) and dried ($MgSO_4$).

The solvent was removed under reduced pressure and the residue was purified

by preparative t.l.c. to give unchanged starting material (30 mg),

characterized by comparison with authentic sample.

3.   Isomerization of 1-Methylbenzo[6,7]bicyclo[3.2.1]octa-3,6-dien-2-one
      (4-20):

A solution of the compound (4-20) either in boiling trifluoroacetic

acid or in concentrated sulphuric acid and quenching with ice-cooled water,

on prolonged treatments caused a slow change in the substrate to unidentified

products.   The product ratio was determined by the [1]H n.m.r. analysis,

however, at short intervals the starting material remained unchanged.

4.   Isomerization of 1-Methylbenzobarrelen-2-one (4-21):

A solution of the compound (4-21) either in boiling trifluoroacetic

acid or in concentrated sulphuric acid, at short intervals remained unchanged.

On prolonged treatments, only the unidentifiable tar was obtained, which

could not be characterized.

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5.   Acid-Catalysed Rearrangements of 2,3-Dimethyl-1-methoxytetrachloro-
     benzobarrelene (2-3):

A.   In Trifluoroacetic Acid:

A solution of the compound (2-3) (1.0 g, 2.86 mmole) in trifluoroacetic

acid (experiment 1A) gave:

i)   1,8-Dimethyltetrachlorobenzo[3,4]bicyclo[3.2.1]octa-3,6-dien-2-one

[1,2,3,4-tetrachloro-5,8-dihydro-8,12-dimethyl-5,8-methanobenzocyclohepten-

9(1H)-one] (4-22): (467 mg, 47%) m.p. 136-37° (from ethanol) (Found: C, 49.9;

H, 2.9%; $C_{14}H_{10}Cl_4O$ requires C, 50.0; H, 2.95%) M$^+$ (Mass spectrometry): 336.

^{1}H n.m.r. τ (CDCl$_3$): 3.39 (q, 1H, $\underline{J}$ = 7.0 Hz); 3.58 (dd, 1H, $\underline{J}$ = $\underline{J}$ = 2.2 Hz)

4.95 (dd, 1H, $\underline{J}$ = $\underline{J}$ = 2.2 Hz); 7.91 (s, 3H); 7.85-8.22 (m, 1H); and 9.12

(d, 3H, $\underline{J}$ = 7.0 Hz). ν_{max} KBr: 3080, 2975, 2940, 2900, 2880, 1705, 1535,

1452, 1360, 1326, 1245, 1230, 1205, 1140, 1025, 1000, 890, 870, 840, 745,

720, and 685 cm^{-1}.

ii)   3-exo-4-Dimethyltetrachlorobenzobarrelen-2-one[1,2,3,4-tetrachloro-

5,8-dihydro-8,11-exo-dimethyl-5,8-ethenonaphthalen-12(1H)-one] (4-24):

(127 mg, 13%), m.p. 141-42° (from ethanol). (Found: C, 49.9; H, 3.0%·

$C_{14}H_{10}Cl_4O$ requires C. 50.0: H, 2.97%) [M$^+$-42] (Mass spectrometry): 280.

^{1}H n.m.r. τ (CDCl$_3$): 3.39 (t, 1H, $\underline{J}$ = 7.0 Hz); 3.75 (dd, 1H, $\underline{J}$ = $\underline{J}$ = 2.2 Hz);

4.91 (dd, 1H, $\underline{J}$ = $\underline{J}$ = 2.2 Hz); 7.63 (m, 1H); 7.91 (s, 3H); 8.83 (d, 3H,

$\underline{J}$ = 7.0 Hz). ν_{max} KBr: 3065, 3020, 2975, 2935, 2880, 1725, 1603, 1450, 1370,

1280, 1170, 1135, 1090, 1005, 925, 830, 750, 710, and 690 cm^{-1}.

iii)   3-endo-,4-Dimethyltetrachlorobenzobarrelen-2-one[1,2,3,4-tetrachloro-

5,8-dihydro-8,11-endo-dimethyl-5,8-ethenonaphthalen-12(1H)-one] (4-23):

·(80 mg, 8%), m.p. 143-44° (from ethanol) [M$^+$-42] (Mass spectrometry): 280.

^{1}H n.m.r. τ (CDCl$_3$):   3.35 (t, 1H, $\underline{J}$ = 7.0 Hz); 3.56 (dd, 1H, $\underline{J}$ = 2.2 Hz,

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$\underline{J}$ = 2.2 Hz); 4.93 (dd, 1H, $\underline{J}$ = $\underline{J}$ = 2.2 Hz); 7.89 (s, 3H); 7.96 (m, 1H); and 9.12 (d, 3H, $\underline{J}$ = 14 Hz). ν_{max} KBr: 3070, 3025, 2970, 2942, 2870, 1728, 1605, 1455, 1365, 1330, 1252, 1230, 1205, 1142, 1025, 1006, 892, 874, 840, 750, 712, and 695 cm^{-1}.

iv) 1,8-Dimethyltetrachlorobenzo[6,7]bicyclo[3.2.1]octa-3,6-dien-2-one-[1,2,3,4-tetrachloro-5,9-dihydro-9,12-dimethyl-5,9-methanobenzocyclohepten-8(1H)-one] (4-25): (245 mg, 25%), m.p. 155-56° (from ethanol). (Found: C, 49.9; H, 2.9%; $C_{14}H_{10}Cl_4O$ requires C, 50.0; H, 2.97%) M^{+} (mass spectrometry) 336. ^{1}H n.m.r. τ (CDCl$_3$): 2.4-2.72 (m, 1H); 4.38 (d, 1H, $\underline{J}$ = 9.0 Hz); 6.32 (d, 1H, $\underline{J}$ = 7.0 Hz); 7.12 (q, 1H, $\underline{J}$ = 9.0 Hz); 8.32 (s, 3H); and 8.95 (d, 3H, $\underline{J}$ = 7.0 Hz). ν_{max} KBr: 3050, 2975, 2940, 2880, 1690, 1460, 1365, 1280, 1240, 1213, 1150, 1075, 1018, 942, 860, 810, 775, 722, and 680 cm^{-1}.

B.   In Concentrated Sulphuric Acid:

The compound (2-3) (1.0 g, 2.860 mmole) in concentrated sulphuric acid (15 ml) (experiment 1$\underline{C}$) gave:

i)   1,8-Dimethyltetrachlorobenzo[3,4]bicyclo[3.2.1]octa-3,6-dien-2-one (4-22), (384 mg, 40%), characterized by comparison with authentic sample.

ii)   A mixture of 3,4-dimethyltetrachlorobenzobarrelen-2-ones [(4-23) and (4-24)] (182 mg, total yield: 19%), characterized by comparison with authentic material.

iii) 1,8-Dimethyltetrachlorobenzo[6,7]bicyclo[3.2.1]octa-3,6-dien-2-one (4-25) (150 mg, 26%), characterized by comparison with authentic sample.

6.   Catalytic Hydrogenation of 1,8-Dimethyltetrachlorobenzo[3,4]bicyclo-[3.2.1]octa-3,6-dien-2-one (4-22):

A suspension of palladised charcoal [10% palladium on charcoal, 0.015 g]

in a solution of the ketone (4-22) (0.100 g, 0.290 mmole) in ethanol (25 ml) was stirred under a positive pressure of hydrogen for 6 h. The reaction mixture was filtered through celite and the filtrate was evaporated under reduced pressure. The residue was purified by column chromatography to give: 1,8-dimethyltetrachlorobenzo[3,4]bicyclo[3.2.1]octa-3,6-ene-2-one (4-22'): (100 mg, 98%), m.p. 150-51° (from ethanol). M^+ (Mass spectrometry): 338. ^{1}H n.m.r. τ (CDCl$_3$): 5.72 (m, 1H); 7.42 (s, 1H); 7.55-8.05 (m, 6H); 8.16 (s, 3H); 9.09 (d, 3H, $\underline{J}$ = 7.0 Hz). ν_{max} KBr: 3010, 2970, 2935, 2870, 1725, 1450, 1365, 1320, 1272, 1215, 1190, 1090, 995, 945, 890, 800, 750, and 670 cm^{-1}.

7. Catalytical Hydrogenation of 1,8-Dimethyltetrachlorobenzo[6,7]bicyclo-[3.2.1]octa-3,6-dien-2-one (4-25):

The compound (4-25) (0.100 g, 0.290 mmole) was catalytically hydrogenated as explained in experiment 6, to give: 1,8-dimethyltetrachloro-benzo[6,7]bicyclo[3.2.1]octa-3,6-ene-2-one (4-25'): (100 mg, 98%), m.p. 160-61° (from ethanol). M^+ (Mass spectrometry): 338. ^{1}H n.m.r. τ (CDCl$_3$): 5.74 (m, 1H); 6.62 (m, 1H); 7.52-8.12 (m, 6H); 8.48 (s, 3H); and 8.96 (d, 3H, $\underline{J}$ = 7.0 Hz). ν_{max} KBr: 3015, 2975, 2940, 2878, 1720, 1450, 1370, 1280, 1220, 1115, 1075, 1018, 950, 812, 787, 745, 708, and 670 cm^{-1}.

8. Isomerization of 1,8-Dimethyltetrachlorobenzo[3,4]bicyclo[3.2.1]octa-3,6-dien-2-one (4-22):

The ketone (4-22) did not give any other product either in trifluoro-acetic acid or concentrated sulphuric acid. At much longer time period treatment only the unidentifiable tar was obtained.

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9.   Isomerization of 1,8-Dimethyltetrachlorobenzo[6,7]bicyclo[3.2.1]-
     octa-3,6-dien-2-one (4-25):

The ketone (4-25) did not give any other product on treatment with either trifluoroacetic acid or concentrated sulphuric acid; however, at longer periods unidentifiable tar was obtained.

10. Acid-Catalysed Rearrangements of 2,3-Dimethyl-1-Methoxybenzobarrelene
     (3-33).

A.   In Trifluoroacetic Acid:

A solution of 2,3-dimethyl-1-methoxybenzobarrelene (3-33) (1.2 g, 5.660 mmole) in trifluoroacetic acid (15 ml) (experiment 1A) gave:

i)   1,8-Dimethylbenzo[3,4]bicyclo[3.2.1]octa-3,6-dien-2-one [5,8-dihydro-8,12-dimethyl-5,8-methanobenzocyclohepten-9(1H)one] (4-28): (448 mg, 41%), m.p. 60-61° (from ethanol) (Found: C, 84.6; H, 7.0%; $C_{14}H_{14}O$ requires C, 84.84; H, 7.07%) $M^{+\cdot}$ (Mass spectrometry): 198. ^{1}H n.m.r. τ (CDCl$_3$): 2.63-3.02 (m, 4H); 3.45 (q, 1H, $|\underline{J}|$ = 7.0 Hz); 3.62 (dd, 1H, $\underline{J}$ = $\underline{J}$ = 2.2 Hz); 5.62 (dd, 1H, $\underline{J}$ = $\underline{J}$ = 2.2 Hz); 7.96 (q, 1H, $|\underline{J}|$ = 7.0 Hz); 8.32 (s, 3H); and 9.35 (d, 3H, $\underline{J}$ = 7.0 Hz), ν_{max} KBr: 3040, 2975, 2910, 2870, 1704, 1535, 1450, 1360, 1326, 1245, 1230, 1190, 1140, 1020, 990, 890, 840, 745, and 720 cm^{-1}.

ii) 3,4-Dimethylbenzobarrelen-2-one [5,8-dihydro-8,11-dimethyl-5,8-ethenonaphthalen-12(1H)-one] (4- 29): (272 mg, 25%), m.p. 78-79° (from n-hexane) (Found: C, 84.3; H, 7.0%; $C_{14}H_{14}O$ requires C, 84.84; H, 7.07%). $[M^{+\cdot} - 56]$ (Mass spectrometry): 142. ^{1}H n.m.r. τ (CDCl$_3$): 2.56-2.91 (m, 4H); 3.26-3.57 (m, 1H) 3.58-3.90 (m, 1H); 5.58 (dd, 1H, $\underline{J}$ = $\underline{J}$ = 2.2 Hz); 7.92 (m, 1H); 8.25 (s, 3H); and 8.83 (d, 3H, $\underline{J}$ = 7.0 Hz). ν_{max} KBr: 3065, 2975, 2935, 1725, 1603, 1450, 1370, 1280, 1170, 1135, 1090, 1005, 915, 830, 750, 710 and 690 cm^{-1}.

iii) 1,8-Dimethylbenzo[6,7]bicyclo[3.2.1]octa-3,6-dien-2-one[5,9-dihydro-9,12-dimethyl-5,9-methanobenzocyclohepten-8(1H)-one] (4-31):

(312 mg), 28%), m.p. 106-107° (from ethanol). (Found: C, 84.5; H, 7.0%; $C_{14}H_{14}O$ requires C, 84.84; H, 7.07%): M⁺ (Mass spectrometry): 198. ¹H n.m.r. τ (CDCl₃): 2.42-3.08 (m, 4H); 4.51 (d, 1H, $\underline{J}$ = 9.0 Hz); 6.61 (d, 1H, $\underline{J}$ = 7.0 Hz); 7.06 (q, 1H, $|\underline{J}|$ = 7.0 Hz); 8.31 (m, 1H); 8.57 (s, 3H); and 9.06 (d, 3H, $\underline{J}$ = 7.0 Hz). ν_{max} KBr: 3080, 3060, 3030, 2980, 2945, 2880, 1678, 1475, 1382, 1370, 1258, 1222, 1175, 1140, 1120, 1020, 900, 875, 830, 805, 770, 715, and 703 cm⁻¹.

B. In Concentrated Sulphuric Acid:

The ketone (3-33) (1.0 g, 4.715 mmole) in concentrated sulphuric acid (98%, 20 ml) (experiment 1.C) gave:

i) 1,8-Dimethylbenzo[3,4]bicyclo[3.2.1]octa-3,6-dien-2-one (4-28) (336 mg, 36%).

ii) 3,4-Dimethylbenzobarrelen-2-one (4-29) (205 mg, 22%); and

iii) 1,8-Dimethylbenzo[6,7]bicyclo[3.2.1]octa-3,6-dien-2-one (4-31) (233 mg, 25%); all these compounds were characterized by comparison with authentic material.

11. Isomerization of 1,8-Dimethylbenzo[3,4]bicyclo[3.2.1]octa-3,6-dien-2-one (4-28):

The ketone (4-28) did not give any other product either in trifluoroacetic acid (24 h) or in concentrated sulphuric acid (2 h); however, at much longer periods unidentifiable tar was obtained.

12. Isomerization of 3,4-Dimethylbenzobarrelen-2-one (4-29):

The ketone (4-29) did not isomerize either in trifluoroacetic acid

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(24 h) or in concentrated sulphuric acid (3 h), to give any other product.

13.   Isomerization of 1,8-Dimethylbenzo[6,7]bicyclo[3.2.1]octa-3,6-dien-2-one (4-31):

An attempted isomerization of the ketone (4-31) either in trifluoro-acetic acid (24 h) or in concentrated sulphuric acid (3 h) failed to give any other product; however, at much longer periods, only the decomposed material was obtained.

14.   Acid-Catalysed Rearrangements of 2,6-Dimethyl-1-Methoxytetrafluoro-benzobarrelene (2-5).

A.   In Trifluoroacetic Acid:

The compound (2-5) (1.5 g, 5.28 mmole) in trifluoroacetic acid (25 ml) (experiment 1.A) gave:

i)   1,7-Dimethyltetrafluorobenzo[3,4]bicyclo[3.2.1]octa-3,6-dien-2-one [1,2,3,4-tetrafluoro-5,8-dihydro-7,8-dimethyl-5,8-methanobenzocyclohepten-9(1H)-one] (4-34): (1.0 g, 73%), m.p. 50-51° (from ethanol) (lit.[2] m.p. 50-51°). M$^+$ (Mass spectrometry): 270. ^{1}H n.m.r. τ (CDCl$_3$): 3.6-3.85 (m, 1H); 5.9-6.15 (m, 1H); 7.25-7.75 (m, 2H); 8.35 (d, 3H, $\underline{J}$ = 1.6 Hz); and 8.69 (s, 3H). ν_{max} KBr: 2980, 2940, 2875, 1707, 1620, 1504, 1477, 1440, 1380, 1365, 1325, 1268, 1005, 971, 940, 894, 843, 810, and 737 cm^{-1}.

ii)   1,3-Dimethyltetrafluorobenzo[6,7]bicyclo[3.2.1]octa-3,6-dien-2-one [1,2,3,4-tetrafluoro-5,9-dihydro-7,9-dimethyl-5,9-methanobenzocyclohepten-9(1H)-one] (4-35): (394 mg, 28%) m.p. 48-50° (from hexane) (lit.[2] m.p. 50-51°) M$^+$ (Mass spectrometry): 270. ^{1}H n.m.r. τ (CDCl$_3$): 2.8-3.1 (m, 1H); 5.95-6.3 (m, 1H); 7.45 (d, 2H, $\underline{J}$ = 2.5 Hz); and 8.4-8.45 (m, 6H). ν_{max} KBr: 2940, 2872, 1685, 1500, 1486, 1448, 1378, 1316, 1098, 1053, 1043, 1018, 961, 946, 898, and 874 cm^{-1}.

