A

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Jerzy A. Zabkiewicz

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SUMMARY

The subject matter of this thesis (the elucidation of the mechanism of the aromatisation of diacetylenes and related species) may be divided into three sections, each dealing respectively with the aromatisation, by treatment with strong base, of linear diacetylenes, cyclic C_8 diacetylene equivalents, and cyclic C_{12} or C_{14} diacetylenes or their equivalents.

The aromatisation of deca-1,9-diyne and deca-4,6-diyne is described in the first section: this is followed by a detailed examination of the requirements for base catalysed isomerisation of octa-1,7-diyne. The products from the latter reaction, aromatic and non-aromatic, are identified, and the non-aromatic ones are also synthesised for comparison. These olefinic by-products are also treated with base under similar conditions in an attempt to elucidate the mechanism of their transformation, and their products are likewise identified. Treatment of octa-1,7-diyne under various reaction conditions also leads to the establishment of conditions necessary for the formation of aromatic products only. A rationale based upon the findings in the course of this work and recent related literature reports, is put forward for the formation of both the aromatic and non-aromatic species.

The results obtained from the first part of this work are

utilised in the following work on the related isomerisation of cyclooctadiyne equivalents. Dehydrobromination of tetrabromocyclooctanes (one of the two isomers obtained has its structure proved by X-ray analysis) with an excess of strong base yields benzocyclobutene and styrene, as well as other products. The analogous isomerisation of cyclooctatetraene itself yields the same major products, and these are isolated and identified. Various reaction conditions are also tried, but complete control of reaction products is not achieved. A mechanistic interpretation for the formation of the various products is again presented.

The third section deals with the similar preparation and dehydrobromination of the hexa- and tetrabromocyclododecanes, as well as the base catalysed isomerisation of cyclotetradeca-1,8-diyne. The products are again identified, and a mechanism for their formation is put forward. The synthetic potential of these reactions is discussed briefly.

INTRODUCTION

The Formation of Benzenoid Compounds from Unsaturated Systems.

Controversy and speculation have marked the progress of the concept of aromaticity over the last century since Kekule's original proposal for the structure of benzene, followed a year later by Berthelot's[1] "simple" synthesis of it from three molecules of acetylene. The facade of simplicity presented by this reaction concealed extremely effectively its profound complexity, so much so that it is only recently that the ramifications of the reaction have become understood - and in the process have helped to place one of organic chemistry's fundamentals on a solid basis of facts. Indeed, this reaction is a perfect example of evidence supporting the original theories of aromaticity, and yet still completely explicable against the background of knowledge available today.

Of necessity, the original speculations about the nature of aromaticity depended on the practical results available at that time, and as such, emphasis was placed on the types of reactions that "aromatic" compounds underwent, rather than the degree of reactivity possible with a certain arrangement of double bonds, though on reflection this is implied. Accordingly, examples of reactions carried out then and now are quite numerous, their comparison is direct, but understanding now the theory and degree of reactivity possible, not only are the products predetermined, but starting materials and products are interconvertible, even though they may be classified as aromatic or olefinic.

Berthelot's original trimerisation of acetylene[1] in 1866, (re-examined in 1960, and found to produce also toluene, o-xylene, styrene, naphthalene and other polynuclear hydrocarbons[2]) was followed by other similar reactions,[3,4] $\left[(1) \longrightarrow (2);\ R = H,\ R^1 = CH_3, \text{ and } R = R^1 = CH_3\right]$ but there the matter rested for many decades while the properties of "aromatics" were evaluated and aromatic reactivity formulated. Aromatic compounds were produced by a variety of methods and reagents, but all had a preformed six-membered ring - or caused it to be formed in the course of a cyclisation reaction involving a carbonyl or its equivalent. Dehydrogenation reactions utilising selenium, sulphur or palladium, were all known, but even now their route (involving free radicals) is poorly understood.

Due to the intense interest in terpene chemistry prevalent at that time, it is not surprising to find the odd example of aromatisation amongst some of their reactions - as for instance carvone (3) and eucarvone (4) (itself an isomer of carvone) were known to give thymol (5) on treatment with acid.[5,6.] Later work[7] on these compounds produced evidence that the rearrangement of carvone hydrobromide (6) to eucarvone (4) proceeded via a bicyclic form (7). So, (with hindsight) it seems strange that the possible existence of this route in reverse was not recognised, that preformed six-membered rings were not necessary precursors of aromatic rings. (The analagous conversion of the dibromocarane (8) to *p*-cymene (10), probably via the bicyclic form (9) has also been observed recently[8]).

This long lull, with its paucity of practical results, finally ended about twenty-five years ago, when organic chemistry, possessing an abundance of theories on aromaticity (produced by mathematicians and physical chemists), finally obtained the practical means to test them, due largely to the development of the spectroscopies and various new reagents and equipment - largely by-products of the two major wars during that period.

As in all evolving sciences, the techniques had changed from the scientifically brutal to the subtle, and though knowledge on dehydrogenation methods had been extended, and understanding of the catalytic requirements gave some control of the end products (e.g. the formation of ethylbenzene from 1-vinylcyclohexene (11) over platinum at 200°[9]), this bore no comparison to the advantages that the advent of new catalysts and especially tracer experiments brought to this sphere. Thorough investigation by Pines and his associates has shown that with the appropriate catalysts (various silicates and alkaline or acidic aluminas) and at the correct reaction temperatures, hydrogenation and dehydrogenation can occur very readily.[10,11] Also, the use of macrocyclic hydrocarbons (instead of cyclohexane species) by Prelog *et al.*[12,13] has produced a variety of polyaromatic compounds depending on the starting material (outlined below).

cyclononane $\xrightarrow{\text{Pd/C } 400^\circ}$ indene

cyclododecane $\longrightarrow$ acenaphthene, acenaphthalene

cyclotridecane $\longrightarrow$ fluorene

cycloheptadecane $\longrightarrow$ 1,2-benzofluorene

Realisation that it was not necessary to start with a cyclic compound to cause aromatisation has produced some striking results, as for instance, fifty-two, mainly aromatic, compounds were identified from the pyrolysis of n-decane.[14] The sophisticated work on catalytic transformation over chromia-alumina by Pines et al. using ^{14}C labelled n-octane has led to the identification of ethylbenzene and all the xylenes, together with cyclooctane and methylcycloheptane[15] (after selective hydrogenation)! Moreover, the aromatics could be prepared from either of the last two, the radioactive assay corroborating the postulated mechanism, (Scheme I), where 1 - 6, 1 - 7, or 1 - 8 ring closure led to the appropriate and distinct end products.