B.   In Concentrated Sulphuric Acid:

The compound (2-5) (1.0 g, 3.52 mmole) in concentrated sulphuric acid (15 ml) (experiment 1.C) gave:

i)   1,3-Dimethyltetrafluorobenzo[6,7]bicyclo[3.2.1]octa-3,6-dien-2-one (4-35): (176 mg, 18%) m.p. 49-50°, characterized by comparison with authentic sample.

ii)   7-Methyltetrafluorobenzo[3,4]bicyclo[3.2.1]octa-3-ene-2-onyl-1,7-sultone [5,6,7,8-tetrafluoro-9,10-dihydro-10a-methyl-3H-3a,9-methanobenzo[5,6]-cyclohept-[1,2-d][1,2]oxathiol-4[10aH]-one-2,2-dioxide]* (4-41):   (840 mg, 70%), m.p. 170-171° (from ethanol).   (Found: C, 48.0; H, 2.8; $C_{14}H_{10}F_4SO_4$ requires C, 48.00; H, 2.85%); $M^{\ddot{+}}$ (Mass spectrometry): 350. ^1H n.m.r. τ (CDCl$_3$): 5.5-5.65 (d, 1H, $\underline{J}$ = 14.0 Hz); 5.82-6.12 (m, 1H), 6.5-6.66 (d, 1H, $\underline{J}$ = 14.0 Hz), 6.9-7.3 (m, 2H); 7.4-7.7 (m, 1H); 7.72-8.04 (m, 1H); and 8.54 (s, 3H). ν_{max} KBr: 3020, 2985, 2975, 2930, 2850, 1703, 1635, 1510, 1485, 1375, 1360, 1210, 1140, 1105, 1085, 1050, 955, 900, 860, 812, and 767 cm^{-1}.

C.   In Aqueous Sulphuric Acid

The compound (2-5) (0.20 g, 0.760 mmole) in aqueous sulphuric acid (80%, 15 ml) gave:

i)   unreacted starting material (2-5) (10 mg, 5%);

ii)   1,3-Dimethyltetrafluorobenzo[6,7]bicyclo[3.2.1]octa-3,6-dien-2-one (4-35) (28 mg, 16%); and

iii)   7-Methyltetrafluorobenzo[3,4]bicyclo[3.2.1]octa-3-ene-2-onyl-1,7-sultone (4-41) (140 mg, 57%);   all the compounds were characterized by comparison with authentic material.

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* As suggested by Dr. A.D. McNaught, as discussed before.

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15.   Isomerization of 1,7-Dimethyltetrafluorobenzo[3,4]bicyclo[3.2.1]-
       octa-3,6-dien-2-one (4-34).

    A.   In Trifluoroacetic Acid:

       The ketone (4-34) (0.100 g, 3.70 mmole) in boiling trifluoroacetic
acid (5 ml) (24 h) gave:

i)   unchanged starting material (4-34) (48 mg, 48%), as shown by t.l.c. and
^{1}H n.m.r., and

ii)   1-Methyl-7-methylenetetrafluorobenzo[3,4]bicyclo[3.2.1]oct-3-ene-2-one
(4-40), (44 mg, 44%) m.p. 60-61° (from ligroin 60-80°) (lit.^{2} m.p. 60-61°),
$\overset{+}{\text{M}}\cdot$ (Mass spectrometry): 270. ^{1}H n.m.r. τ (CDCl$_3$): 4.75-5.0 (m, 1H); 6.1-6.4
(m, 2H); 6.8-7.6 (m, 2H); 7.8-8.0 (m, 2H); and 8.65 (s, 3H). ν_{max} KBr: 2980,
2945, 1703, 1635. 1510, 1470, 1367, 1340, 1290, 1140, 1093, 1010, 990, 937,
905, 825, and 730 cm^{-1}.

    B.   In Concentrated Sulphuric Acid:

       The ketone (4-34) (0.20 g, 7.40 mmole) in concentrated sulphuric acid
(5 ml) gave: 5,6,7,8-tetrafluoro-9,10-dihydro-10a-methyl-3H-3a,9-methanobenzo-
[5,6]cyclohept[1,2-d][1,2]oxathiol-4[10aH]-one-2,2-dioxide] (4-41) (240 mg,
97%), characterized by comparison with authentic sample.

16.   Isomerization of 1-Methyl-7-methylenetetrafluorobenzo[3,4]bicyclo-
       [3.2.1]oct-3-ene-2-one   (4- 40).

    A.   In Trifluoroacetic Acid:

       The compound (4-40) (0.50 g, 1.35 mmole) in boiling trifluoroacetic
acid (3 ml) gave:

i)   1,7-Dimethyltetrafluorobenzo[3,4]bicyclo[3.2.1]octa-3,6-dien-2-one (4-34)

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(25 mg, 50%), as shown by t.l.c. and ^{1}H n.m.r., and ii) unchanged starting material (4-40) (48 mg, 49%), as shown by ^{1}H n.m.r. and t.l.c. identical to the authentic sample.

B. In Concentrated Sulphuric Acid:

The compound (4-40) (0.50 g, 1.35 mmole) in concentrated sulphuric acid (2 ml) gave: 7-methyltetrafluorobenzo[3,4]bicyclo[3.2.1]octa-2-ene-2-onyl-1,7-sultone (4-41) (60 mg, 96%), characterized by comparison with authentic sample.

17. Acid-Catalysed Rearrangements of 2,6-Dimethyl-1-methoxytetrachlorobenzobarrelene (2-8).

A. In Trifluoroacetic Acid:

The compound (2-8) (2.0 g, 5.70 mmole) in boiling trifluoroacetic acid (30 ml) (2 h) gave:

i) 1,7-Dimethyltetrachlorobenzo[3,4]bicyclo[3.2.1]octa-3,6-dien-2-one-[1,2,3,4-tetrachloro-5,8-dihydro-7,8-dimethyl-5,8-methanobenzocyclohepten-9(1H)-one] (4-36): (768 mg, 40%) m.p. 140-42° (from ethanol) (Found: C, 50.3; H, 3.2%; $C_{14}H_{10}Cl_4O$ requires: C, 50.0; H, 3.0%); M$\overset{+}{\cdot}$ (Mass spectrometry): 336. ^{1}H n.m.r. τ (CDCl$_3$): 3.74 (m, 1H); 5.75 (m, 1H); 7.46 (m, 2H, $\underline{J}$ = 2.2 Hz); 8.38 (d, 3H, $\underline{J}$ = 1.6 Hz); and 8.65 (s, 3H). ν_{max} KBr: 2970, 2930, 2870, 1690, 1530, 1440, 1355, 1310, 1232, 1155, 1105, 1010, 990, 810, and 710 cm^{-1}.

ii) 1,3-Dimethyltetrachlorobenzo[6,7]bicyclo[3.2.1]octa-3,6-dien-2-one-[1,2,3,4-tetrachloro-5,9-dihydro-7,9-dimethyl-5,9-methanobenzocyclohepten-9(1H)-one] (4-37): (950 mg, 50%), m.p. 151-52° (from ethanol) (Found: C, 49.9; H, 2.9%; $C_{14}H_{10}Cl_4O$ requires: C, 50.0; H, 3.0%), M$\overset{+}{\cdot}$ (Mass spectrometry): 336. ^{1}H n.m.r. τ (CDCl$_3$): 2.82 (m, 1H); 6.11 (m, 1H); 7.36 (m, 2H); 8.30 (s, 3H);

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and 8.34 (d, 3H, $\underline{J}$ = 1.6 Hz). ν_{max} KBr: 3070, 2970, 2938, 2870, 1665, 1455, 1427, 1377, 1320, 1250, 1198, 1172, 1122, 1018, 905, 881, 775, 766, and 730 cm^{-1}.

B.   In Concentrated Sulphuric Acid:

The compound (2-8) (1.0 g, 2.86 mmole) in concentrated sulphuric acid (98%, 15 ml) (experiment 1.C) gave:

i)   1,3-Dimethyltetrachlorobenzo[6,7]bicyclo[3.2.1]octa-3,6-dien-2-one (4-37), (650 mg, 66%),m.p. 151-52° (from ethanol), characterized by comparison with authentic sample;

ii)   an unidentifiable tar (200 mg).

C.   In Aqueous Sulphuric Acid (80%):

The compound (2-8) (0.100 g, 0.286 mmole) in aqueous sulphuric acid (80%, 5 ml) gave: 1,3-Dimethyltetrachlorobenzo[6,7]bicyclo[3.2.1]octa-3,6-dien-2-one (4-37), (60 mg, 64%), characterized by comparison with authentic sample.

18.   Isomerization of 1,7-Dimethyltetrachlorobenzo[3,4]bicyclo[3.2.1]octa-3,6-dien-2-one (4-36):

The ketone (4-36) (0.20 g, 0.590 mmole) in boiling trifluoroacetic acid (5 ml) (experiment 1.A) gave:

i)   unchanged starting material (4-36) (108 mg, 54%), as shown by t.l.c. and ^{1}H n.m.r.

ii)   1-Methyl-7-methylenetetrachlorobenzo[3,4]bicyclo[3.2.1]octa-3,6-ene-2-one[1,2,3,4-tetrachloro-5,8-dihydro-7-methylene-8-methyl-5,8-methanobenzo-cycloheptan-9(1H)-one] (4-43):   (76 mg, 38%) m.p. 149-50° (from ethanol)

(Found: C, 50.7; H, 2.9%; $C_{14}H_{10}Cl_4O$ requires, C, 50.0; H, 2.97%), M⁺

(Mass spectrometry): 336. [1]H n.m.r. τ (CDCl$_3$): 4.91 (m, 1H);

7.08 (m, 2H); 7.48 (m, 2H); 7.81 (m, 2H); and 8.50 (d, 3H, J = 2.2 Hz).

ν_{max} KBr 2970, 2930, 2910, 2875, 1690, 1535, 1442, 1370, 1312, 1232, 1203,

1155, 1106, 1012, 992, 810, and 716 cm^{-1}.

19. Isomerization of 1-Methyl-7-methylenetetrachlorobenzo[3,4]bicyclo-
     [3.2.1]octa-3,6-ene-2-one (4-43).

The ketone (4-43) (0.050 g, 0.145 mmole) in boiling trifluoroacetic
acid (3 ml) gave:

i)   1,7-Dimethyltetrachlorobenzo[3,4]bicyclo[3.2.1]octa-3,6-dien-2-one (4-36)
(25 mg, 50%), as shown by t.l.c. and [1]H n.m.r., and

ii) unchanged starting material (4-43) (22 mg, 44%), characterized by
comparison with authentic sample.

20. Acid-Catalysed Rearrangements of 2,6-Dimethyl-1-methoxybenzobarrelene
     (3-36).

A.   In Trifluoroacetic Acid:

The compound (3-36) (2.5 g, 11.8 mmole) in trifluoroacetic acid
(25 ml) (experiment 1.A) gave:

i)   1,7-Dimethylbenzo[3,4]bicyclo[3.2.1]octa-3,6-dien-2-one[5,8-dihydro-
7,8-dimethyl-5,8-methanobenzocyclohepten-9(1H)-one] (4-38): (1.42 g, 62%),

b.p. 105-106°/4 mm. (Found: C, 84.4; H, 6.9%; $C_{14}H_{14}O$ requires C, 84.8;

H, 7.07%), M⁺ (Mass spectrometry): 198. [1]H n.m.r. τ (CDCl$_3$): 1.94-2.14

(m, 1H); 2.52-3.01 (m, 3H); 3.67 (m, 1H); 6.45 (m, 1H); 7.41 (m, 2H, |J| =

1.6 Hz); 8.34 (s, 3H); and 8.66 (s, 3H). ν_{max} oil; 3050, 3020, 2960, 2930,

2860, 1686, 1600, 1440, 1370, 1290, 1270, 1225, 1190, 1115, 1070, 1003, 952,

894, 812, 758, and 700 cm^{-1}.

ii)   1,3-Dimethylbenzo[6,7]bicyclo[3.2.1]octa-3,6-dien-2-one[5,9-dihydro-7,9-dimethyl-5,9-methanobenzocyclohepten-8(1$\underline{H}$)-one] (4-39):   (720 mg, 31%), m.p. 104-105° (from ethanol).   (Found: C, 84.8; H, 7.2%;   C$_{14}$H$_{14}$O requires C, 84.84; H, 7.07%) M$^{\cdot+}$ (Mass spectrometry): 198. ^{1}H n.m.r. τ (CDCl$_{3}$): 2.62-2.97 (m, 5H); 6.35 (m, 1H); 7.39 (m, 2H); 8.41 (s, 3H); and 8.43 (d, 3H, $\underline{J}$ = 1.6 Hz). ν_{max} KBr: 3060, 3015, 2960, 2915, 2860, 1660, 1462, 1450, 1370, 1340, 1307, 1180, 1070, 942, 905, 825, 750, and 710 cm^{-1}.

B.   In Concentrated Sulphuric Acid:

The compound (3-36) (2.5 g, 11.8 mmole) in concentrated sulphuric acid (98%, 25 ml) (experiment 1.$\underline{C}$) gave:

i)   1,3-Dimethylbenzo[6,7]bicyclo[3.2.1]octa-3,6-dien-2-one (4-39) (700 mg, 29%), m.p. 104-105° (from ethanol), characterized by comparison with authentic sample.

ii)   2-Methyl-4-acetonyl-α-tetralone (4-46):   (490 mg, 19%) m.p. 92-93° (from ethanol).   (Found: C, 77.6; H, 7.4%.   C$_{14}$H$_{16}$O$_{2}$ requires C, 77.7%; H, 7.4%) M$^{\cdot+}$ (Mass spectrometry): 216 (diastereoisomeric mixture of diketones): ^{1}H n.m.r. τ (CDCl$_{3}$): 1.85-2.05 (m, 1H); 2.4-2.9 (m, 3H); 6.15-6.5 (m, 1H); 6.95-7.25 (m, 2H); 7.28-7.52 (m, 1H); 7.82 (s, 3H) [7.72 (s, 3H)]; 7.84-8.5 (m, 2H); and 8.75 (d, 3H, $\underline{J}$ =9.0 Hz). ν_{max} KBr: 3055, 2980, 2960, 2925, 2875, 2860, 2840, 1708, 1680, 1600, 1480, 1405, 1360, 1285, 1225, 1160, 995, 965, 910, 780, 745, and 715 cm^{-1}.

iii)   7-Methylbenzo[3,4]bicyclo[3.2.1]octa-8-ene-2-onyl-1,7-sultone [9,10-dihydro-10a-methyl-3$\underline{H}$;3a,9-methanobenzo[5,6]cyclohept[1,2-d][1,2]oxathiol-4(10a$\underline{H}$)-one-2,2-dioxide] (4-45) (1.5 g, 48%), m.p. 173-74° (from ethanol). (Found: C, 60.4; H, 5.1%; C$_{14}$H$_{14}$SO$_{4}$ requires C, 60.4; H, 5.0%) M$^{\cdot+}$ (Mass

spectrometry): 278. ^{1}H n.m.r. τ (CDCl$_3$): 1.85-2.15 (m, 1H); 2.25-2.74 (m, 3H); 5.51 (d, 1H, |$\underline{J}$| = 14 Hz); 6.19-6.45 (m, 1H); 6.55 (d, 1H, |$\underline{J}$| = 14 Hz); 6.94-7.23 (m, 2H); 7.36-7.6 (m, 1H); 7.75-8.05 (m, 1H); and 8.6 (s, 3H).

ν_{max} KBr: 3010, 2970, 2880, 1693, 1600, 1460, 1425, 1385, 1328, 1268, 1240, 1190, 1153, 1120, 1070, 960, 870, 850, 810, 765, 750, 695, and 665 cm^{-1}.

21.   Isomerization of 1,7-Dimethylbenzo[3,4]bicyclo[3.2.1]octa-3,6-dien-2-one (4-38).

A.   In Trifluoroacetic Acid:

The ketone (4-38) (300 mg, 1.51 mmole) in boiling trifluoroacetic acid (5 ml) (experiment 1.$\underline{A}$) gave:

i)   an unchanged starting material (4-38) (0.152 g, 51%), as shown by t.l.c. and ^{1}H n.m.r.

ii)   1-Methyl-7-methylenebenzo[3,4]bicyclo[3.2.1]octa-3-ene-2-one[5,8-dihydro-7-methylene-8-methyl-5,8-methanobenzocycloheptan-9(1H)-one] (4-44): (132 mg, 44%) m.p. 55-56° (from hexane)   (Found: C, 84.4; H, 7.0%; C$_{14}$H$_{14}$O requires C, 84.84; H, 7.1%); M^{+} (Mass spectrometry): 198. ^{1}H n.m.r. τ (CDCl$_3$): 1.85-2.15 (m, 1H); 2.36-3.05 (m, 3H); 4.86 (m, 1H); 7.39 (m, 2H); 7.68 (s, 2H); 8.34 (m, 2H); and 8.56 (s, 3H). ν_{max} oil: 3020, 2965, 2930, 2860, 1688, 1603, 1442, 1370, 1290, 1270, 1190, 1116, 1072, 1008, 955, 895, 812, 758 and 704 cm^{-1}.

B.   In Concentrated Sulphuric Acid:

The ketone (4-38) (0.200 g, 1.01 mmole) in concentrated sulphuric acid (5 ml) (experiment 1.$\underline{C}$) gave:

i)   2-Methyl-4-acetonyl-α-tetralone (4-46): (40 mg, 19%), m.p. 92-93° (from iso-octane), characterized by comparison with authentic sample.

ii)   9,10-Dihydro-10a-methyl-3$\underline{H}$-3a,9-methanobenzo[5,6]cyclohept[1,2-d][1,2]-

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oxathiol-4(10a<u>H</u>)-one-2,2-dioxide (4-45): (110 mg, 41%), m.p. 173-74° (from ethanol), as shown by t.l.c. and ^{1}H n.m.r.

C.   In Aqueous Sulphuric Acid:

The ketone (4-38) (0.200 g, 1.01 mmole) in aqueous sulphuric acid (80%, 4.0ml) gave:

i)   an unchanged starting material (5%), as shown by t.l.c. and ^{1}H n.m.r.

ii)   2-Methyl-4-acetonyl-α-tetralone (4-46), (35 mg, 17%), as shown by t.l.c. and ^{1}H n.m.r.

iii)   9,10-dihydro-10a-methyl-3<u>H</u>-3a,9-methanobenzo[5,6]cyclohept[1,2-d][1,2]-oxathiol-4(10a<u>H</u>)-one-2,2-dioxide (4-45), (100 mg, 37%), characterized by comparison with authentic sample.

22.   <u>Isomerization of 1-Methyl-7-methylenebenzo[3,4]bicyclo[3.2.1]octa-3-ene-2-one (4-44)</u>.

A.   In Trifluoroacetic Acid:

The ketone (4-44) (0.20 g, 1.01 mmole) in boiling trifluoroacetic acid (4 ml) (experiment 1.A) gave:

i)   1,7-Dimethylbenzo[3,4]bicyclo[3.2.1]octa-3,6-dien-2-one (4-38): (100 mg, 50%), characterized by comparison with authentic sample.

ii)   an unchanged starting material (4-44) (49%), as shown by t.l.c. and ^{1}H n.m.r.

B.   In Concentrated Sulphuric Acid:

The ketone (4-44) (0.100 g, 0.50 mmole) in concentrated sulphuric acid (3 ml) gave:

i)   diastereoisomeric mixture of diketones: 2-methyl-4-acetonyl-α-tetralone

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(4-46): (20 mg, 18%), characterized by comparison with authentic sample:

ii)   9,10-Dihydro-10a-methyl-3$\underline{H}$-3a,9-methanobenzo[5,6]cyclohept[1,2-d][1,2]-
oxathiol-4(10a$\underline{H}$)-one-2,2-dioxide (4-45):   (48 mg, 36%), characterized by
comparison with authentic sample.

23.   <u>Isomerization of 1,3-Dimethylbenzo[6,7]bicyclo[3.2.1]octa-3,6-dien-</u>
       <u>2-one</u> (4-39).

       An attempted isomerization of the ketone (4-39) (0.20 g , 1.01 mmole)
either in trifluoroacetic acid or in concentrated sulphuric acid failed to
give any other products.   Treatment at much longer periods,only decomposed
products were obtained.

24.   <u>Reactions Using Deuteriated Solvents.</u>

   A.   <u>In Trifluoroacetic Acid:</u>

       A solution of 2,6-dimethyl-1-methoxybenzobarrelene (3-36) (0.50 g,
2.36 mmole) in deuteriated trifluoroacetic acid (98%, 5 ml) (experiment 1.$\underline{A}$)
gave:

i)   1,7-Dimethylbenzo[3,4]bicyclo[3.2.1]octa-3,6-dien-2-one (4-50) (246 mg,
53%), oil. [1]H n.m.r. τ (CDCl$_3$): 1.95-2.20 (m, 1H); 2.42-3.65 (m, 3H); 4.92
(m, 1H). d_9: 12.2%; d_8: 14.2%; d_7: 14.8%.

ii)   1,3-Dimethylbenzo[6,7]bicyclo[3.2.1]octa-3,6-dien-2-one (4-49) (141 mg,
30%), m.p. 104-105° (from ethanol); [1]H n.m.r. τ (CDCl$_3$): 2.60-2.97 (m, 4H);
6.35 (m, 1H); 7.39 (m, 1H); 8.16 (m, 1H); and 8.43 (m, 3H). d_1: 24.4%;
d_2: 34.8%; d_3: 26.2%; d_4: 14.6%.

   B.   <u>In Concentrated Sulphuric Acid:</u>

       A suspension of 2,6-dimethyl-1-methoxybenzobarrelene (3-36) (0.50 g,

2.36 mmole) in deuteriated sulphuric acid (96%, 5 ml) (experiment 1.C) gave:

i)   1,3-Dimethylbenzo[6,7]bicyclo[3.2.1]octa-3,6-dien-2-one (4-49) (132 mg, 29%), m.p. 104-105° (from ethanol). d_1: 20.8%; d_2: 36.7%; d_3: 27.9%; d_4: 14.6%.

ii)   Diastereoisomeric mixture of diketones: 2-Methyl-4-acetonyl- -tetralone (4-52):   (97 mg, 19%), m.p. 92-93°. [1]H n.m.r. τ (CDCl$_3$): 1.84-2.06 (m, 1H); 2.41-2.92 (m, 3H); 6.32 (m, 1H). d_{10}: 2.6%; d_9: 4.3%; d_8: 8.2%; d_7: 10.4%.

iii)   9,10-Dihydro-10a-methyl-3H̲-3a,9-methanobenzo[5,6]cyclohept[1,2-d][1,2]-oxathiol-4(10aH̲)-one-2,2-dioxide (4-53): (201 mg, 31%), m.p. 173-74°. [1]H n.m.r. τ (CDCl$_3$): 1.84-2.02 (m, 1H); 2.26-2.72 (m, 3H); 6.32 (m, 1H). d_9: 9.60%; d_8: 10.2%; d_7: 12.4%; d_6: 16.3%.

C.   Isomerization of 1,7-Dimethylbenzo[3,4]bicyclo[3.2.1]octa-3,6-dien-2-one (4-50):

The ketone (4-50)   (0.10 g, 0.53 mmole) in deuteriated sulphuric acid (96%, 1 ml) gave:

i)   Epimeric mixture of 2-methyl-4-acetonyl-α-tetralone (4-52) (21 mg, 19%), m.p. 92-93°, characterized by comparison with authentic sample.
d_{10}: 2.6%; d_9: 3.9%; d_8: 5.7%; d_7: 8.4%; d_6: 12.5%.

ii)   9,10-Dihydro-10a-methyl-3H̲-3a,9-methanobenzo[5,6]cyclohept[1,2-d][1,2]-oxathiol-4(10aH̲)-one-2,2-dioxide (4-53): (47 mg, 32%) m.p. 173-74°, characterized by comparison with authentic sample.
d_9: 8.8%; d_8: 9.7%; d_7: 11.7%; d_6: 15.7%.

25.   Reaction of 1,7-Dimethylbenzo[3,4]bicyclo[3.2.1]octa-3,6-dien-2-one
      (4-38) with Sulphur trioxide-Dioxan Complex.

A solution of the ketone (4-38) (0.10 g, 0.505 mmole) in dichloro-
methane (5 ml) was added dropwise to a suspension of $SO_3-O^+C_4H_8O$ complex[*]
(0.20 g) in dichloromethane (10 ml), maintaining the temperature ca. -70°.
The temperature of the reaction mixture was brought to room temperature and
was allowed to stir for 24 h.   The reaction mixture was then carefully
quenched with crushed ice (ca. 50 g) and extracted with dichloromethane
(3 x 20 ml).   The combined extracts were dried ($MgSO_4$) and evaporated under
reduced pressure.   The residue on purification gave:

i)   9,10-Dihydro-10a-methyl-3H-3a,9-methanobenzo[5,6]cyclohept[1,2-d][1,2]-
oxathiol-4(10aH)-one-2,2-dioxide (4-45):   (18 mg, 12.5%), m.p. 173-74°,
characterized by comparison with authentic sample.

ii)   1,5-Dihydro-3a,5-dimethyl-1H-1,5-methanonaphtho[2,1-C][1,2]oxathiol-
4-(3aH)-one-3,3-dioxide (4-48):   (72 mg, 50%), m.p. 204-205° (from ethanol).
(Found: C, 60.4; H, 5.1%; $C_{14}H_{14}SO_4$ requires C, 60.4; H, 5.0%); M$^+$ (Mass
spectrometry): 278. [1]H n.m.r. τ ($CDCl_3$): 2.3-2.8 (m, 4H); 4.62-4.88 (m, 1H);
5.54-5.78 (d, 1H, $|J|$ =15 Hz); 7.46-7.62 (d, 1H, J = 15 Hz); 7.75-8.18 (m, 1H);
8.37 (s, 3H); and 8.58 (s, 3H). ν_{max} KBr: 3010, 2980, 2940, 2880, 2860,
1735, 1472, 1450, 1375, 1350, 1339, 1252, 1185, 1145, 1110, 1060, 980, 950,
910, 865, 835, 760, and 698 cm^{-1}.

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[*] $SO_3-O^+C_4H_8O$ Complex: A solution of freshly distilled sulphur trioxide
(2.9 g, 3.6 mmole) in trichloroethylene (8.0 ml) was added slowly to
anhydrous dioxan (3.12 g, 3.6 mmole) in trichloroethylene (4 ml) while
maintaining the temperature ca.-10°. The SO_3-dioxan complex promptly
precipitated.

26. Reaction of 1,3-Dimethylbenzo[6,7]bicyclo[3.2.1]octa-3,6-dien-2-one (4-39) with Sulphur trioxide-Dioxan Complex.

The ketone (4-39) (0.10 g, 0.505 mmole) on treatment with sulphur trioxide-dioxan (0.200 g) in dichloromethane (20 ml) as explained in experiment 25 gave: 1,5-dihydro-3a,5-dimethyl-1H-1,5-methanonaphtho-[2,1-C][1,2]-oxathiol-4-(3a,H)-one-3,3-dioxide (4-48): (105 mg, 73%), m.p. 204-205$^{\text{o}}$ (from ethanol), characterized by comparison with authentic sample.

27. Reaction of 2,6-Dimethyl-1-methoxybenzobarrelene (3-36) with Sulphur trioxide-Dioxan Complex.

An attempted reaction between the compound (3-36) (0.10 g, 0.490 mmole) with sulphur trioxide-dioxan complex (0.20 g) failed to give any product. An unchanged starting material was obtained as shown by t.l.c. and ^{1}H n.m.r.

28. Acid-Catalysed Rearrangements of 2,6-Dimethyl-1-hydroxybenzobarrelene (3-39).

A. In Trifluoroacetic Acid:

The compound (3-39) (0.30 g, 1.48 mmole) in trifluoroacetic acid (5 ml) (experiment 1.A) gave:

i) 1,7-Dimethylbenzo[3,4]bicyclo[3.2.1]octa-3,6-dien-2-one (4-38):(100 mg, 35%), oil, characterized by comparison with authentic sample.

ii) 1,3-Dimethylbenzo[6,7]bicyclo[3.2.1]octa-3,6-dien-2-one (4-39): (112 mg, 36%), m.p. 104-105$^{\text{o}}$ (from ethanol), as shown by t.l.c. and ^{1}H n.m.r.

iii) brown tar (52 mg), which could not be identified.

B.   In Concentrated Sulphuric Acid:

The compound (3-39) (0.10 g, 0.493 mmole) in concentrated sulphuric acid (98%, 5 ml) (experiment 1.C) gave:

i)   1,3-Dimethylbenzo[6,7]bicyclo[3.2.1]octa-3,6-dien-2-one (4-39): (17 mg, 19%), m.p. 103-105°, as shown by t.l.c. and ^{1}H n.m.r.

ii)   9,10-Dihydro-10a-methyl-3H-3a,9-methanobenzo[5,6]cyclohept[1,2-d][1,2]-oxathiol-4(10aH)-one-2,2-dioxide (4-45): (47 mg, 32%), m.p. 173-74°, characterized by comparison with authentic sample.

iii)   brown tar (42 mg), which could not be identified.

29.   Preparation of 1-N,N-Dimethylamino-3,4-dihydronaphthalene (4-55).

A mixture of α-tetralone (4-54) (14.6 g, 100.0 mmole) and dimethylamine (13.5 g, 300.0 mmole) in dry benzene (200 ml) was treated with titanium chloride (9.5 g) in n-hexane (50 ml) over a period of 30 minutes at ca. 0 $\pm$ 5°. The mixture was stirred at room temperature for 28 h and the progress of the reaction was followed by ^{1}H n.m.r. The reaction mixture was filtered and the solvent was removed under reduced pressure. The residual oil was fractionally distilled to give: 1-N,N-dimethylamino-3,4-dihydronaphthalene (4-55): (14.0 g, 80%), b.p. 76°/0.5 mm Hg, (Found: C, 83.3; H, 8.6; N, 8.3%; $C_{12}H_{15}N$ requires C, 83.23; H, 8.5; N, 8.17%): M^+ (Mass spectrometry): 173. ^{1}H n.m.r. τ (CDCl$_3$): 2.45-2.92 (m, 4H); 4.77 (t, 1H, $|J|$ = 4.5 Hz); 7.41 (s, 6H); and 7.52-7.95 (m, 4H). ν_{max} oil 3060, 3020, 2940, 2880, 2830, 2780, 1620, 1482, 1452, 1365, 1340, 1302, 1198, 1146, 1070, 1035, 932, 850, 790, 768, 742, and 705 cm^{-1}.

30.   Preparation of 1-Pyrrolidino-3,4-dihydronaphthalene (4-57).

A mixture of α-tetralone (4-54) (14.6 g, 100.0 mmole), pyrrolidine

(50 ml), p-toluenesulphonic acid (0.5 g) in benzene (300 ml) was heated under reflux. Water was removed as formed by azeotropic distillation in a Dean-Stark trap. Sodium acetate (10 g) was added and the reaction mixture was filtered. The solvent was evaporated under reduced pressure and the residual oil was fractionally distilled to give: 1-pyrrolidino-3,4-dihydro-naphthalene (4-57): (15.4 g, 76%), b.p. 118°/0.4 mm Hg. (Found: C, 84.4; H, 8.4; N, 6.8%; $C_{14}H_{17}N$ requires C, 84.5; H, 8.5; N, 6.98%): M^{+} (Mass spectrometry): 199. ^1H n.m.r. τ (CDCl$_3$): 2.4-3.0 (m, 4H); 4.83 (t, 1H, $|J|$ = 4.5 Hz); 7.02 (m, 4H); 7.21-7.45 (m, 2H); 7.58-7.94 (m, 2H); and 7.96-8.30 (m, 4H). ν_{max} oil: 3060, 3020, 2970, 2930, 2880, 2825, 1620, 1485, 1426, 1370, 1320, 1285, 1178, 1135, 1102, 1038, 940, 870, 790, 770, 742, and 680 cm^{-1}.