Work of this type has led to the development of the theory of surface catalysis, where adsorbtion of the reagents on the substrate is compulsory for reaction. (In the previous illustrations, the substrate also participated by hydrogenating or dehydrogenating the primary species). In particular, development of transition metal chemistry has produced the sensationally efficient series of Ziegler type catalysts, with which unsaturated hydrocarbons form π-bonded complexes, thereby facilitating molecular condensation.

An outstanding example from some of the earlier work was without doubt the commercially applicable polymerisation of acetylene to cyclooctatetraene by Reppe et al.[16] over nickel cyanide in tetrahydrofuran solution. A more pertinent example[17] is the trimerisation of dimethylacetylene to hexamethylbenzene over a triphenylchromium catalyst in tetrahydrofuran, where the mechanistic route is envisaged as shown in Scheme II.

The uses and mechanism of this type of reaction have been reviewed,[17,18,19] and the formation of the aromatic system is explained by a stepwise replacement of the tetrahydrofuran ligands of the triphenylchromium complex (12) to form the "tetramethylcyclobutadiene" metal complex (13), which can then undergo an external Diels Alder addition of dimethylacetylene, to give the hexamethylbenzene on rearrangement and liberation of the original triphenylchromium.

A similar reaction is the trimerisation of vinylacetylene,[20] where the acetylene group is the reactive portion, to give (14) and (15) (using tri-isobutylaluminium/titaniumtetrachloride catalyst at -10°) respectively - and again explicable by the same mechanism. Not only can simple aromatic compounds be formed, but by a judicious choice of catalysts, either aromatisation or linear polymerisation can occur,[21] and even bi- or tricyclic structures, such as (16) (from diphenylacetylene using triethylaluminium/titanium tetrachloride) can be easily obtained.[22]

These reactions are directly comparable with Berthelot's original, differing only in the reaction conditions and in scope of application. However, recognition of the mechanism, and the resulting awareness that classical concepts of aromaticity are not sufficient to explain the properties of these new intermediates, or the formation of the end products, has resulted in a deliberate quest for similar anomalies.

Hence the reaction[23] of dimethylacetylene dicarboxylate (18) with the tetramethylcyclobutadiene (17), (generated in situ) gave a compound identified as 3,4,5,6-tetramethyldimethylphthalate (20), presumably formed via the valence bond isomer (19). Even more remarkable is the fact that (19) has been generated by the reaction of zinc with its dibromo derivative (21), and is quite stable[24] (though heating it at 130° for a short time will convert it completely to (20)). More astonishing still is the reverse direct conversion of a benzene nucleus into a bicyclic "Dewar benzene" form,[25] (admittedly by irradiation), as typified by the change of (22) into (23).

As a consequence of these studies, the actual synthesis of "Dewar benzene" (26) came as no surprise,[26] but as the inevitable. [The method is outlined in Scheme III, (24)→(26)]. Further work in this field has been carried out since then by Arnett and Bollinger[27] and Viehe *et al.*[28,29] with the tetra-tert-butyl benzene (27) (Scheme IV) and the compounds resulting from trimerisation of 1-fluoro-2-tert-butylacetylene [(29), Scheme V]. In the former series a Dewar benzene (27a) is obtained and a

Ladenburg structure (28) postulated; in the latter, not only a Dewar benzene (30a), but an analogous Ladenburg structure (30b) are actually obtained!

More recent work has also confirmed the feasibility of converting a double bond into a cyclopropane ring - and vice versa - as previously postulated in the earlier eucarvone work. In one case,[30] sodio-eucarvone was reacted with triphenylmethylchloride, and yielded the bicyclic derivative (31), which is closely related to (7), a postulated intermediate. Examples of light catalysed conversion of double bond systems into a cyclopropane are provided by the conversion of cycloocta-1,5-diene (32) to the bicyclic structure[31] (33) and the racemisation of (34) and (36) which Vogel et al.[32] maintain can only occur via (35).

The reversibility of the non-benzenoid benzenoid conversion is clearly demonstrated by the reaction of benzene with diazomethane to give cyclohepta-1,3,5-triene,[33] and substantiated still further by the analogous reactions of compounds (37) and (40) to give the previously unobtainable oxepins[34,35] (39) and (42) . However, the importance of substituents should be emphasised, for in a previously quoted example [(8) → (10)] and in the conversion[36] of (43) to (44) (as opposed to the preparation of cycloheptatriene from benzene, an exactly analogous route) the preferred state is aromatic. Thus, under the conditions employed, the presumed intermediate (41) does not give rise to phenol.

The obvious lesson in these examples (and many more are being recognised now) is that reversibility is the common denominator, and as such it is possible to start from either aromatic or olefin and convert one into the other as required. The word "aromatic" can no longer be used to imply extraordinary properties, but only to describe the difference in degree of reactivity and stability to different reagents. (An admirable discussion and proof is offered in E. Clar's book,[37] "Polycyclic Hydrocarbons" Vol. I). An illustration is provided by the difference in stability between benzocyclobutene (45) relative to its valence bond isomer *o*-quinodimethane (46). The latter has been postulated[38] as a reactive intermediate, but only very recently identified as a breakdown species[39] in a mass spectrometer - although there are several reactions in which benzocyclobutene apparently participates through the intermediacy of the *o*-quinodimethane form (see p.10).

Viewed against this background of knowledge, the results obtained originally by workers in this department (Harkin,[41] Rosenfeld,[42] and Eglinton[107]) during the attempted repetition of Perkin's original work[40] no longer seems doubtful or incomprehensible. The observed aromatisation of dipropargylacetic acid (47) to *m*-toluic acid (48), and the later extensions of this reaction (by refluxing in strong base) to simple diacetylenes,[42,43] has shown that the reaction is a general one. What was not known was the mechanism, and this, together with the identification of other cyclisation products, has now been elucidated, (though not without some difficulty), and is dealt with in the first part of this thesis.

Very recent work on the isomerisation of diynes and polyynes has underlined the versatility of this reaction, and aromatisation occurs very readily in some cases, as demonstrated by the now classic work of Sondheimer and his co-workers on the formation of annulenes.[44,45.] They found that base treatment of the cyclic compound,[44] cyclooctadeca-1,3,7,9,13,15-hexayne (49) yielded triphenylene (50), a result analogous to the formation[45] of 10-diphenylsuccindene (52) from the cyclic C_{16} diene-tetrayne (51). Similar results have also been obtained by Hubert and Dale in their study of cyclic polyenes and polyynes. These workers applied the aromatisation reaction to a series of cyclic diynes, and obtained the corresponding 1,2-polymethylenebenzenes in quite high yields[46] [(53) → (54)], thereby corroborating the results of some initial studies made by McCrae[47] and Willis[43] in the course of their doctoral studies.