31.   Preparation of 2-Methyl-α-tetralone (4-58).

A.   From 1-N,N-Dimethylamino-3,4-dihydronaphthalene (4-55):

A mixture of the compound (4-55) (8.60 g, 5.00 mmole) and methyl iodide (10.6 g, 15.00 mmole) was heated under reflux in chloroform (50 ml) for 6 h.   The white crystalline mass formed was filtered, washed with chloroform (2 x 10 ml) and the combined filtrate was evaporated under reduced pressure.   The residual oil was fractionally distilled to give α-tetralone (4-54) (46%), as shown by t.l.c., g.l.c. and ^1H n.m.r.

The white crystalline mass (4.2 g, 50%) was characterized as tetramethylammonium iodide: (Found: C, 23.78; H, 5.9; N, 6.9%; Calc. for $C_4H_{12}NI$ C, 23.78; H, 5.97; N, 6.96%).

B.   From 1-Pyrrolidino-3,4-dihydronaphthalene (4-57):

A mixture of the compound (4-57) (5.0 g, 25.12 mmole) and methyl iodide (9.6 g, 67.60 mmole) in dry chloroform (50 ml) was heated under reflux for 8 h.   The mixture was diluted with water (15 ml) and the two layers were

separated. The organic phase was separated, dried ($MgSO_4$) and evaporated under reduced pressure. The residue was fractionally distilled to give: 2-methyl-α-tetralone (4-58): (3.2 g, 80%), b.p. $98^{\circ}/0.3$ mm. (lit.[25] b.p. $98^{\circ}/0.3$ mm), characterized by comparison with authentic sample.

Semicarbazone of 2-methyl-α-tetralone, m.p. 198-99° (lit.[25] m.p. 199°).

32. Preparation of 2-Methyl-4-acetonyl-α-tetralone (4-46).

A. Using Anhydrous Manganic acetate and pent-1-en-4-one (4-67):

A mixture of propiophenone (1.34 g, 10.05 mmole), pent-1-en-4-one (4-67) (1.26 g, 10.0 mmole) and manganic acetate (0.67 g, 3.0 mmole) in glacial acetic acid (25 ml) containing 10 % potassium acetate was heated at $90\pm5^{\circ}$ until the brown manganic colour had disappeared. The reaction mixture was diluted with ether (100 ml), extracted with water (5 x 100 ml); saturated sodium chloride (2x50 ml) and dried ($MgSO_4$-Na_2CO_3). The solvent was evaporated under reduced pressure and the residual oil was separated by preparative t.l.c. to give:

i) 1,5-Dioxo-1-phenylhexane: (560 mg, 26%), b.p. 84-$85^{\circ}/0.4$ mm Hg.

ii) 6-Benzoyl-2-oxo-hept-4-ene: (430 mg, 20%), b.p. 115-$16^{\circ}/0.4$ mm Hg.

iii) 2-Methyl-4-acetonyl-α-tetralone (4-46): (122 mg, 5.6%), m.p. 92-93°, identical to the material obtained previously [Experiment 20.B(ii) p.234].

iv) An unidentifiable oil: (380 mg), b.p. 126-$27^{\circ}/0.4$ mm Hg.

B. Using Anhydrous Manganic acetate and pent-1-en-4-ol (4-65):

A mixture of propiophenone (1.34 g, 10.05 mmole), penten-4-ol (1.28 g, 10.0 mmole), and manganic acetate (0.67 g, 3.0 mmole) in glacial acetic acid (40 ml) containing 10% potassium acetate as explained above gave:

i) 1,5-Dioxo-1-phenylhexane (300 mg, 14%), b.p. 85-86° (0.4 mm Hg.).

ii)　4-Hydroxy-6-benzoyl-heptan-2-one; (340 mg, 15.5%), b.p. 115-17°/0.4 mm Hg.

iii)　6-Benzoyl-2-oxo-hept-4-ene; (460 mg, 21%), b.p. 180°/0.4 mm Hg.

iv)　2-Methyl-4-acetonyl-α-tetralone (4-46); (165 mg, 6.2%) m.p. 92-93°, characterized by comparison with authentic sample.

C.　Using Anhydrous Manganic acetate and Penten-4-acetate

(Methyl ester of allyl methyl carbinol) (4-68):

A mixture of propiophenone (1.34 g, 10.05 mmole), pent-1-en-4-acetate (1.28 g, 10.0 mmole) and manganic acetate (1.34 g, 6.0 mmole) in glacial acetic acid (40 ml) containing 10% potassium acetate as explained earlier gave:

i)　1,5-Dioxo-1-phenyl-hexane (4-70); (440 mg, 20%), b.p. 85-86°/0.4 mm Hg.

ii)　4-Acetoxy-6-benzoyl-heptan-2-one (4-71): (460 mg, 21%), b.p. 114-17°/0.4 mm Hg.

iii)　6-Benzoyl-2-oxo-hept-4-ene (4-72): (390 mg, 18%), b.p. 129-30°/0.4 mm Hg.

iv)　2-Methyl-4-acetonyl-α-tetralone (4-46): (200 mg, 92%), m.p. 92-93°, as shown by t.l.c. and ^{1}H n.m.r.

D.　Using Manganic acetate dihydrate and Penten-4-ol (4-65):

A mixture of propiophenone (2.68 g, 20.10 mmole), penten-4-ol (2.56 g, 20.0 mmole) and manganic acetate dihydrate (2.68 g, 10.0 mmole) in glacial acetic acid (40 ml) containing 10% potassium acetate as explained earlier gave: 2-methyl-4-acetonyl-α-tetralone (4-46) in 10% yield, characterized by comparison with authentic material.

33.   Acid-Catalysed Rearrangements of 2,5-Dimethyl-1-methoxybenzobarrelene
      (3-34).

A.   In Trifluoroacetic Acid:

      A solution of the compound (3-34) (1.5 g, 7.07 mmole) in trifluoro-
acetic acid (25 ml) (experiment 1.A) gave:

i)   1,6-Dimethylbenzo[3,4]bicyclo[3.2.1]octa-3,6-dien-2-one[5,8-dihydro-
6,8-dimethyl-5,8-methanobenzocyclohepten-9(1H)-one] (4-73): (126 mg, 9%),
b.p. 102-103°/4 mm.   (Found: C, 84.7; H, 6.9%. $C_{14}H_{14}O$ requires   C, 84.84;
H, 7.07%), M^{+} (Mass spectrometry):198. ^{1}H n.m.r. τ (CDCl$_3$): 1.85-2.05 (dd,
1H,|$\underline{J}$|= 1.6 Hz; |$\underline{J}$| = 6.8 Hz); 2.3-2.9 (m, 3H); 3.45-3.85 (m, 1H, |$\underline{J}$| = 7.0 Hz);
6.61-6.35 (m, 1H); 7.55-7.96 (m, 2H); 8.6 (d, 3H*); and 8.63 (s, 3H). ν_{max} oil:
3070, 2975, 2935, 2870, 1690, 1600, 1455, 1378, 1285, 1240, 1195, 1080, 985,
960, 855, 815, 770, 740, and 715 cm^{-1}.

ii)   A mixture of two isomeric ketones, which were separated by multiple
elution, to give:

(a)   1,4-Dimethylbenzobarrelen-2-one[5,8-dihydro-5,8-dimethyl-5,8-etheno-
naphthalen-9(1H)-one] (4-74): (381 mg, 27%), m.p. 69-70° (from ethanol)
(Found: C, 84.7; H, 7.1%. $C_{14}H_{14}O$ requires, C, 84.84; H, 7.07%) [M^{+}-42]
(Mass spectrometry): 156. ^{1}H n.m.r. τ (CDCl$_3$): 2.55-2.95 (m, 4H); 3.69
(q, 2H,|$\underline{J}$|= 7.0 Hz); 7.95 (m, 2H, |$\underline{J}$| = 7.0 Hz); 8.25 (s, 3H); and 8.29 (s, 3H).
ν_{max} KBr: 3050, 2975, 2942, 2880, 1725, 1455, 1385, 1350, 1295, 1255, 1180,
1137, 1080, 1050, 1030, 915, 782, 770, 755, and 692 cm^{-1}.

(b)   1,5-Dimethylbenzobarrelen-2-one[5,8-dihydro-6,8-dimethyl-5,8-etheno-
naphthalen-9(1H)-one] (4-75):   (201 mg, 14%), m.p. 74-75°C (from ethanol).
(Found: C, 84.6; H, 7.1%. $C_{14}H_{14}O$ requires   C, 84.84; H, 7.07%); [M^{+}-42]
(Mass spectrometry): 156. ^{1}H n.m.r. τ (CDCl$_3$): 2.52-2.98 (m, 4H); 4.15-4.32
(m, 1H); 6.06-6.35 (m, 1H, |$\underline{J}$| = 2.2 Hz); 7.55-8.0 (m, 2H); 8.06 (d, 3H,

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*(|$\underline{J}$|= 1.6 Hz.)

$\underline{J}$ = 2.2 Hz); and 8.34 (s, 3H). ν_{max} KBr: 3070, 3042, 2980, 2940, 2880, 1725, 1455, 1390, 1380, 1292, 1115, 1070, 960, 820, 762, 712, and 695 cm^{-1}.

iii) 1,4-Dimethylbenzo[6,7]bicyclo[3.2.1]octa-3,6-dien-2-one[5,9-dihydro-6,9-dimethyl-5,9-methanobenzocyclohepten-8(1H)-one] (4-76): (670 mg, 48%), m.p. 103-104° (from ethanol). (Found: C, 84.7; H, 7.1%. $C_{14}H_{14}O$ requires C, 84.84; H, 7.07%); M$^{\dot{+}}$ (Mass spectrometry): 198. ^{1}H n.m.r. τ (CDCl$_3$): 2.62-3.05 (m, 4H); 4.68-4.82 (m, 1H); 6.49 (m, 1H, $|\underline{J}|$ = 2.2 Hz); 7.46 (m, 2H, $|\underline{J}|$ = 2.2 Hz); 8.0 (s, 3H); and 8.5 (s, 3H). ν_{max} KBr: 3075, 3040, 2985, 2970, 2940, 2875, 1668, 1625, 1455, 1425, 1375, 1320, 1250, 1198, 1174, 1122, 1016, 904, 775, 760, and 730 cm^{-1}.

B.   In Concentrated Sulphuric Acid:

The compound (3-34) (1.5 g, 7.07 mmole) in concentrated sulphuric acid (98%, 10 ml) (experiment 1.$\underline{C}$) gave:

i)   1,6-Dimethylbenzo[3,4]bicyclo[3.2.1]octa-3,6-dien-2-one (4-73): (147 mg, 10%), as shown by t.l.c. and ^{1}H n.m.r.

ii)   1,4-Dimethylbenzobarrelen-2-one (4-74): (234 mg, 17%), characterized by comparison with authentic material.

iii)   1,5-Dimethylbenzobarrelen-2-one (4-75): (195 mg, 14%), as shown by t.l.c. and ^{1}H n.m.r.

iv)   1,4-Dimethylbenzo[6,7]bicyclo[3.2.1]octa-3,6-dien-2-one (4-76): (556 mg, 39%), characterized by comparison with authentic sample;   and

v)   4-Methylbenzo[3,4]bicyclo[3.2.1]oct-3-ene-2-onyl-1,7-sultone[10,10a-dihydro-9-methyl-3H-3a,9-methanobenzo[5,6]cyclohept[1,2-d][1,2]oxathiol-4-(10aH)-one-2,2-dioxide] (4-79): (318 mg, 16%), m.p. 203-204° (from ethanol): (Found: C, 60.3; H, 5.1%. $C_{14}H_{14}SO_4$ requires, C, 60.4; H, 5.0%), M$^{\dot{+}}$ (Mass

spectrometry): 278. ^{1}H n.m.r. τ (CDCl$_3$): 1.7-1.95 (dd, 1H,|$\underline{J}$|= 1.6 Hz;

|$\underline{J}$| = 6.6 Hz); 2.2-2.75 (m, 3H); 5.25-5.47 (m, 1H); 5.71 (d, 1H,|$\underline{J}$|= 14.0 Hz);

6.45 (d, 1H,|$\underline{J}$|= 14.0 Hz); 7.5 (m, 2H); 7.6-7.85 (m, 2H); and 8.55 (s, 3H).

ν_{max} KBr: 3090, 2982, 2945, 2880, 1692, 1600, 1480, 1455, 1437, 1415, 1380,

1355, 1317, 1280, 1260, 1232, 1222, 1180, 1168, 1078, 1015, 987, 967, 872,

840, 805, 770, 740, and 718 cm^{-1}.

C.   In Fluorosulphuric Acid:

The compound (3-34) (0.50 g, 2.36 mmole) in fluorosulphuric acid

(5 ml) at -70° (experiment 1.$\underline{D}$) gave:

i)   1,6-Dimethylbenzo[3,4]bicyclo[3.2.1]octa-3,6-dien-2-one (4-73):

(42 mg, 9%), as shown by t.l.c. and ^{1}H n.m.r.

ii)   1,4-Dimethylbenzobarrelen-2-one (4-74): (170 mg, 36%) characterized

by comparison with authentic sample.

iii)   1,5-Dimethylbenzobarrelen-2-one (4-75): (150 mg, 32%), as shown by

t.l.c. and ^{1}H n.m.r.

iv)   1,4-Dimethylbenzo[6,7]bicyclo[3.2.1]octa-3,6-dien-2-one (4-76): (66 mg,

14%), m.p. 103-104°, characterized by comparison with authentic sample.

34.   Isomerization of 1,6-Dimethylbenzo[3,4]bicyclo[3.2.1]octa-3,6-dien-

2-one (4-73).

The ketone (4-73) failed to isomerize either in trifluoroacetic acid

or in concentrated sulphuric acid (98%) to give any other product. However,

at much longer periods only the decomposed products were obtained which could

not be identified.

35.   Isomerization of 1,4-Dimethylbenzobarrelen-2-one (4-74).

A.   In Trifluoroacetic Acid:

The ketone (4-74) did not give any other product in trifluoroacetic acid even after 72 h. On heating only decomposed products were obtained which could not be identified.

B.   In Concentrated Sulphuric Acid:

The ketone (4-74) (0.10 g, 0.504 mmole) in concentrated sulphuric acid (10 ml) (experiment 1.C) gave:

i)   an unchanged starting material (25 mg), characterized by comparison with authentic sample.

ii)   10,10a-Dihydro-9-methyl-3H-3a,9-methanobenzo[5,6]cyclohept[1,2-d][1,2]-oxathiol-4(10aH)-one-2,2-dioxide (4-79): (84 mg, 60%), m.p. 203-204° (from ethanol), characterized by comparison with authentic sample.

36.   Isomerization of 1,5-Dimethylbenzobarrelen-2-one (4-75).

The ketone (4-75) failed to isomerize either in trifluoroacetic acid or in concentrated sulphuric acid to give any other product. On longer treatment only decomposed products were obtained which could not be identified.

37.   Isomerization of 1,4-Dimethylbenzo[6,7]bicyclo[3.2.1]octa-3,6-dien-2-one (4-76).

An attempted isomerization of the ketone (4-76) either in trifluoroacetic acid or in concentrated sulphuric acid failed to give any other product. No effect was observed even at much longer periods.

38.   Acid-Catalysed Rearrangements of 3,5-Dimethyl-1-methoxytetrachloro-benzobarrelene (2-10).

A.   In Trifluoroacetic Acid:

A solution of the compound (2-10) (1.0 g, 2.860 mmole) in trifluoroacetic acid (15 ml) (experiment 1.A) gave:

i)   4,6-Dimethyltetrachlorobenzobarrelen-2-one[1,2,3,4-tetrachloro-5,8-dihydro-5,7-dimethyl-5,8-ethenonaphthalen-9(1H)-one] (4-82): (860 mg, 94%), m.p. 174-75° (from ethanol). (Found: C, 49.8; H, 3.0%. $C_{14}H_{10}Cl_4O$ requires C, 50.0; H, 2.97%); M$^+$ (Mass spectrometry): 294. ^{1}H n.m.r. τ (CDCl$_3$): 3.9-4.1 (m, 1H); 5.08-5.22 (d, 1H, $|J|$ = 2.2 Hz); 7.75-8.15 (m, 2H); 7.96 (s, 3H); and 8.05 (d, 3H, $|J|$ = 1.6 Hz). ν_{max} KBr: 3020, 2985, 2950, 2930, 2865, 1735, 1445, 1390, 1380, 1365, 1290, 1220, 1175, 1130, 1085, 905, 830, 795, 700, and 650 cm^{-1}.

ii)   an unidentified tar (50 mg).

   B.   In Boiling Trifluoroacetic Acid:

      The compound (2-10) (1.0 g, 2.860 mmole) in boiling trifluoroacetic acid (10 ml) gave:

i)   4,6-Dimethyltetrachlorobenzobarrelen-2-one (4-82): (50 mg, 5%), as shown by t.l.c. and ^{1}H n.m.r.

ii)   1,5-Dimethyl-6-oxa-tetrachlorobenzo[2,3]bicyclo[3.3.1]non-2-ene-7-one (4-83): (930 mg, 93%), m.p. 212-13° (from ethanol). (Found: C, 47.5; H, 3.4%; $C_{14}H_{12}Cl_4O_2$ requires C, 47.45; H, 3.37%), M$^+$ (Mass spectrometry): 354. ^{1}H n.m.r. τ (CDCl$_3$): 6.6-7.21 (m, 2H): 7.41-7.92 (m, 2H); 7.92-8.23 (m, 2H); 8.31 (s, 3H) and 8.42 (s, 3H). ν_{max} KBr: 3050, 2990, 2955, 2930, 2890, 1730, 1460, 1425, 1395, 1385, 1372, 1340, 1315, 1270, 1245, 1210, 1125, 1090, 1060, 990, 975, 870, 810, 715, and 660 cm^{-1}.

   C.   In Concentrated Sulphuric Acid:

      The compound (2-10) (0.500 g, 1.430 mmole) in concentrated sulphuric acid (98%, 10 ml) (experiment 1.C) gave 1,5-Dimethyl-6-oxa-tetrachlorobenzo-

[2,3]bicyclo[3.3.1]non-2-ene-7-one (4-83):   (460 mg, 92%), m.p. 212-13°
(from ethanol), characterized by comparison with authentic sample.

D.   In Aqueous Sulphuric Acid:

The compound (2-10) (0.10 g, 0.286 mmole) in aqueous sulphuric acid
(80%, 10 ml) gave:

i)   unchanged starting material (10 mg), as shown by t.l.c. and [1]H n.m.r.

ii)   4,6-Dimethyltetrachlorobenzobarrelen-2-one (4-82) (20 mg, 18%) as
shown by t.l.c. and [1]H n.m.r., and

iii)   1,5-Dimethyl-6-oxa-tetrachlorobenzo[2,3]bicyclo[3.3.1]non-2-ene-7-one
(4-83):   (50 mg, 48%), m.p. 212-214° (from ethanol) characterized by
comparison with authentic sample.

39.   Isomerization of 4,6-Dimethyltetrachlorobenzobarrelen-2-one (4-82).

A.   In Trifluoroacetic Acid:

The ketone (4-82) (0.15 g, 0.429 mmole) in boiling trifluoroacetic
acid (5 ml) gave: 1,5-Dimethyl-6-oxa-tetrachlorobenzo[2,3]bicyclo[3.3.1]-
non-2-ene-7-one (4-83):   (130 mg, 87%), m.p. 212-214° (from methanol), as
shown by t.l.c. and [1]H n.m.r.

B.   In Concentrated Sulphuric Acid:

The ketone (4-82) (0.05 g, 0.143 mmole) in concentrated sulphuric
acid (5 ml) gave: 1,5-Dimethyl-6-oxa-tetrachlorobenzo[2,3]bicyclo[3.3.1]-
non-2-ene-7-one (4-83):   (40 mg, 80%), as shown by t.l.c. and [1]H n.m.r.

40.   Reduction of 1,5-Dimethyl-6-oxa-tetrachlorobenzo[2,3]bicyclo[3.3.1]-
        non-2-ene-7-one (4-83).

The lactone (4-83) (0.50 g, 1.410 mmole) in ether (25 ml) was added

250.

dropwise to a suspension of lithium aluminium hydride (0.10 g) in ether (20 ml) and the mixture was stirred for 1 h.   Dilute sulphuric acid (2$\underline{N}$, 15 ml) was then slowly added and the two layers were separated. The aqueous phase was extracted with ether (2x25 ml) and the combined extracts were dried (MgSO$_4$).   The solvent was evaporated under reduced pressure and the residue on purification gave: <u>1,3-Dimethyl-3-hydroxy-1-(2'-hydroxyethyl)-5,6,7,8-tetrachloro-1,2,3,4-tetrahydronaphthalene</u> (4-87): (490 mg, 96%) m.p. 100-101° (from ethanol).   (Found: C, 46.8; H, 4.4%;   C$_{14}$H$_{16}$Cl$_4$O$_2$ requires C, 46.92; H, 4.47%); M$^{\ddot{+}}$ (Mass spectrometry): 358. ^{1}H n.m.r. τ (CDCl$_3$): 5.54 (broad hump, 2H); 6.21-6.72 (m, 2H); 6.75-8.21 (m, 6H); 8.51 (s, 3H); and 8.73 (s, 3H). ν_{max} KBr: 3380, 3025, 2990, 2950, 2890, 1650, 1565, 1465, 1425, 1380, 1350, 1300, 1242, 1165, 1125, 1065, 978, 935, 905, 840, 780, and 690 cm^{-1}.

41.   <u>Oxidation of 1,3-Dimethyl-3-hydroxy-1-(2'-hydroxyethyl)-5,6,7,8-tetrachloro-1,2,3,4-tetrahydronaphthalene (4-87)</u>:

A solution of diol (4-87) (0.10 g, 0.279 mmole) in acetone (10 ml) was treated with Jone's reagent* dropwise until a yellow colour remained for 5 minutes.   The mixture was diluted with water (20 ml) and the aqueous phase was extracted with ether (4x25 ml).   The combined extracts were dried (MgSO$_4$) and evaporated under reduced pressure.   The residue on purification gave: 1,5-Dimethyl-6-oxa-tetrachlorobenzo[2,3]bicyclo[3.3.1]non-2-ene-7-one (4-83): (95 mg, 95%), m.p. 212-214° (from ethanol), characterized by comparison with authentic sample.

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* <u>Jone's Reagent</u>: Chromium trioxide (26.72 g) was dissolved in concentrated sulphuric acid (23 ml) and the mixture was diluted with water to 100 ml.

42.   Acid-Catalysed Rearrangements of 3,5-Dimethyl-1-methoxybenzobarrelene
       (3-35).

A.   In Trifluoroacetic Acid:

        A solution of the compound (3-35) (1.5 g, 7.07 mmole) in trifluoro-
acetic acid (25 ml) (experiment 1.A) gave: 4,6-Dimethylbenzobarrelen-2-one-
[5,8-dihydro-5,7-dimethyl-5,8-ethenonaphthalen-9(1H)-one] (4-84): (1.30 g,
96%), oil. (Found: C, 84.4; H, 7.2%; $C_{14}H_{14}O$ requires, C, 84.84; H, 7.07%),
M$^+$ (Mass spectrometry): 156. ^{1}H n.m.r. τ (CDCl$_3$): 2.6-3.12 (m, 4H); 4.02-4.22
(m, 1H); 5.85-6.12 (m, 1H); 7.81-8.51 (m, 2H); 8.06 (d, 3H, |$\underline{J}$| = 1.6 Hz);
and 8.2 (s, 3H). ν_{max} oil: 3080, 3040, 2975, 2940, 2920, 2880, 1730, 1460,
1410, 1385, 1300, 1230, 1175, 1127, 1030, 930, 830, 810, 768, 750, and
655 cm^{-1}.

B.   In Boiling Trifluoroacetic Acid:

        The compound (3-35) (0.50 g, 2.358 mmole) in boiling trifluoroacetic
acid (10 ml) gave:

i)   4,6-Dimethylbenzobarrelen-2-one (4-84): (50 mg, 9%), as shown by t.l.c.
and ^{1}H n.m.r.

ii)   1,5-Dimethyl-6-oxa-benzo[2,3]bicyclo[3.3.1]non-2-ene-7-one (4-85):
(460 mg, 89%), m.p. 140-41° (from ethanol). (Found: C, 77.5; H, 7.5%;
$C_{14}H_{16}O_2$ requires C, 77.78; H, 7.41%), M$^+$ (Mass spectrometry): 216. ^{1}H n.m.r.
τ (CDCl$_3$): 2.5-3.12 (m, 4H); 6.98 (s, 2H); 7.4-7.63 (m, 2H); 7.66-8.25 (m, 2H);
8.49 (s, 3H); and 8.60 (s, 3H). ν_{max} KBr: 3025, 2980, 2970, 2935, 2910,
2880, 1720, 1485, 1460, 1445, 1380, 1335, 1318, 1295, 1260, 1230, 1160, 1145,
1120, 1050, 995, 975, 965, 930, 900, 805, 780, and 735 cm^{-1}.

C.   In Concentrated Sulphuric Acid:

The compound (3-35) (0.50 g, 2.358 mmole) in concentrated sulphuric acid (10 ml) (experiment 1.C) gave: 1,5-Dimethyl-6-oxa-benzo[2,3]bicyclo-[3.3.1]non-2-ene-7-one (4-85): (475 mg, 94%), m.p. 140-41$^{\text{o}}$ (from ethanol), characterized by comparison with authentic sample.

43.   Isomerization of 4,6-Dimethylbenzobarrelen-2-one (4-84).

A.   In Trifluoroacetic Acid:

The ketone (4-84) (0.10 g, 0.505 mmole) in boiling trifluoroacetic acid (5 ml) gave: 1,5-Dimethyl-6-oxa-benzo[2,3]bicyclo[3.3.1]non-2-ene-7-one (4-85): (98 mg, 96%), as shown by t.l.c. and ^{1}H n.m.r.

B.   In Concentrated Sulphuric Acid:

The ketone (4-84) (0.05 g, 0.252 mmole) in concentrated sulphuric acid (3 ml) gave: 1,5-Dimethyl-6-oxa-benzo[2,3]bicyclo[3.3.1]non-2-ene-7-one (4-85): (50 mg, 98%), characterized by comparison with authentic sample.

44.   Reduction of 1,5-Dimethyl-6-oxa-benzo[2,3]bicyclo[3.3.1]non-2-ene-7-one (4-85):

A solution of the lactone (4-85) (0.10 g, 0.462 mmole) on reduction with lithium aluminium hydride (30 mg) in dry ether (30 ml) (experiment 40) gave: 1,3-Dimethyl-3-hydroxy-1-(2'-hydroxyethyl)-1,2,3,4-tetrahydronaphthalene (4-88): (140 mg, 95%), m.p. 100-101$^{\text{o}}$ (from ethanol). (Found: C, 76.16; H, 9.1%; $C_{14}H_{20}O_2$ requires, C, 76.38; H, 9.15%); M^{+} (Mass spectrometry): 220. ^{1}H n.m.r. τ (CDCl$_3$): 2.6-3.06 (m, 4H); 6.15-6.45 (t, 2H, $|J|$ = 6.0 Hz), 7.16 (s, 2H); 7.45 (broad hump, 2H); 7.6-7.96 (m, 2H); 8.0-8.42 (m, 2H); and 8.68 (s, 3H);and 8.70(s,3H). ν_{max} oil: 3370, 3080, 3030, 2990, 2890, 1495, 1460, 1387, 1225, 1175, 1140, 920, 900, 770, and 675 cm^{-1}.

45.   Oxidation of 1,3-Dimethyl-3-hydroxy-1-(2'-hydroxyethyl)-1,2,3,4-tetra-
      hydronaphthalene (4-88).

A solution of the diol (4-88) (0.08 g, 0.369 mmole) in dichloromethane

(10 ml) was stirred for 1 h with pyridinium chlorochromate (0.323 g, 1.50

mmole) in dichloromethane (10 ml). The mixture was diluted with ether (25 ml)

and the supernatant liquid was decanted from the gum. The combined organic

phase was passed through celite pad and evaporated under pressure to give:

1,5-Dimethyl-6-oxa-benzo[2,3]bicyclo[3.3.1]non-2-ene-7-one (4-85):   (75 mg,

96%), m.p. 140-41°, characterized by comparison with authentic sample.

46.   Acid-Catalysed Rearrangements of 2,3,5-Trimethyl-1-methoxytetrachloro-
      benzobarrelene (2-12).

   A.   In Trifluoroacetic Acid:

      A solution of the compound (2-12) (1.5 g, 4.12 mmole) in boiling

trifluoroacetic acid (25 ml) (experiment 1.A) gave:

i)   an unidentified product (60 mg);

ii)   1,4,6-Trimethyltetrachlorobenzo[6,7]bicyclo[3.2.1]octa-3,6-dien-2-one-

[1,2,3,4-tetrachloro-5,9-dihydro-6,9,12-trimethyl-5,9-methanobenzocyclohepten-

8(1H)-one] (4-93): (245 mg, 17%), m.p. 183-84° (from ethanol).   (Found:

C, 51.1; H, 3.4%; $C_{15}H_{12}Cl_4O$ requires   C, 51.43; H, 3.43%), M$^{\overset{+}{\cdot}}$ (Mass

spectrometry): 350. ^{1}H n.m.r. τ (CDCl$_3$): 4.81 (s, broad, 1H); 6.62 (s, 1H);

6.91-7.64 (q, 1H, $|\underline{J}|$ = 6.6 Hz); 7.92 (s, 3H); 8.43 (s, 3H); and 8.97 (d, 3H,

$|\underline{J}|$ = 6.6 Hz). ν_{max} KBr: 3050, 2990, 2970, 2950, 2930, 2890, 1680, 1630,

1465, 1435, 1380, 1360, 1330, 1290, 1255, 1220, 1170, 1120, 1030, 950, 880,

825, 780, 710, and 645 cm^{-1}.

iii)   an unidentified product (85 mg);   and

iv)   1,4,6-Trimethyltetrachlorobenzobarrelen-2-one[1,2,3,4-tetrachloro-5,8-

dihydro-5,7,8-trimethyl-5,8-ethenonaphthalen-9(1H)-one (4-94): (825 mg, 55%), m.p. 135-36° (from ethanol). (Found: C, 51.2; H, 3.4%; $C_{15}H_{12}Cl_4O$ requires, C, 51.43; H, 3.43%), $M^{\overset{+}{\cdot}}$ (Mass spectrometry): 350 (loss of 42). ^{1}H n.m.r. τ (CDCl$_3$): 4.37 (s, 1H); 6.41-7.45 (q, 2H, $|\underline{J}|$ = 7.2 Hz); 7.96 (s, 3H); 8.62 (s, 3H); and 8.71 (s, 3H). ν_{max} KBr: 3020, 2990, 2960, 2940, 2920, 2890, 2860, 1715, 1635, 1435, 1375, 1300, 1268, 1185, 1110, 985, 870, 845, 775, 730, and 670 cm^{-1}.

B. In Concentrated Sulphuric Acid:

The compound (2-12) (1.5 g, 4.12 mmole) in concentrated sulphuric acid (96%, 25 ml) (experiment 1.C) gave:

i) an unidentified product (80 mg);

ii) 1,4,6-Trimethyltetrachlorobenzo[6,7]bicyclo[3.2.1]octa-3,6-dien-2-one (4-93): (265 mg, 18%), m.p. 182-84° (from ethanol), characterized by comparison with authentic sample;

iii) an unidentified sample (40 mg);

iv) 1,4,6-Trimethyltetrachlorobenzobarrelen-2-one (4-94): (616 mg, 41%), m.p. 135-36° (from ethanol), characterized by comparison with authentic sample; and

v) 1,5,8-Trimethyl-6-oxa-1',2',3',4'-tetrachlorobenzo[2,3]bicyclo[3.3.1]-non-2-ene-7-one (4-95): (270 mg, 18%), m.p. 190-91° (from ethanol). (Found: C, 48.9; H, 3.7%; $C_{15}H_{14}Cl_4O_2$ requires, C, 48.91; H, 3.80%), $M^{\overset{+}{\cdot}}$ (Mass spectrometry): 368. ^{1}H n.m.r. τ (CDCl$_3$): 6.4-6.82 (m, 2H); 7.07 (s, 1H); 7.3-7.65 (m, 2H, $|\underline{J}|$ = 7.0 Hz); 7.70-7.95 (m, 1H); 8.11 (s, 3H); 8.42 (s, 3H); and 8.62 (d, 3H, $|\underline{J}|$= 1.6 Hz). ν_{max} KBr: 3050, 2990, 2950, 2890, 2870, 1720, 1460, 1390, 1335, 1315, 1235, 1220, 1150, 1115, 1090, 1025, 975, 890, 835, 805, 785, and 710 cm^{-1}.