The C_{12} cyclic diyne was the smallest ring system studied by any of these authors - only very recently[48] has a similar aromatisation been achieved within a smaller ring system [(55) → (57) via (56)]. The synthesis of benzenoid compounds from a smaller ring size - namely the eight-membered ring - was therefore examined. The C_8 benzenoid, benzocyclobutene (45), though known for some time - in fact a 7,8-dibromobenzocyclobutene (59) was synthesised in 1910 by Finkelstein, although this fact was not published till fifty years later[49] - had never been obtained by isomerisation of another hydrocarbon. Finkelstein's method has been recently verified by Cava and Napier,[50,51,52] who not only synthesised the dibromo derivative (59) from (58), but also succeeded in converting it to the parent hydrocarbon (45) from the dibromide. (Excellent reviews on this and related reactions are given by Baker[55] and Baker and McOmie[53,54]). Another synthetic method developed by Cava, the pyrolytic elimination of sulphur dioxide from the appropriate precursors to yield assorted benzocyclobutene systems, is illustrated in the preparation[56,57,58] of compounds (61), (65), and (70). The very interesting observation was made that compound (70) arose via the formation of the 1,2-naphthoquinodimethane (69) - the corresponding Diels-Alder adduct of this intermediate actually being isolated. Incidentally, an interesting example occurs in the preparation[59] from (71) of (72) - a rather exotic benzocyclobutene derivative - but again the aromatic ring is preformed, though the synthesis does involve a transannular ring closure to yield the required four-membered ring.

In general, dehalogenation or dehydrohalogenation of halogenated cyclic precursors can produce ring contraction or expansion - for which analogous hydrocarbon reactions are now known. For example, the ring contraction[60,61] on dehydrobromination of (73) or (74) to (75) has been matched[62] by the expansion subsequent upon the solvolysis of (76) to (77) (as well as (78) by direct replacement of the tosyl group).

Reaction of cyclooctatetraene (79) with chlorine[63] gives the dichloride (80), which is converted to β-chlorostyrene (81) on heating[63,64] - but not to the hoped-for benzocyclobutadiene. This would seem to be an example of the instability of the four-membered ring system. However cyclohepta-1,3,5-triene and dichlorocarbene give (82) which can be converted by heat to the required 7-chlorobenzocyclobutene[65] (83).

In a very recent example,[66] removal of four moles of hydrogen bromide from 1,2,5,6-tetrabromocyclooctane (84) by potassium tert-butoxide in dimethylsulphoxide at room temperature, resulted in the formation of styrene as well as the expected cyclo octatetraene - but no benzocyclobutene. (This work has been checked in the present study (p. 56), and benzocyclobutene has been found, though the reaction temperature determines the yield). Hence it is not improbable that cyclooctatetraene - or one of its valency isomers - could be a precursor in the rearrangement needed to produce the aromatic benzocyclobutene system.

It seems preferable to postulate cyclooctatetraene, rather than cycloocta-1,5-diyne, for cyclooctyne is the smallest cycloalkyne so far isolated.[67,68.] As will be demonstrated later, (e.g. p. 14), valence bond isomers of the same molecule can exist and react similarly. The tetrabromide (84) could conceivably give rise to a mixture of isomeric carbocycles which could act as precursors for the formation of benzocyclobutene - and indeed Willis[69] identified benzocyclobutene as a major product. This sequence, from cycloocta-1,5-diene (available on the ton scale commercially), provides a simple two-stage synthesis of benzo-

:cyclobutene.

This work has been extended in the second section of this thesis, and the other products also obtained - either under similar or different conditions - are elucidated. The precise configuration and conformation of one of the starting tetrabromides have been determined by X-ray crystallography and those of the other isomer discussed. The structures of other cyclic monobromo and dibromo compounds have also been examined.

The detection of a trace of cyclooctatetraene amongst the reaction products from the dehydrobromination of (84) suggests that cyclooctatetraene itself might take part in this reaction. This compound, first synthesised by Willstätter,[70] produced and made easily available by Reppe's method involving the tetramerisation of acetylene[16] (analogous to the trimerisation of acetylene to benzene[1]), has had its relatively short, but rather weird chemistry ably reviewed several times.[71,72].

For instance, on irradiation cyclooctatetraene gives benzene, styrene, acetylene, bicyclo[4·2·0]octa-2,4,7-triene and cycloocta-1,3,5-triene as well as polymer.[73,74,75]. Oxidation produces benzoic, phthalic and terephthalic acids[16] and even tropylium salts have been isolated.[76,77]. Recent interesting examples[78,79] of its transannular reactions are illustrated in the conversion of (85) to (86) and (87) to (89) - presumed to go via (88). Again addition of a mole of bromine to cyclooctatetraene results in the dibromide (90). However, dehydrobromination[80,64,82] of this compound reforms the cyclooctatetraene system (91), rather than convert it to an aromatic type.

The interconversion of benzene and its valence bond isomers has already been discussed - the eight-membered ring and the bicyclic [4ˑ2ˑ0] systems are likewise interconvertible. Thus in the reaction[83] of (92) with maleic anhydride, the identity of the intermediate (93) could be deduced from the product (94). A similar intermediate (96) must exist in the conversion of (95) to (77):[85] the intermediacy of this o-quinodimethane type of compound is further demonstrated by the formation of (97) and (98) respectively from benzocyclobutene.[86] It must be mentioned that the seemingly analogous reaction[84] of (99) to (100) does not appear to proceed via this type of intermediate, but rather by direct bimolecular condensation, followed by rearrangement.

Valence bond tautomerism between cyclooctatetraene and benzocyclobutene appears to be a distinct possibility - analogous to the well-known cycloocta-1,3,5-triene (101) - bicyclo[4ˑ2ˑ0]octa-2,4-diene (102) example.[87,88.] Indeed, as in the cycloocta-1,3,5-triene series, where this compound (101) has been very recently obtained from the linear octa-1,3,5,7-tetraene[89] (103), so the conversion of the acyclic ene-diyne (108) to various polycyclic dimers of (46) has also been achieved.[38] Incidentally, the acyclic tetraene (103a) has been postulated as an intermediate in the conversion of (104) to (105)[90] (Scheme VI) and of (106) to (107)[91] (Scheme VII).

Finally, the original observation by Reppe[16] in his massive study of cyclooctatetraene, that the valence isomer (109) could exist transiently and could be trapped as its Diels Alder adduct has been corroborated[92] by the isolation of (110) (formed by addition of dichlorocarbene to cyclooctatetraene and subsequent hydrogenation). Theoretical and kinetic studies[93,94] have also shown that Diels Alder adducts must proceed via the form (109). In fact, the related compounds (111) and (112)[95,96] and the compound (109) itself[97] have been successfully synthesised. These facts provide a rationale for Willis' conversion[43] of cyclooctatetraene into benzocyclobutene, with compound (109) acting as an intermediate.

Sondheimer's classic work on the annulenes,[98] and their relevance to the concept of aromaticity is well known. Recent developments[99,100,101,102] have shown that in large rings (more than fourteen carbon atoms) there is considerable stability inherent in a fully conjugated system, or in one having appropriately positioned double or triple bonds.

Various attempts to prepare a C_{12} annulene have verified the properties predicted for this compound, i.e. general instability, explosive decomposition, formation of bicyclic or aromatic compounds. It has yet to be isolated, though it may indeed exist. Aromatisation of cyclododeca-1,7-diyne , or its double-bond equivalent, on treatment with base should be facile, and a 1,2-benzocyclopolymethylene compound (54) or related species should result.

Transannular reaction is feasible; for example, palladium at 400° converts cycloalkanes into various aromatic compounds.[12,13]. Again, cyclododeca-1,7-diyne, ((53), m = n = 4), can form a [6:4:0] bicyclic system[103] (113), and (114) can be converted[104] to the doubly bridged compound (115). Moreover, Sondheimer has obtained,[45,46] as by-products, triphenylene (50) and 10-diphenylsuccindene (52) from the C_{18} and C_{16} unsaturated carbocycles (49) and (51) respectively. By-products, even of a tricyclic nature, are also obtained in a similar fashion from the C_{14} annulene and C_{14} cyclic diyne.[99,105.] Under more forcing conditions the C_{14} and C_{12} diynes afford the appropriate 1,2-benzocyclopolymethylene compounds.[46.]

The extreme ease of formation[106] - and resultant commercial availability - of the isomeric cyclododecatrienes [(116), (117) and, in trace amount, (118)] from the trimerisation of 1,3-butadiene over the appropriate catalyst (e.g. titanium tetrachloride / aluminium pentachloride) - has made these cyclic hydrocarbons the obvious starting materials for the synthesis of a cyclic C_{12} triyne - or its equivalent. Initial studies were carried out by McCrae[47] - bromination and dehydrobromination giving aromatic material amongst other things. A re-examination and extension of this reaction is the object of the last part of this doctoral work.

DISCUSSION

Historical Introduction

Speculation about the nature of "ψ-m-toluic acid" and its remarkable transformations, as described by Perkin and Simonsen,[108] led Eglinton and his co-workers to attempt a repetition of this early work.[41,42] Although this was unsuccessful, it led subsequently to the discovery that one of the possible structures for this compound, hepta-1,6-diyne-4-carboxylic acid (47), itself could be transformed into *m*-toluic acid (48) by the action of aqueous potassium hydroxide.[41] This observation proved to be so interesting that this same rearrangement was attempted with, and successfully extended to, the corresponding hydrocarbon hepta-1,6-diyne (119; $n = 3$). This compound yielded toluene after isomerisation with base.[42] In order to examine the generality and structural requirements of this unusual rearrangement, Willis extended it to a series of diacetylenic hydrocarbons[43] (119; $n = 4,5,6,10,17$).

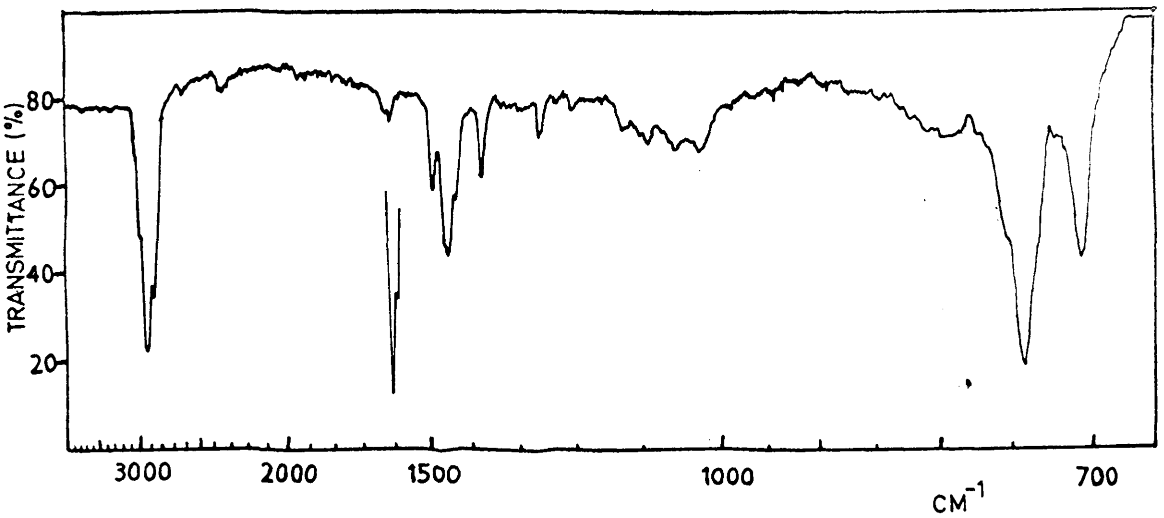
A survey by him showed that various examples existed of the base catalysed prototropic rearrangements of acetylenes to allenes or dienes. Furthermore, it was known that the triple bond was more stable in the 2- than in the 1- position of an alkyl chain, and that the migration was considerably facilitated (as in double bond migration) if it led to a conjugated system as the end product.

These facts led Willis to a reappraisal of the relative effectiveness of various base-solvent systems in promoting the prototropic rearrangement of hepta-1,6-diyne to toluene. By refluxing the hydrocarbon with the basic system for suitable periods he discovered that systems containing a free hydroxyl group were ineffective. In contrast, both sodamide and potassium tert-butoxide in diglyme were effective. (It should be pointed out that later work by Sondheimer[98] and Hubert and Dale[101] has shown that potassium tert-butoxide in tert-butanol *can* be used to effect rearrangement, but only for specific systems, or at higher pressures and concentrations than tried by Willis. Furthermore, the latter authors[99] have successfully carried out similar rearrangements of cyclic diynes with dimethylsulphoxide as solvent.