C.   In Aqueous Sulphuric Acid:

The compound (2-12) (0.50 g, 1.37 mmole) in aqueous sulphuric acid (80%, 25 ml) gave:

i)   an unchanged starting material (100 mg);

ii)   1,4,6-trimethyltetrachlorobenzo[6,7]bicyclo[3.2.1]octa-3,6-dien-2-one (4-93): (92 mg, 18%), m.p. 182-83°, as shown by t.l.c. and ^{1}H n.m.r.

iii)   1,4,6-Trimethyltetrachlorobenzobarrelen-2-one (4-94): (160 mg, 30%), m.p. 135-36°, as shown by t.l.c. and ^{1}H n.m.r.

iv)   1,5,8-Trimethyl-6-oxa-1',2'-tetrachlorobenzo[2,3]bicyclo[3.3.1]non-2-ene-7-one (4-95): (116 mg, 24%), m.p. 190-91°; characterized by comparison with authentic sample.

D.   In Fluorosulphuric Acid:

The compound (2-12) (0.10 g, 0.274 mmole) in fluorosulphuric acid (3 ml) at -70° (experiment 1.D) gave:

i)   an unidentified product (10 mg);

ii)   1,4,6-Trimethyltetrachlorobenzo[6,7]bicyclo[3.2.1]octa-3,6-dien-2-one (4-93): (15 mg, 17%), as shown by t.l.c. and ^{1}H n.m.r.

iii)   1,4,6-Trimethyltetrachlorobenzobarrelen-2-one (4-94): (52 mg, 58%), m.p. 135-36°, as shown by t.l.c. and ^{1}H n.m.r.

iv)   an unidentified material (10 mg).

47.   Isomerization of 1,4,6-Trimethyltetrachlorobenzobarrelen-2-one (4-94).

A.   In Trifluoroacetic Acid:

The ketone (4-94) (0.10 g, 0.275 mmole) in boiling trifluoroacetic acid (5 ml) (100 h) gave:

256.

i)   an unchanged starting material (40 mg);

ii)   1,5,8-Trimethyl-6-oxa-1',2'-tetrachlorobenzo[2,3]bicyclo[3..3.1]non-
2-ene-7-one (4-95):   (35 mg, 30%), m.p. 190-91°, characterized by comparison
with authentic sample.

B.   In Concentrated Sulphuric Acid:

The ketone (4-94) (0.10 g, 0.275 mmole) in concentrated sulphuric
acid (10 ml) gave:

i)   unchanged starting material (10 mg);

ii)   1,5,8-Trimethyl-6-oxa-1',2'-tetrachlorobenzo[2,3]bicyclo[3.3.1]non-
2-ene-7-one (4-95):   (67 mg, 60%), characterized by comparison with
authentic sample.

48.   Reduction of 1,5,8-Trimethyl-6-oxa-1',2'-tetrachlorobenzo[2,3]-
bicyclo[3.3.1]non-2-ene-7-one (4-95).

The lactone (4-95) (0.20 g, 0.592 mmole) was reduced with lithium
aluminium hydride (0.40 g) in ether (40 ml) (experiment 40) gave: 1,3-
dimethyl-3-hydroxy-1-(2'-hydroxypropyl)-5,6,7,8-tetrachloro-1,2,3,4-
tetrahydronaphthalene (4-101):   (190 mg, 94%), m.p. 140-41° (from ethanol)
M^{+} (Mass spectrometry): 372. ν_{max} KBr: 3405, 3025, 2990, 2980, 2890, 1658,
1570, 1462, 1425, 1380, 1325, 1305, 1245, 1165, 1040, 980, 935, 905, 840,
810, 775, and 692 cm^{-1}.

49.   Oxidation of 1,3-Dimethyl-3-hydroxy-1-(2'-hydroxypropyl)-5,6,7,8-
tetrachloro-1,2,3,4-tetrahydronaphthalene (4-101).

A solution of the diol (4-101) (0.08 g, 0.213 mmole) was oxidized
with Jone's reagent in acetone (20 ml) (experiment 41) gave: 1,5,8-

257.

Trimethyl-6-oxa-1',2'-tetrachlorobenzo[2,3]bicyclo[3.3.1]non-2-ene-7-one
(4-95): (70 mg, 89%), m.p. 190-91°, characterized by comparison with
authentic material.

50. Acid-Catalysed Rearrangements of 2,3,5-Trimethyl-1-methoxybenzo-
    barrelene (3-37).

A. In Trifluoroacetic Acid:

A solution of the compound (3-37) (1.2 g, 5.310 mmole) in trifluoro-
acetic acid (20 ml) (experiment 1.A) gave:

i) an unidentified product (40 mg);

ii) 1,4,6-Trimethylbenzobarrelen-2-one[5,8-dihydro-5,7,8-trimethyl-5,8-
dihydro-5,7,8-trimethyl-5,8-ethenonaphthalen-9(1H)-one](4-97): (860 mg,
78%), m.p. 65-66° (from ethanol): (Found: C, 84.6; H, 7.6%; $C_{15}H_{16}O$
requires, C, 84.9; H, 7.55%);[M$^+$-42] (Mass spectrometry):170.^{1}H n.m.r. τ (CDCl$_3$):
2.62-3.32 (m, 4H); 3.85-4.31 (d, 1H, $|J|$ = 7.2 Hz) 7.62-8.6 (m, 2H);
8.3 (s, 3H); 8.40 (s.3H); and 8.51 (s.3H). ν_{max} KBr: 3080, 3050, 2980,
2950, 2930, 2890, 1730, 1460, 1445, 1390, 1320, 1300, 1263, 1175, 1148, 1120,
1090, 1070, 1050, 1035, 820, 795, 770, and 755 cm^{-1};

iii) an unidentified oil (60 mg); and

iv) 1,4,6-Trimethylbenzo[6,7]bicyclo[3.2.1]octa-3,6-dien-2-one[5,9-dihydro-
6,9,12-trimethyl-5,9-methanobenzocyclohepten-8(1H)-one] (4-96): (126 mg, 11%),
m.p. 97-98° (from ethanol): (Found: C, 84.6; H, 7.5%; $C_{15}H_{16}O$ requires,
C, 84.90; H, 7.55%); M$^+$ (Mass spectrometry): 212. ^{1}H n.m.r. τ (CDCl$_3$):
2.55-3.16 (m, 4H); 4.7-4.9 (q, 1H, $|J|$ = 7.2 Hz); 6.75 (s, 1H); 7.05 (q, 1H,
$|J|$ = 7.2 Hz); 7.9 (d, 3H, $|J|$ = 1.6 Hz); 8.6 (s, 3H); and 9.06 (d, 3H, $|J|$ =
7.2 Hz). ν_{max} KBr: 3050, 2985, 2950, 2925, 2890, 1672, 1460, 1440, 1380,
1330, 1255, 1222, 1165, 1118, 1020, 890, 835, 795, 762, and 726 cm^{-1}.

B.   In Concentrated Sulphuric Acid:

The compound (3-37) (1.0 g, 4.42 mmole) in concentrated sulphuric

acid (15 ml) (experiment 1.C) gave:

i)   an unidentified oil (60 mg);

ii) 1,4,6-Trimethylbenzobarrelen-2-one (4-97) (150 mg, 13%) m.p. 65-66$^{\rm O}$,

as shown by t.l.c. and ^{1}H n.m.r.

iii)   1,4,6-Trimethylbenzo[6,7]bicyclo[3.2.1]octa-3,6-dien-2-one (4-96):

(175 mg, 18%) m.p. 97-98$^{\rm O}$, characterized by comparison with authentic material.

iv)   1,5,8-Trimethyl-6-oxa-benzo[2,3]bicyclo[3.3.1]non-2-ene-7-one (4-98):

(450 mg, 46%) m.p. 139-40$^{\rm O}$ (from ethanol). (Found: C, 77.9; H, 7.9%;

$C_{15}H_{18}O_2$ requires, C, 78.2; H, 7.83%); $M^{\overset{+}{\cdot}}$ (Mass spectrometry): 230. ^{1}H n.m.r.

τ (CDCl$_3$): 2.52-3.06 (m, 4H); 6.95 (q, 1H, $\underline{J}$ = 7.2 Hz); 7.62 (d, 1H, $|\underline{J}|$ =

2.2 Hz); 7.75-8.25 (m, 2H); 8.52 (s, 3H); 8.62 (m, 3H); and 8.78 (d, 3H,

$|\underline{J}|$ = 2.2 Hz). ν_{max} KBr: 3080, 3030, 2990, 2950, 2890, 1728, 1495, 1460,

1420, 1390, 1370, 1340, 1305, 1268, 1225, 1160, 1130, 1065, 1040, 1010, 985,

930, 820, 765, 725, and 675 cm^{-1}.

C.   In Aqueous Sulphuric Acid:

The compound (3-37) (0.10 g, 0.442 mmole) in aqueous sulphuric acid

(80%, 5 ml) gave:

i)   1,4,6-Trimethylbenzobarrelen-2-one (4-97): (20 mg, 19%); as shown by

t.l.c. and ^{1}H n.m.r.

ii)   1,4,6-Trimethylbenzo[6,7]bicyclo[3.2.1]octa-3,6-dien-2-one (4-96):

(23 mg, 22%), characterized by comparison with authentic sample, and

iii)   1,5,8-Trimethylbenzo[2,3]bicyclo[3.3.1]non-2-ene-7-one (4-98):

(25 mg, 21%), characterized by comparison with authentic sample.

259.

51.   Isomerization of 1,4,6-Trimethylbenzobarrelen-2-one (4-97).

    A.   In Trifluoroacetic Acid:

        The ketone (4-97) (0.10 g, 0.424 mmole) in boiling trifluoroacetic

acid (5 ml) gave:

i)   unchanged starting material (18 mg);

ii)   1,5,8-Trimethylbenzo[2,3]bicyclo[3.3.1]non-2-ene-7-one (4-98): (74 mg,

70%), characterized by comparison with authentic sample.

    B.   In Concentrated Sulphuric Acid:

        The ketone (4-97) (0.10 g, 0.424 mmole) in concentrated sulphuric

acid (5 ml) gave: 1,5,8-Trimethylbenzo[2,3]bicyclo[3.3.1]non-2-ene-7-one

(4-98): (89 mg, 85%), characterized by comparison with authentic sample.

52.   Reduction of 1,5,8-Trimethylbenzo[2,3]bicyclo[3.3.1]non-2-ene-7-one
        (4-98).

        The lactone (4-98) (0.20 g, 0.87 mmole) was reduced with lithium

aluminium hydride (0.020 g) in ether (40 ml) (experiment 48) and gave:

1,3,4-Trimethyl-3-hydroxy-1-(2'-hydroxypropyl)-1,2,3,4-tetrahydronaphthalene

(4-102): (190 mg, 93%), m.p. 108-9 (from ethanol); M^{+} (Mass spectrometry):

234.

53.   Oxidation of 1,3,4-Trimethyl-3-hydroxy-1-(2'-hydroxypropyl)-1,2,3,4-
        tetrahydronaphthalene (4-102).

        A solution of the diol (4-102) (0.080 g, 0.342 mmole) was oxidized

with pyridinium chlorochromate (0.216 g) in dichloromethane (40 ml) (experiment

49) gave: 1,5,8-Trimethylbenzo[2,3]bicyclo[3.3.1]non-2-ene-7-one (4-98):

(65 mg, 83%), characterized by comparison with authentic material.

54. Acid-Catalysed Rearrangements of 2,3,5,6-Tetramethyl-1-methoxytetra-chlorobenzobarrelene (2-14).

A. In Trifluoroacetic Acid:

A solution of the compound (2-14) (1.0 g, 2.645 mmole) in trifluoro-acetic acid (15 ml) (experiment 1.A) (24 h) gave:

i) 1,6,7,8-Tetramethyltetrachlorobenzo[3,4]bicyclo[3.2.1]octa-3,6-dien-2-one[1,2,3,4-tetrachloro-5,8-dihydro-6,7,8,10-tetramethyl-5,8-methanobenzo-cyclohepten-9(1H)-one] (4-105): (60 mg, 6%), m.p. 167-68° (from ethanol). (Found: C, 52.30; H, 3.6%; $C_{16}H_{14}Cl_4O$ requires, C, 52.80; H, 3.84%), M^+ (Mass spectrometry): 364. ^1H n.m.r. τ (CDCl$_3$): 4.87 (s, 1H); 7.53 (q, 1H, $\underline{J}$=7.0H);8.27 (s, 3H); 8.36 (s, 3H); 8.78 (s, 3H); and 9.11 (d, 3H, $|\underline{J}|$ = 7.0 Hz). ν_{max} KBr: 3035, 2990, 2950, 2890, 2855, 1702, 1603, 1540, 1458, 1365, 1288, 1225, 1150, 1092, 1015, 920, 812, 765, 725, 718, and 675 cm^{-1}.

ii) 1,3,4,6-endo-Tetramethyltetrachlorobenzo[7,8]bicyclo[2.2.2]octa-5,7-dien-2-one[1,2,3,4-tetrachloro-5,8-dihydro-5,7,8,10-endo-tetramethyl-5,8-ethenonaphthalen-9(1H)-one] (4-107): (100 mg, 10%), m.p. 171-72° (from ethanol). (Found: C, 52.50; H, 3.8%; $C_{16}H_{14}Cl_4O$ requires, C, 52.80; H, 3.84%); M^+ (Mass spectrometry): 364. ^1H n.m.r. τ (CDCl$_3$): 4.14 (m, 1H); 7.85 (m,1H); * ;8.18 (d, 3H, $|\underline{J}|$ = 1.6 Hz); and 8.87 (d, 3H, $|\underline{J}|$ = 7.2 Hz). ν_{max} KBr: 3040, 2990, 2960, 2890, 2870, 1732, 1462, 1392, 1375, 1355, 1285, 1226, 1175, 1125, 1085, 982, 910, 860, 845, 827, 785, and 792 cm^{-1}.

iii) 1,3,4,6-exo-Tetramethyltetrachlorobenzo[7,8]bicyclo[2.2.2]-octa-5,7-dien-2-one[1,2,3,4-tetrachloro-5,8-dihydro-5,7,8,10-exo-tetramethyl-5,8-ethenonaphthalen-9(1H)-one] (4-106): (120 mg, 12%), m.p. 182-83° (from ethanol). (Found: C, 53.3; H, 3.9%; $C_{16}H_{14}Cl_4O$ requires, C, 52.80; H, 3.84%), M^+ (Mass spectrometry): 364. ^1H n.m.r. τ (CDCl$_3$): 3.95 (m, 1H);

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* 7.94 (s, 3H); and 7.95 (s, 3H).

7.75-8.05 (m, 7H); 8.18 (d, 3H, $|\underline{J}|$ = 1.6 Hz); and 9.06 (d, 3H, $|\underline{J}|$ = 7.2 Hz).

ν_{max} KBr: 3055, 3000, 2975, 2950, 2910, 1735, 1460, 1440, 1400, 1355, 1315, 1280, 1260, 1228, 1170, 1135, 1100, 1045, 980, 905, 855, 830, 798, 745, and 715 cm^{-1}.

iv)   <u>1,3,4,8-Tetramethyltetrachlorobenzo[6,7]bicyclo[3.2.1]octa-3,6-dien-2-one[1,2,3,4-tetrachloro-5,9-dihydro-6,7,9,12-tetramethyl-5,9-methanobenzo-cyclohepten-8(1H)-one]</u> (4-108):   (150 mg, 15%), m.p. 163-64° (from ethanol); (Found: C, 52.4; H, 3.8%; $C_{16}H_{14}Cl_4O$ requires, C, 52.80; H, 3.84%), M$\overset{+}{\cdot}$ (Mass spectrometry): 364. ^{1}H n.m.r. τ (CDCl$_3$): 6.48 (s, 1H); 7.25 (q, 1H, $|\underline{J}|$ = 6.2 Hz); 7.88 (s, 3H); 8.37 (s, 6H); and 9.03 (d, 3H, $|\underline{J}|$ = 7.0 Hz).