As potassium tert-butoxide in diglyme was found to be the most effective reagent (isomerisations employing sodamide showed the presence of allenic and ethylenic intermediates), Willis used it in all his subsequent isomerisations. In general, the basic medium was prepared just before use as an opalescent dispersion, by refluxing freshly prepared potassium tert-butoxide (previously heated at 160° under reduced pressure until sublimation started) with ten times its weight of diglyme. The diyne and this reagent were then heated under reflux (in an atmosphere of nitrogen) for the requisite period (4 - 15 hrs.). The reaction mixture was then diluted with water and extracted with n-pentane. Repeated washing of this extract with water, drying, and concentration gave the hydrocarbons resulting from the isomerisation.

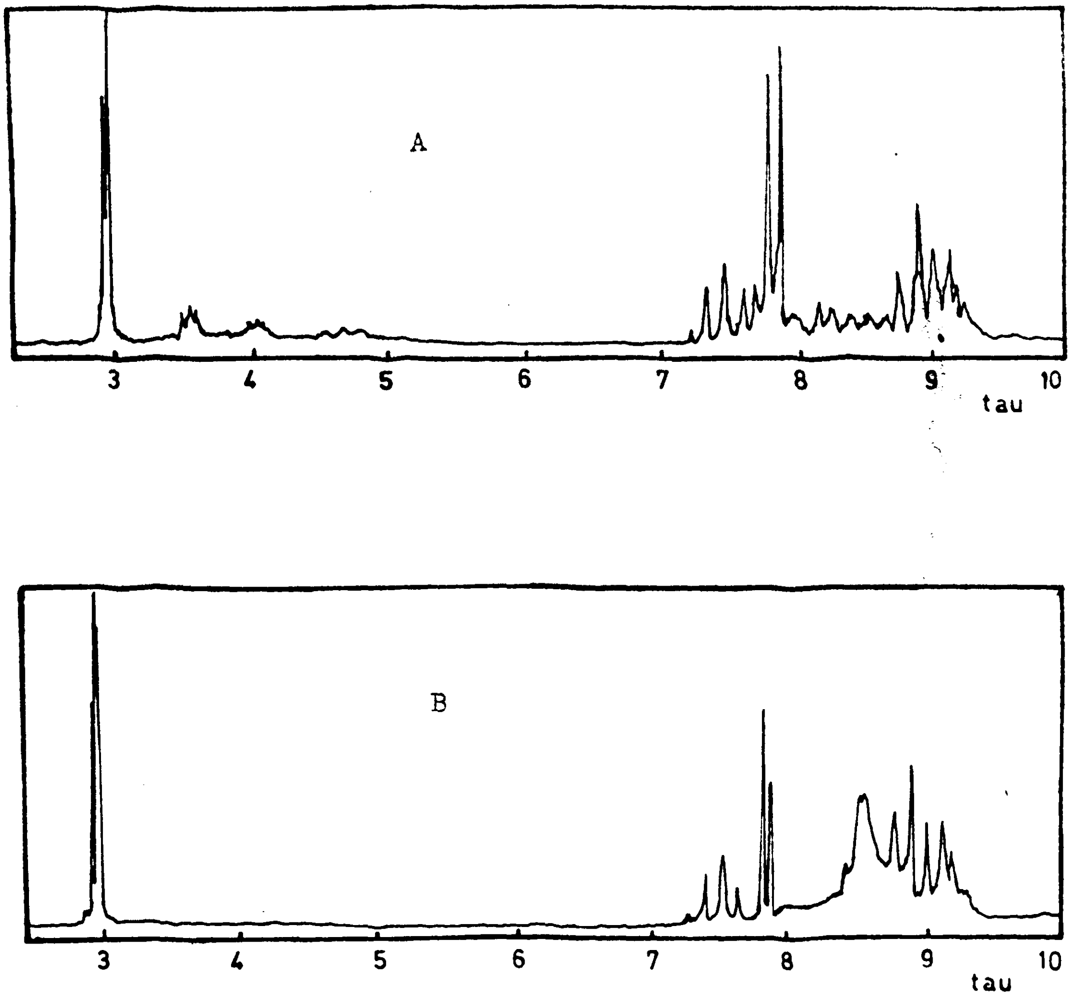
Using this method,[43,107,109] a variety of straight chain α,ω-diacetylenes (119; n = 4, 5, 6, 10, 17) gave products consisting mainly of the isomeric o-dialkylbenzenes, the total conversion being in most cases about 65%. The aromatic products were detected by their absorption in the infra-red spectrum at 750 and 690 cm.$^{-1}$, due to o-disubstituted and mono-substituted benzenes respectively; by permanganate oxidation to phthalic and benzoic acids respectively, and by comparative g.l.c. studies with authentic alkylbenzenes where feasible . This rearrangement was not confined to the terminal diacetylenes; thus nona-2,7-diyne gave the same proportions of n-propylbenzene and o-ethylmethylbenzene as did nona-1,8-diyne (119; n = 5). Conjugated diynes underwent the rearrangement with equal ease; thus both octa-3,5-diyne and octa-1,7-diyne produced similar proportions of ethylbenzene and o-xylene.

These were the facts known about this rearrangement at the commencement of these doctoral studies. There was no doubt that aromatic products were formed; whether they were the only products formed was rather doubtful, for several of the infra-red spectra and g.l.c. traces showed inexplicable peaks - indeed, the longer the chain length the more intermediates would need to be formed. The mechanistic route of this reaction was still complete conjecture, though several could be postulated by analogy with known reactions of acetylenes. The isomeric pair deca-1,9-diyne and deca-4,6-diyne were chosen for a further more detailed study of the reaction.



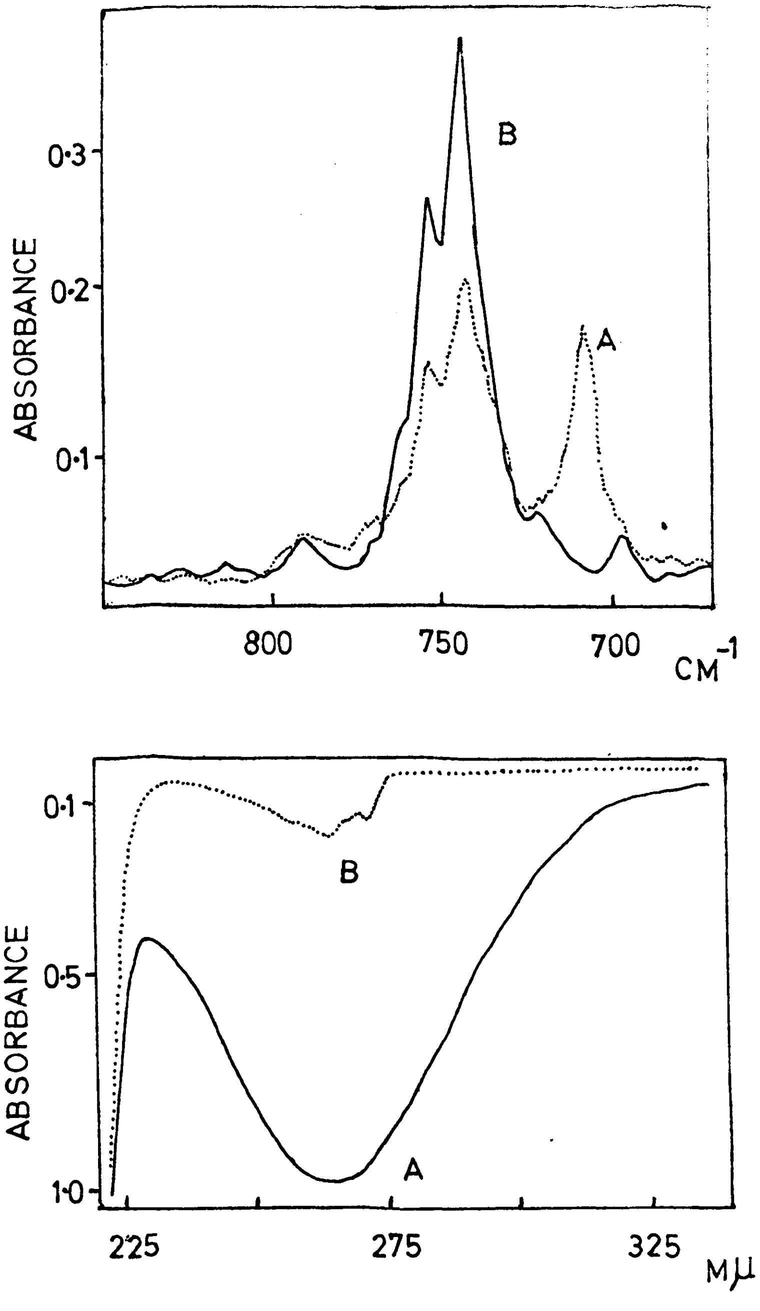
Infrared spectrum of the primary products of base catalysed isomerisation of deca-1,9-diyne (liquid film)

Figure 1.



N.m.r. spectra of the primary (A) and hydrogenated (B) products from the base catalysed isomerisation of deca-4,6-diyne (CCl_4 solution).

Figure 2.



Infrared and ultraviolet spectra of primary (A) and hydrogenated (B) product from the isomerisation of deca-1,9-diyne.

Infrared: Cell path 0.51 cm.; CS_2 solution, 4.6 and 11.1 mg./ml. respectively of A and B.

Ultraviolet: Cell path 0.1 and 0.2 cm.; cyclohexane solution, 0.64 and 0.79 mg./ml. respectively of A and B.

Figure 3.

SECTION I

The Preparation and Isomerisation of the Decadiynes

Deca-1,9-diyne and deca-4,6-diyne were synthesised by the standard methods outlined in the experimental section (p. 89), and their purity checked by g.l.c. They were then treated with the reagent described previously (in a 1:7 molar ratio, diyne to base) for 12 - 18 hrs. The reaction products, as characterised by their infra-red (Fig.1) and ultra-violet absorptions were remarkably similar, both being indicative of aromatic material ($\nu_{max.}^{film}$ 740, 710 cm.$^{-1}$ for both; $\lambda_{max.}^{c.hexane}$ 265 mμ, ε = 1,900 and 2,800 respectively). The intensity of the ultra-violet absorption of the product from deca-4,6-diyne was stronger than that for the deca-1,9-diyne product, but in both cases, the absorptions were stronger than those expected for simple benzenoid systems.

The presence of other unsaturated (and conjugated) products was therefore inferred, and this view was confirmed by the n.m.r. spectra of both products (Fig. 2a, again both practically identical), in which the presence of ethylenic constituents was clearly shown by vinylic proton absorption over the region 3.5 - 4.9τ, as well as aromatic products (2.8 - 3.0τ). These olefinic properties disappeared completely when the mixture was catalytically hydrogenated [under conditions which left the benzenoid components unscathed (Fig. 2b)]. A marked decrease in the intensity of the 710 cm.$^{-1}$ absorption in the infra-red (which must have

TABLE I

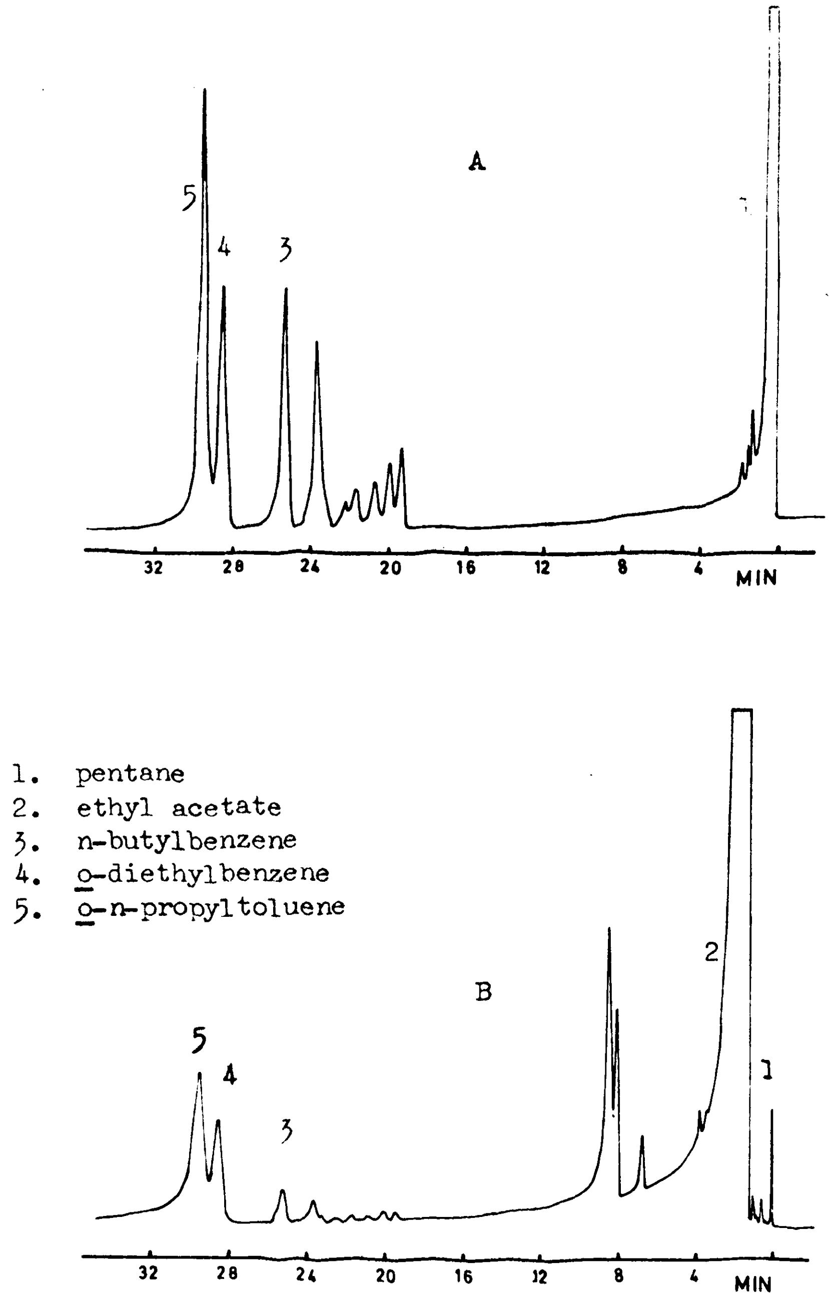
Retention times (R_T) and composition (%) data of primary and hydrogenated Decadiyne isomerisation products.