ν_{max} KBr: 3030, 2990, 2970, 2945, 2885, 1675, 1638, 1445, 1390, 1372, 1360, 1330, 1292, 1215, 1155, 1108, 1025, 982, 950, 875, 856, 806, 782, 762, 715, and 680 cm^{-1}.

v)   <u>1,3,4,8-Tetramethyltetrachlorobenzo[6,7]tricyclo[3.2.1.0^{2,8}]oct-6-ene-4-one[1,2,3,4-tetrachloro-5,6,7,9-tetrahydro-6,7,9,12-tetramethyl-[10,11]-benzocyclopropa[cd]pentalen-8(1H)-one]</u> (4-109):   (340 mg, 32%), m.p. 161-62° (from ethanol).   (Found: C, 52.6; H, 3.8%; $C_{16}H_{14}Cl_4O$ requires, C, 52.7; H, 3.8%); M$\overset{+}{\cdot}$ (Mass spectrometry): 364. ^{1}H n.m.r. τ (CDCl$_3$): 7.25-7.6 (q, 1H, $\underline{J}$ = 7.2 Hz);   7.62 (s, 1H); 8.29 (s, 3H); 8.58 (d, 6H, $\underline{J}$ = 2.2 Hz); and 9.24 (d, 3H, $\underline{J}$ = 7.2 Hz). ν_{max} KBr: 3070, 2998, 2990, 2950, 2890, 1750, 1465, 1380, 1370, 1356, 1295, 1265, 1230, 1215, 1165, 1135, 1065, 985, 952, 860, 830, 800, 775, 745, and 655 cm^{-1}.

vi)   <u>1,3,4,5-Tetramethyltetrachlorobenzo[7,8]bicyclo[3.3.0]octa-3,7-dien-2-one[1,2,3,4-tetrachloro-9,12-dihydro-6,7,9,12-tetramethylbenzo[10,11]-cyclopent[9,12]inden-8(1H)-one]</u> (4-110):   (60 mg, 5%), m.p. 159-60° (from ethanol).   (Found: C, 52.7; H, 3.9%; $C_{16}H_{14}Cl_4O$ requires, C, 52.75; H, 3.9%),

$M^{+\cdot}$ (Mass spectrometry): 364. ^{1}H n.m.r. τ (CDCl$_3$): 6.52-7.32 (q, 2H, $|\underline{J}|$ = 7.0 Hz); 7.98 (s, 3H); 8.33 (s, 3H); 8.47 (s, 3H); and 8.71 (s, 3H). ν_{max} KBr: 3010, 2985, 2950, 2925, 2890, 2870, 1715, 1660, 1535, 1445, 1385, 1332, 1300, 1261, 1240, 1182, 1145, 1115, 1090, 1020, 940, 851, 780, 745, and 675 cm^{-1}.

B.   In Boiling Trifluoroacetic Acid:

The compound (2-14) (1.0 g, 2.645 mmole) in boiling trifluoroacetic acid (15 ml) (experiment I$\underline{B}$) gave:

i)   1,6,7,8-Tetramethyltetrachlorobenzo[3,4]bicyclo[3.2.1]octa-3,6-dien-2-one (4-105): (60 mg, 6%), as shown by t.l.c. and ^{1}H n.m.r.

ii)   1,3,4,6-endo-Tetramethyltetrachlorobenzo[7,8]bicyclo[2.2.2]octa-5,7-dien-2-one (4-107): (90 mg, 9%), characterized by comparison with authentic sample.

iii)   1,3,4,6-exo-Tetramethyltetrachlorobenzo[7,8]bicyclo[2.2.2]octa-5,7-dien-2-one (4-106): (120 mg, 12%), characterized by comparison with authentic sample.

iv)   1,3,4,8-Tetramethyltetrachlorobenzo[6,7]bicyclo[3.2.1]octa-3,6-dien-2-one (4-108): (160 mg, 16%), as shown by t.l.c. and ^{1}H n.m.r.; and

v)   1,3,4,5-Tetramethyltetrachlorobenzo[7,8]bicyclo[3.3.0]octa-3,7-dien-2-one[1,2,3,4-tetrachloro-9,12-dihydro-6,7,9,12-tetramethylbenzo[10,11]-cyclopent[9,12]inden-8(1$\underline{H}$)-one] (4-110): (500 mg, 53%), m.p. 159-60°, characterized by comparison with authentic sample.

C.   In Concentrated Sulphuric Acid:

The compound (2-14) (1.0 g, 2.645 mmole) in concentrated sulphuric acid (98%, 15 ml) and chloroform (15 ml) gave:

263.

i)   1,6,7,8-Tetramethyltetrachlorobenzo[3,4]bicyclo[3.2.1]octa-3,6-dien-2-one (4-105): (25 mg, 2.5%), characterized by comparison with authentic sample.

ii)   <u>1,3,5,6-Tetramethyltetrachlorobenzo[7,8]bicyclo[2.2.2]octa-5,7-dien-2-one[1,2,3,4-tetrachloro-5,8-dihydro-6,7,8,10-tetramethyl-5,8-ethenonaphthalen-9(1H)-one]</u> (4-112): (460 mg, 45%), m.p. 170-72° (from ethanol). (Found: C, 52.5; H, 3.8%; $C_{16}H_{14}Cl_4O$ requires, C, 52.75; H, 3.8%); $M^{\ddagger}$ (Mass spectrometry): 364. ^{1}H n.m.r. τ (CDCl$_3$): 6.91 (d, 1H, $\underline{J}$ = 2.2 Hz); 7.36 (m, 1H); 8.36 (s, 3H); 8.47 (s, 3H); 8.62 (s, 3H); and 8.63 (d, 3H, $\underline{J}$ = 7.0 Hz). ν_{max} KBr: 2980, 2945, 2930, 2890, 1730, 1560, 1460, 1385, 1325, 1280, 1225, 1180, 1103, 1025, 985, 903, 815, 788, 758, and 732 cm^{-1}.

iii)   1,3,4,6-Tetramethyltetrachlorobenzo[7,8]bicyclo[2.2.2]octa-5,7-dien-2-one (4-107): (50 mg, 5%); m.p. 182-83°, characterized by comparison with authentic sample.

iv)   1,3,4,8-Tetramethyltetrachlorobenzo[6,7]bicyclo[3.2.1]octa-3,6-dien-2-one (4-108): (140 mg, 14%), as shown by t.l.c., i.r. and ^{1}H n.m.r., and

v)   1,3,4,5-Tetramethyltetrachlorobenzo[7,8]bicyclo[3.3.0]octa-3,7-dien-2-one (4-110): (290 mg, 29%), characterized by comparison with authentic sample.

D.   In Fluorosulphuric Acid:

The compound (2-14) (0.80 g, 2.116 mmole) in fluorosulphuric acid (5 ml) and dichloromethane (5 ml) gave:

i)   1,6,7,8-Tetramethyltetrachlorobenzo[3,4]bicyclo[3.2.1]octa-3,6-dien-2-one (4-105): (40 mg, 5%), as shown by t.l.c., i.r., ^{1}H n.m.r. and mass spectrometry.

ii)   1,3,4,6-<u>endo</u>-Tetramethyltetrachlorobenzo[7,8]bicyclo[2.2.2]octa-5,7-dien-2-one (4-107): (100 mg, 12%), m.p. 171-72°, characterized by comparison with authentic sample.

iii)   1,3,4,6-<u>exo</u>-Tetramethyltetrachlorobenzo[7,8]bicyclo[2.2.2]octa-5,7-dien-2-one (4-106): (110 mg, 11%), as shown by t.l.c., mixed m.p., and ^{1}H n.m.r.

iv)   1,3,4,8-Tetramethyltetrachlorobenzo[6,7]bicyclo[3.2.1]octa-3,6-dien-2-one (4-108): (129 mg, 14%), as shown by t.l.c., i.r., and ^{1}H n.m.r., and

v)   <u>1,3,4,8-Tetramethyltetrachlorobenzo[6,7]tricyclo[3.2.1.0^{2,8}]oct-6-ene-4-one[1,2,3,4-tetrachloro-5,6,7,9-tetrahydro-6,7,9,12-tetramethyl-[10,11]-benzocyclopropa[cd]pentalen-8(1<u>H</u>)-one]</u> (4-109):   (360 mg, 47%), m.p. 161-62° (from ethanol), characterized by comparison with authentic sample.

55.   <u>Isomerization of 1,3,4,6-Tetramethyltetrachlorobenzo[7,8]bicyclo[2.2.2]-octa-5,7-dien-2-one</u> [(4-106) and (4-107)].

A.   <u>In Trifluoroacetic Acid</u>:

The mixture of ketones [(4-106) and (4-107)] (0.10 g, 0.274 mmole) in boiling trifluoroacetic acid (5 ml) (24 h) gave:

i)   The mixture of an unchanged ketone (32 mg), characterized by comparison with authentic sample.

ii)   1,3,4,5-Tetramethyltetrachlorobenzo[7,8]bicyclo[3.3.0]octa-3,7-dien-2-one (4-110): (42 mg, 40%), as shown by t.l.c., i.r., mixed m.p. and ^{1}H n.m.r.

B.   <u>In Concentrated Sulphuric Acid</u>:

The mixture of ketones [(4-106) and (4-107)] (0.10 g, 0.274 mmole) in concentrated sulphuric acid (5 ml) and chloroform (5 ml) gave:

i)   1,3,5,6-Tetramethyltetrachlorobenzo[7,8]bicyclo[2.2.2]octa-5,7-dien-2-one (4-112): (45 mg, 42%), characterized by comparison with authentic sample; and

ii)   1,3,4,5-Tetramethyltetrachlorobenzo[7,8]bicyclo[3.3.0]octa-3,7-dien-2-one (4-110): (29 mg, 27%, m.m.p. 159-60°, characterized by comparison with authentic sample.

C.   In Fluorosulphuric Acid:

The mixture of ketones [(4-106) and (4-107)] (0.05 g, 0.137 mmole) in fluorosulphuric acid (3 ml) at -70°, gave:

i)   1,3,4,8-Tetramethyltetrachlorobenzo[6,7]tricyclo[3.2.1$0^{2,8}$]oct-6-ene-4-one (4-109):   (36 mg, 70%), m.p. 161-62° (from ethanol), as shown by comparison with authentic sample;   and

ii)   an unidentified tar (10 mg).

56.   Isomerization of 1,3,4,8-Tetramethyltetrachlorobenzo[6,7]-tricyclo-[3.2.1$0^{2,8}$]oct-6-ene-4-one (4-109):

A.   In Trifluoroacetic Acid:

The ketone (4-109) (0.10 g, 0.274 mmole) in boiling trifluoroacetic acid (5 ml) gave: 1,3,4,5-Tetramethyltetrachlorobenzo[7,8]bicyclo[3.3.0]-octa-3,7-dien-2-one (4-110), (72 mg, 72%), characterized by comparison with authentic sample.

B.   In Concentrated Sulphuric Acid:

The ketone (4-109) (0.05 g, 0.137 mmole) in concentrated sulphuric acid (3 ml) (experiment 1.C) gave: 1,3,4,5-Tetramethyltetrachlorobenzo[7,8]-bicyclo[3.3.0]octa-3,7-dien-2-one (4-110): (42 mg, 84%), as shown by t.l.c., i.r., mixed m.p., and [1]H n.m.r.

57. Isomerization of 1,3,5,6-Tetramethyltetrachlorobenzo[7,8]bicyclo-
[2.2.2]octa-5,7-dien-2-one (4-110).

The ketone (4—110) failed to isomerize either in boiling trifluoro-
acetic acid or concentrated sulphuric acid to give any other product. At
much longer periods only the decomposed products were obtained, which could
not be identified.

58. Acid-Catalysed Rearrangements of 2,3,5,6-Tetramethyl-1-methoxybenzo-
barrelene (3-38).

A. In Trifluoroacetic Acid:

The compound (3-38) (1.0 g, 4.167 mmole) in trifluoroacetic acid
(20 ml) (experiment 1.A) gave:

i) 1,6,7,8-Tetramethylbenzo[3,4]bicyclo[3.2.1]octa-3,6-dien-2-one[5,8-
dihydro-6,7,9,12-tetramethyl-5,8-methanobenzocyclohepten-9(1H)-one] (4-113):
(92 mg, 9.6%), oil. M^{+} (Mass spectrometry): 226. ^{1}H n.m.r. τ (CDCl$_3$):
2.09 (m, 1H); 2.56-3.04 (m, 3H); 6.32 (s, 1H); 7.28 (q, 1H); 8.49 (s, 3H);
8.53 (s, 3H); 8.78 (s, 3H); and 9.15 (d, 3H, $\underline{J}$ = 7.0 Hz), ν_{max} oil: 3080,
2995, 2950, 2950, 1688, 1603, 1460, 1385, 1310, 1215, 1165, 1038, 975, 905,
815, 774, and 724 cm^{-1}.

ii) 1,3,4,6-endo-Tetramethylbenzo[7,8]bicyclo[2.2.2]octa-5,7-dien-2-one-
[5,8-dihydro-5,7,8,10-endo-tetramethyl-5,8-ethenonaphthalen-9(1H)-one] (4-114):
(170 mg, 18%), m.p. 62-63° (from n-hexane). (Found: C, 84.8; H, 7.9%;
$C_{16}H_{18}O$ requires, C, 84.94; H, 7.96%). M^{+} (Mass spectrometry): 226. ^{1}H n.m.r.
τ (CDCl$_3$): 2.62-2.98 (m, 4H); 6.1 (m, 1H); 7.88 (q, 1H, $\underline{J}$ = 7.0 Hz); 8.22
(s, 3H); 8.33 (s, 3H); 8.38 (s, 3H); and 8.84 (d, 3H, $\underline{J}$ = 7.0 Hz). ν_{max} KBr:
3045, 2995, 2955, 2896, 1728, 1462, 1380, 1302, 1225, 1175, 1135, 1040, 975,
875, 850, 765, and 675 cm^{-1}.

iii) 1,3,4,6-exo-Tetramethylbenzo[7,8]bicyclo[2.2.0]octa-5,7-dien-2-one-

[5,8-dihydro-5,7,8,10-exo-tetramethyl-5,8-ethenonaphthalen-9(1H)-one] (4-115):

(216 mg, 23%), m.p. 66-67° (from iso-octane). (Found: C, 85.2; H, 7.7%;

$C_{16}H_{18}O$ requires, C, 84.94; H, 7.96%); M^{+} (Mass spectrometry): 226. ^{1}H n.m.r.

τ (CDCl$_3$): 2.63-2.99 (m, 4H); 3.93 (m, 1H); 7.92 (q, 1H, $\underline{J}$ = 7.0 Hz); 8.24 (s, 3H);

8.35 (s, 3H); 8.37 (s, 3H), and 9.35 (d, 3H, $\underline{J}$ = 8.0 Hz). ν$_{max}$ oil 3080,

3045, 2950, 2890, 1730, 1460, 1442, 1390, 1330, 1290, 1225, 1132, 1105,

1038, 975, 875, 848, 828, 760, and 675 cm^{-1}.

iv) 1,3,4,8-Tetramethylbenzo[6,7]bicyclo[3.2.1]octa-3,6-dien-2-one-

[5,9-dihydro-6,7,9,12-tetramethyl-5,9-methanobenzocyclohepten-8(1H)-one]

(4-116): (207 mg, 22%), m.p. 87-88° (from ethanol). (Found: C, 84.8; H, 7.8%;

$C_{16}H_{18}O$ requires C, 84.94; H, 7.96%); M^{+} (Mass spectrometry): 226. ^{1}H n.m.r.

τ (CDCl$_3$): 2.72-3.12 (m, 4H); 7.68 (s, 1H); 7.94 (q, 1H, $\underline{J}$ = 7.0 Hz);

8.62 (s, 3H); 8.66 (s, 3H); 8.76 (s, 3H), and 9.52 (d, 3H, $\underline{J}$ = 14 Hz). ν$_{max}$

KBr: 3090, 3042, 2996, 2958, 2898, 1671, 1460, 1389, 1332, 1228, 1170, 1103,

1028, 980, 895, 870, 775, 715, and 680 cm^{-1}.

B. In Concentrated Sulphuric Acid:

The compound (3-38) (1.0 g, 4.167 mmole) in concentrated sulphuric

acid (15 ml) (experiment 1.C) gave:

i) 1,6,7,8-Tetramethylbenzo[3,4]bicyclo[3.2.1]octa-3,6-dien-2-one (4-113):

(75 mg, 8%), as shown by t.l.c., i.r., and ^{1}H n.m.r.

ii) 1,3,4,6-Tetramethylbenzo[7,8]bicyclo[2.2.2]octa-5,7-dien-2-one (4-115):

(150 mg, 16%), as shown by t.l.c., i.r., and ^{1}H n.m.r.

iii) 1,3,4,8-Tetramethylbenzo[6,7]bicyclo[3.2.1]octa-3,6-dien-2-one (4-116):

(200 mg, 21%), characterized by comparison with authentic sample.

iv) 1,4,5,8-Tetramethyl-6-oxa-benzo[2,3]bicyclo[3.3.1]non-2-ene-7-one

(4-117): (500 mg, 50%) m.p.135-36°(from ethanol). (Found: C, 78.6; H, 8.1%; $C_{16}H_{20}O_2$ requires, C, 78.67; H, 8.2%); M^+ (Mass spectrometry): 244. ^{1}H n.m.r. τ (CDCl$_3$): 2.54-2.93 (m, 4H); 6.7-7.22 (m, 1H); 7.34-7.74 (m, 1H); 7.86 (m, 2H); 8.5 (s, 3H); 8.52 (s, 3H); and 8.82 (m, 6H). ν_{max} KBr: 3080, 3045, 3000, 2960, 2895, 1732, 1492, 1465, 1390, 1375, 1330, 1255, 1203, 1175, 1162, 1148, 1112, 1070, 1040, 980, 957, 922, 780, 760, 720, and 690 cm^{-1}.