Sample	Retention Times (mins.) and % composition											
Deca-1, 9-diyne mixture				19.2	19.7	20.4	21.8	22.0	23.4	25.0	28.1	29.2
%				4	5	3	2	2	10	18	20	37
Deca-1, 9-diyne hydrogenated mixture	6.7	8.0	8.4	19.4	20.0	20.8	21.8	22.3	23.8	25.4	28.6	29.6
%	10	10	18	2	2	1	0	0	9	9	17	28
Deca-4, 6-diyne mixture				19.4	19.8	20.6	22.0	22.2	23.6	25.2	28.4	29.5
%				6	5	3	3	2	14	19	17	31
Deca-4, 6-diyne hydrogenated mixture	6.6	8.0	8.4	19.4	19.9	20.6	21.6	22.4	23.6	25.2	28.5	29.5
%	6	22	32	1	1	0	1	0	3	4	12	18
n-butylbenzene										24.9		
o-diethylbenzene											28.3	
o-*n*-propylmethylbenzene												29.2

been due to cis double bonds) was also noted, and the ultra-violet spectrum was now of greatly reduced intensity and more characteristic of aromatic compounds (Fig. 3).

G.l.c. analysis, using high resolution capillary columns, of the primary reaction mixtures showed the presence of n-butylbenzene, o-n-propylmethylbenzene, and o-diethylbenzene, the last two predominating. (Fig. 4a). However, these were by no means the only peaks to appear; at least six further products were indicated on the trace for each diyne. Similar traces were obtained for the hydrogenated primary products (Fig. 4b), but they did not contain any n-decane, thereby proving that the primary olefinic constituents were most likely to be cyclic and not straight chain compounds.

The percentage compositions of the primary and hydrogenated mixtures, as well as the peak assignments, are given in Table I. The close correspondence of the aromatic isomers in both primary mixtures is clearly demonstrated, but there appear to be discrepancies between the hydrogenated samples, possibly as a result of the incomplete hydrogenation of the deca-1,9-diyne mixture. As the percentage of n-butylbenzene and o-diethylbenzene drops drastically, so other materials must be present, hidden in the peaks assigned to these compounds. Likewise the decrease in size of the unidentified peaks and the emergence of new ones with markedly shorter retention times, probably means that these are the unsaturated cyclics converted into only three saturated parent compounds.

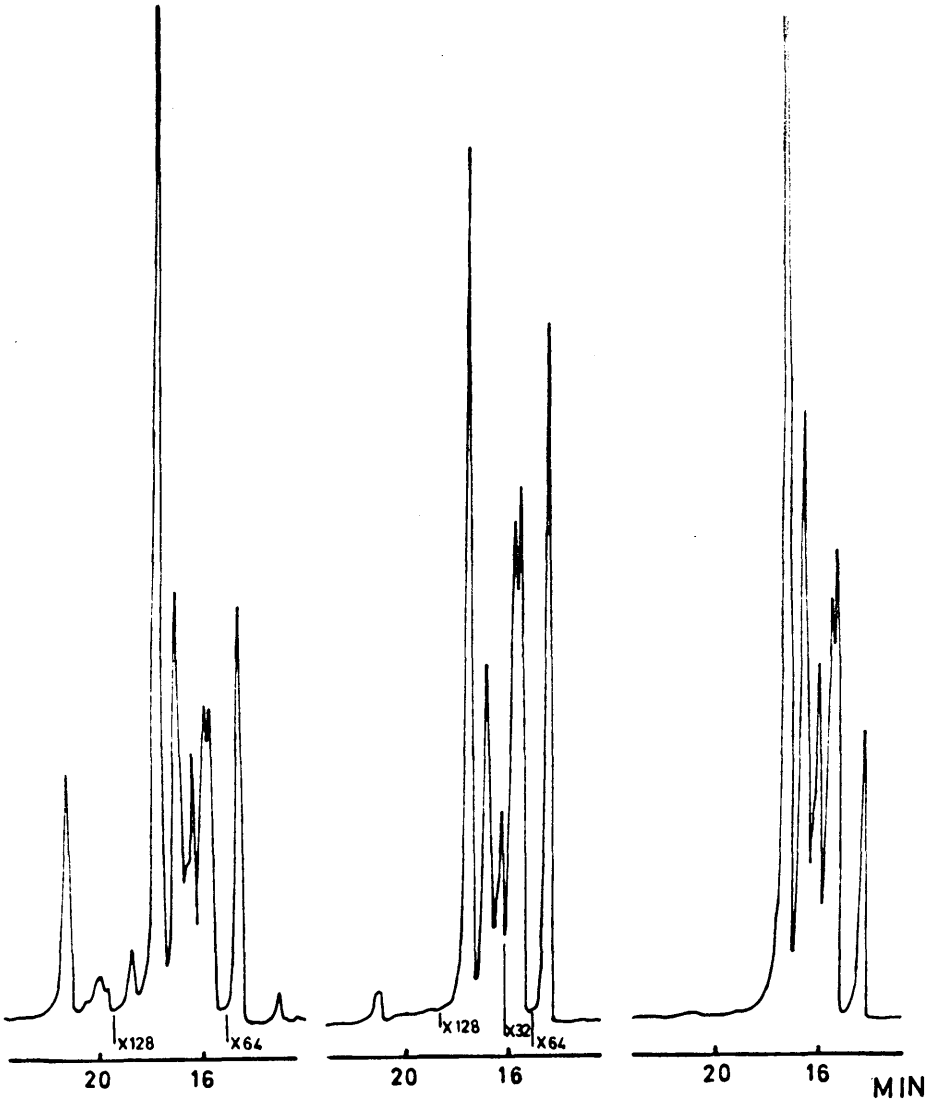


1. pentane
2. ethyl acetate
3. n-butylbenzene
4. o-diethylbenzene
5. o-n-propyltoluene

G.l.c. of primary (A) and hydrogenated (B) product from the isomerisation of deca-4,6-diyne.