C.   In Fluorosulphuric Acid:

The compound (3-38) (0.50 g, 2.080 mmole) in dichloromethane (10 ml) on treatment with fluorosulphuric acid (3 ml) gave:

i)   1,6,7,8-Tetramethylbenzo[3,4]bicyclo[3.2.1]octa-3,6-dien-2-one (4-113): (47 mg, 10%), characterized by comparison with authentic sample.

ii)   1,3,4,6-Tetramethylbenzo[7,8]bicyclo[2.2.2]octa-5,7-dien-2-one (4-114/115): (240 mg, 51%), as shown by t.l.c. and ^{1}H n.m.r.

iii)   1,3,4,8-Tetramethylbenzo[6,7]bicyclo[3.2.1]octa-3,6-dien-2-one (4-116): (90 mg, 19%), as shown by t.l.c., i.r. and ^{1}H n.m.r.

59.   Isomerization of 1,3,4,6-Tetramethylbenzo[7,8]bicyclo[2.2.2]octa-5,7-dien-2-one (4-114,115).

A.   In Trifluoroacetic Acid:

The ketones (4-114,115) (0.10 g, 0.442 mmole) in boiling trifluoro-acetic acid (3 ml) gave: 1,4,5,8-Tetramethyl-6-oxa-benzo[2,3]bicyclo[3.3.1]-non-2-ene-7-one (4-117):   (82 mg, 80%), characterized by comparison with authentic sample.

B.   In Concentrated Sulphuric Acid:

The ketones (4-114,115) (0.10 g, 0.442 mmole) in concentrated sulphuric acid (5 ml) gave: 1,4,5,8-Tetramethyl-6-oxa-benzo[2,3]bicyclo[3.3.1]non-2-ene-

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7-one (4-117): (86 mg, 83%), characterized by comparison with authentic sample.

60.   Isomerization of 1,6,7,8-Tetramethylbenzo[3,4]bicyclo[3.2.1]octa-3,6-dien-2-one (4-113).

The ketone (4-113) failed to give any other product either on treatment with trifluoroacetic acid or concentrated sulphuric acid. Treatment at longer periods gave decomposed·products which could not be identified.

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CHAPTER FIVE

Carbon-13   Chemical Shifts of

Benzobarrelene Systems.

Introduction:

In recent years organic chemists have shown particular interest in ^{13}C n.m.r. spectroscopy as a tool for the elucidation of the structures of bicyclic systems. The rigid structural features present in the bicyclo-[2.2.1]heptane and bicyclo[3.2.1]octane systems, has allowed extensive investigations of norbornyl systems.[1] The ^{1}H n.m.r. spectra of norbornyl derivatives have been extensively studied[2-5] and have been the cause of considerable controversy,[6-8] in particular regarding the shielding of -syn and -anti protons.

High resolution N.M.R. spectra of ^{13}C at natural abundance offers in principle many advantages in assigning the structures of these controversial molecules. The spectra are considerably simpler to assign, they are less sensitive to the presence of impurities, their linewidths, and relaxation times give a direct measure of localized intramolecular motion.

As a part of our examination of the effects of molecular geometry on ^{13}C shieldings we have obtained the spectra of bicyclo[2.2.2]octane and bicyclo[3.2.1]octane ring systems. The prime reason for investigating these systems in that the well-defined carbon skeleton allows one to study the shielding variations as a function of molecular geometry. The [2.2.2] and [3.2.1] saturated examples have the additional feature of a flexible six-membered ring permitting an examination of this factor on the shielding trends.[9,10]

In general, the shifts produced by the substituents at carbons within four bonds are of particular interest as potential probes for stereochemical analysis. A possible deficiency in the use of bicyclic systems as models for these perturbations in the contribution of strain to the observed

shieldings, a factor which is difficult to assess.   However, the influence of strain could be revealed in a comparison of the corresponding interactions in a variety of systems, differing in strain energy.[11]

The ^{13}C data are present as substituent parameters, or changes of ring carbon chemical shifts upon introduction of a particular substituent group.   In principle, the prediction of ^{13}C chemical shifts in complicated molecules by analogy with simpler compounds of the same geometry, is at present the practical approach to analysis.

Results and Discussion:

The ^{13}C shieldings for the series of benzobarrelenes and their unsaturated analogues are listed in Tables [5-I to 5-III]. For each derivative, the signal was readily assigned from its characteristic position, δ_C. The bridgehead carbon signals were distinguished by off-resonance decoupling and thus, directly assigned for the sp^2 and sp^3 carbons with the exception of bridgehead carbons (sp^3). The olefinic signal assignments were made by comparison of the observed shieldings with those for the corresponding olefin.

The methine and methylene assignments were made on the basis of the appearance of the pattern of the off-resonance decoupled spectrum and by consideration of shifts caused by the various substituents relative to those found for analogous substitutions in other bicyclic systems. For example, the off-resonance pattern for the bridgehead carbon (C-1) for benzobarrelene (3-30) was a doublet showing two carbons [(C-1) and (C-4)]; however, when hydrogen at (C-1) was replaced by methoxy group, compound (3-31), the carbon (C-4) gave rise to more complex pattern owing to the fact that the protons bonded thereto to form a closely coupled system. The olefinic carbons appeared as singlets or doublets depending upon the environment of the carbon present. It is clear from the general study that the presence of halogen atoms pulled the carbon positions downfield. The position of carbons (C-7) and (C-8) were equally affected by the presence of halogen on the aromatic ring system. The numbering pattern used for the various structures for the assignments are as follows:


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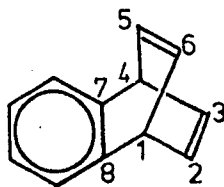
The chemical shifts relative to tetramethylsilane, together with the shifts relative to the parent benzobarrelene (3-30) were determined in chloroform solution, off-resonance proton decoupled spectra being used to assist assignment. The stereochemical assignments for the known compounds are in accord with the observed carbon shifts. It is also interesting to study the effect of substitution on the conformation of the methoxy group at the bridgehead carbon (C-1). The various chemical shifts of the ^{13}C N.M.R. spectra of substituted benzobarrelenes are shown in Tables 5-Ia and 5-Ib. From these results, some of the interesting features are immediately apparent.

(a) The difference between the chemical shifts of carbons 7 and 8 (easily seen as low field singlets in the off-resonance spectrum) are significant.

(b) Proton- and non-proton bearing carbons are easily distinguished by their different relaxation times.

(c) It is generally observed that the resonances of the chlorine-bearing carbons are more intense than those of other non-proton-bearing carbons. This is probably due to the contribution of scalar relaxation to the carbon relaxation.

A considerably larger downfield shift has been observed in certain cases, which could be attributed to the orbital overlap of the substituent.

A variety of bicyclic ketones has been examined by ^{13}C N.M.R. spectroscopy and these carbonyl shieldings are collected in Table 5-II. The presence of carbonyl group exhibits a marked upfield shift relative to its saturated analogous. These upfield shifts may be interpreted in terms of homoconjugative interaction between the olefinic and carbonyl bonds. Such interactions are expected to be strongly dependent on the
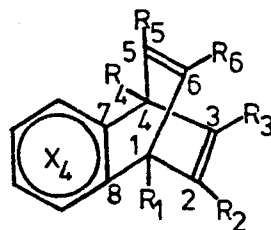
277.

Table 5-1a

Compound No.	X$_4$	Carbon Atom (Multiplicity in Off-Resonance Experiments), Chemical Shift/p.p.m. Downfield from T.M.S., Relative Intensity.													
		C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	R$_1$	R$_2$	R$_3$	R$_4$	R$_5$	R$_6$
(2-47)	Cl$_4$	47.05	139.59	139.59	47.05	139.59	139.59	146.29	146.29	-	-	-	-	-	-
(3-30)	H$_4$	49.19	139.59	139.59	49.19	139.59	139.59	147.52	147.52	-	-	-	-	-	-
(2-1)	Cl$_4$	91.50	137.45	141.02	45.94	137.71	137.19	141.61	141.28	55.50	-	-	-	-	-
(3-31)	H$_4$	89.88	138.42	140.31	48.28	138.94	140.83	137.71	139.66	54.46	-	-	-	-	-
(2-2)	Cl$_4$	92.15	152.98	130.30	45.10	130.56	137.45	130.82	137.64	56.47	14.68	-	-	-	-
(3-32)	H$_4$	90.85	151.55	131.47	47.57	137.30	138.40	146.16	147.65	55.11	14.68	-	-	-	-
(2-3)	Cl$_4$	91.96	145.25	142.19	51.08	137.45	138.55	125.69	137.12	56.28	16.89	11.69	-	-	-
(3-33)	H$_4$	90.53	147.72	145.51	53.74	137.25	138.68	123.28	140.89	55.11	16.70	11.11	-	-	-
(2-4)	Cl$_4$	91.89	152.92	129.72	50.30	147.98	130.17	129.33	147.98	56.21	15.07	-	-	19.43	-
(3-34)	H$_4$	90.40	151.68	129.52	52.96	148.37	130.95	130.37	146.03	54.98	14.68	-	-	19.49	-
(2-8)	Cl$_4$	94.95	151.81	131.86	44.58	132.44	147.52	125.30	147.57	58.42	17.09	-	-	-	17.09
(3-36)	H$_4$	93.45	151.03	123.67	46.79	133.09	148.11	123.76	147.07	57.90	16.37	-	-	-	16.37
(2-10)	Cl$_4$	90.98	130.11	145.77	56.54	147.52	133.42	125.82	145.25	55.11	-	19.43	-	19.43	-
(3-35)	H$_4$	88.90	123.67	148.04	59.20	148.37	132.64	123.02	145.38	54.07	-	19.43	-	19.43	-
(2-12)	Cl$_4$	91.70	146.81	142.32	56.41	145.12	129.72	125.56	138.03	56.15	16.89	11.63	-	19.62	-
(3-37)	H$_4$	90.07	148.04	141.09	59.27	145.38	129.72	123.35	138.23	54.91	16.70	11.17	-	19.62	-
(2-14)	Cl$_4$	94.65	146.44	141.16	57.91	145.55	129.58	125.25	138.37	56.57	17.37	13.45	-	13.45	17.37
(3-38)	H$_4$	92.95	147.06	140.22	59.32	145.72	128.71	123.75	138.71	57.80	17.02	12.81	-	12.81	17.02

(Table 5-Ib)
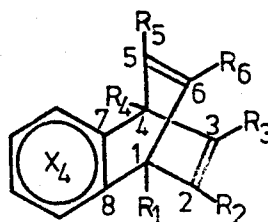
Compound No.	X$_4$	Carbon Atom (Multiplicity in Off Resonance), Chemical Shift/p.p.m. Downfield from T.M.S.													
		C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	R$_1$	R$_2$	R$_3$	R$_4$	R$_5$	R$_6$
(2-48)	Cl$_4$	54.00	137.90	149.67	57.84	147.07	139.59	125.75	138.75	22.03	–	19.17	–	18.32	–
3-40	H$_4$	50.04	122.57	150.32	60.44	148.24	123.48	117.95	137.19	20.14	–	19.30	–	17.41	–
(2-51)	Cl$_4$	66.48	33.59	161.50	48.87	152.59	133.22	124.52	150.45	28.01;	28.85;	29.76;	32.49.		
(3-54)	H$_4$	61.28	34.96	161.50	51.99	153.11	131.41	121.98	149.99	26.77;	28.33;	29.31;	32.69.		
(3-55)		52.90	35.28	154.22	52.51	152.72	128.87	121.66	145.51	26.77;	28.33;	29.57;	33.59.		

relative orientation of the two π bonds. A qualitative assessment of the homoconjugative interactions in terms of the $\sigma\sigma$ and $\pi\pi$ overlap contributions has been put forward by the different authors to account for the stereochemical dependence as well as to illustrate the differences for the various unsaturated systems.

Although less striking, significant differences are found in some J_{CH} values in substituted 9,10-dihydroanthracene derivatives for which the couplings of the β-carbons depend on the orientation of the C-H bond with respect to the substituent. The effect of increasing strain, however, is apparent from the chemical shifts found for the central carbons in triptycene.[12]   The ^{13}C N.M.R. spectra of some of the substituted 9,10-dihydroanthracene derivatives are reported in Table 5-III. Previously reported stereochemical assignments for the known compounds are in accord with the observed carbon shifts.

Table 5-II

Compound No.	X_4	Carbon Atom (Multiplicity in Off-Resonance Experiments), Chemical Shift/p.p.m. Downfield from T.M.S.												
		C-1	C-2	C-3	C-4	C-5	C-6	R+7	C-8	R_1	$(R_2\ R_3)$	R_4	R_5	R_6
(2-17)	Cl_4	91.50	200.23	34.37	37.23	135.05	140.57	131.15	140.57	55.69	-	-	-	-
(2-18)	Cl_4	84.22	40.35	198.54	56.99	128.22	134.72	128.94	138.88	54.72	-	-	-	-
(2-20)	Cl_4	79.92	203.85	43.60	54.85	-	-	-	-	55.50	16.37	-	-	-
(2-19)	Cl_4	74.99	43.86	202.96	55.56	135.43	134.46	129.39	139.07	55.56	-	-	16.44	-
(2-21)	Cl_4	78.44	202.96	38.53	43.54	134.46	139.07	131.21	139.07	55.56	-	-	-	16.44
(2-6)	Cl_4	75.38	206.79	44.97 (38.79)	59.72	136.67	141.61	129.65	138.62	<u>17.93</u>	<u>16.70</u>	-	-	-
(2-11)	Cl_4	47.18	203.02	44.77	63.04	136.47	140.76	-	-	<u>23.98</u>	-	-	19.23	-

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Table 5-III
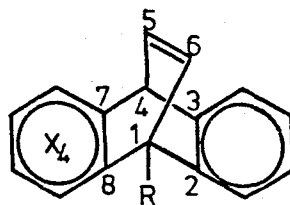
Compound No.	X_4	Carbon Atom (Multiplicity in Off-Resonance Experiments). Chemical Shifts/p.p.m. Downfield from T.M.S.								
		C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	R.
(2-53)	Cl_4	77.81	124.61	125.07	48.74	136.97	135.58	147.12	144.22	$-NMe_2$: 44.84; 42.05.
(3-51)	H_4	75.56	146.31	147.29	51.21	138.94	136.32	147.29	146.31	$-NMe_2$: 42.57
(2-52)	Cl_4	88.89	121.28	137.54	47.60	130.77	144.10	123.23	145.14	$-OMe$ 56.12
(3-50)	H_4	87.53	119.98	137.28	50.26	125.64	144.69	122.64	146.31	$-OMe$ 54.88

EXPERIMENTAL:

Material:

The compounds examined in this study have been described in the previous three chapters.

^{13}C Spectra:

A Jeol FX-100; 90Q and Brücker 20.12 MHz system operating in the Fourier transform mode at 25.2 MHz was employed for the ^{13}C spectra. Carbon types were distinguished by off-resonance decoupling. All compounds were examined as CDCl$_3$ solution (5-15% w/v) containing T.M.S. as an internal standard.

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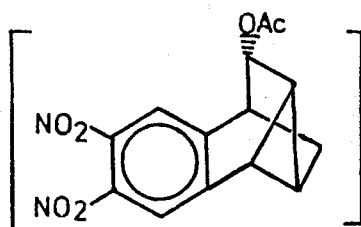
[1 - 54']

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CORRECTION:

In all the experiments, please read as characterised by comparison with an authentic sample.

Compound no. (2-13')

^{1}H n.m.r. τ (CDCl$_3$):

5.3 (m, 1H); 7.98 (m, 3H); 8.05 (s, 3H); 8.2 (m, 3H); and 9.12 (d, 3H, $\underline{J}$ = 7.2 Hz).

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2,2-Ethylenedioxy-1,5-dimethyl-	(2-59)	Me	H	H	H	Me	H	92

Table V continued. Page 50.

Occasional