Conditions: 50 m. poly(ethyleneglycol) capillary, 50°, 18 p.s.i./ 6.0, total flow 55 ml./min.

Figure 4.



After 11 hrs. After 5 hrs. After 1 hr.

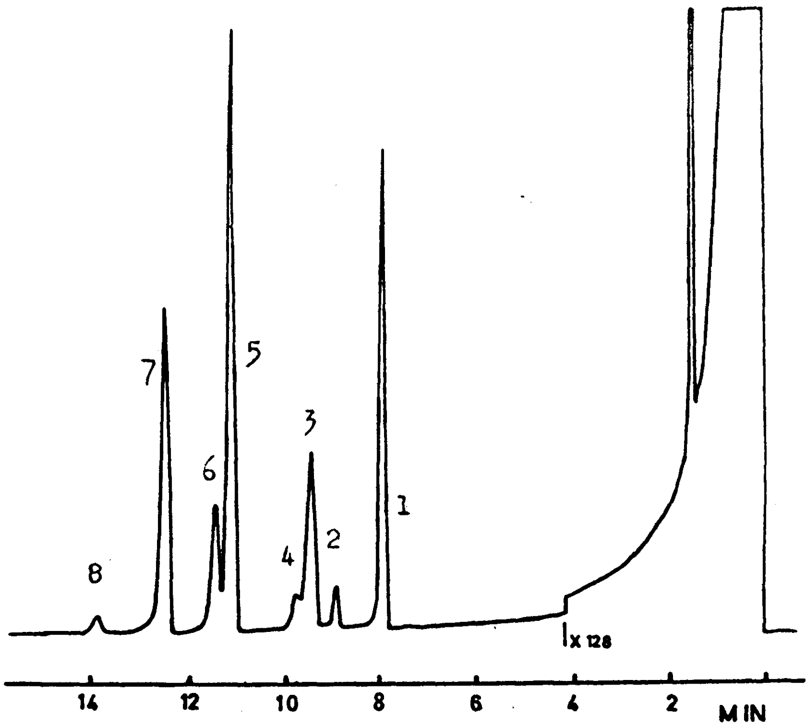
G.l.c. of aliquots from the base catalysed isomerisation of deca-4,6-diyne.

Conditions: 50 m. Ap'L' capillary, 103°, 20.75 p.s.i./7.1, total flow 90 ml./min.

Figure 5.

However, certain unassigned peaks on the traces did not shift completely on hydrogenation, so they could not correspond to any ethylenic products; this point is discussed further in connection with the work on octa-1,7-diyne.

A time study of the isomerisation, involving withdrawal of aliquots at regular intervals and subsequent g.l.c. analysis (in this case using only deca-4,6-diyne) showed that isomerisation occurred very rapidly. Even after one hour the composition of the reaction mixture was essentially the same as after 25 hrs., though some further isomerisation took place towards the end as indicated by the appearance of further minor peaks (Fig. 5). The composition was constant throughout the first ten hours, the proportions of n-butylbenzene, o-diethylbenzene and o-n-propylmethylbenzene being 10% (10%), 17% (16%) and 43% (38%) after 2 hrs. and 10 hrs. respectively.



G.l.c. of the product from the base catalysed isomerisation of octa-1,7-diyne.

Conditions: 50 m. Ap'L' capillary, 81°, 17 p.s.i./5.8, total flow 55 ml./min.

Peak no.	Compounds	R_T (min.)	Composition %
1	ethylbenzene	11.34	21
2		12.38	3
3	*m*- plus *p*-xylene	12.92	16
4		13.26	
5	*o*-xylene	14.56	38
6		14.86	
7		15.9	19
8		17.34	3

Figure 6.

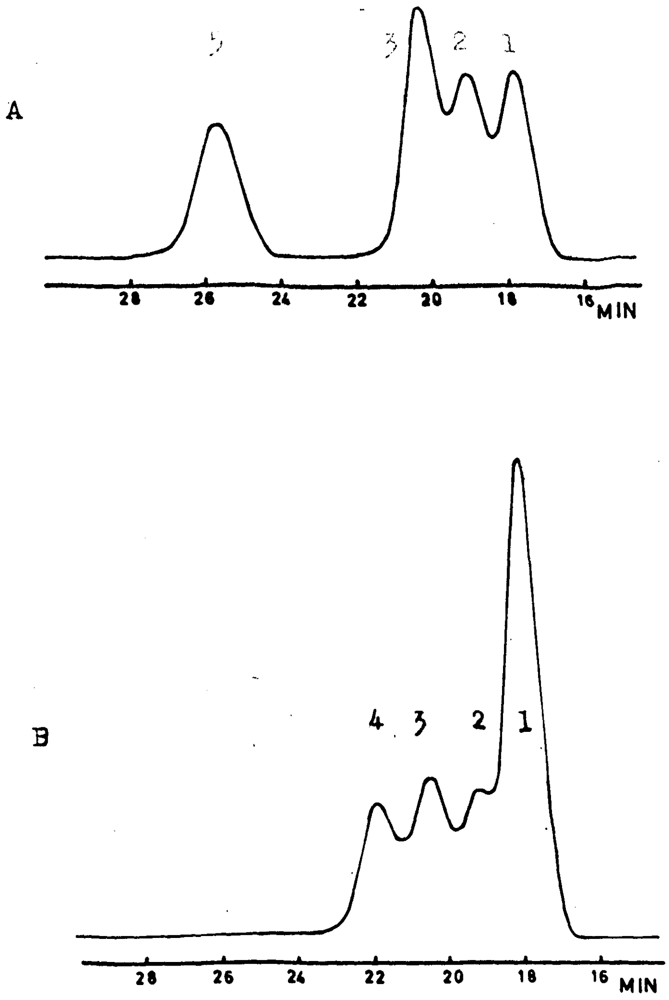
SECTION II

Isomerisation of Octa-1,7-diyne.

In view of the large number of isomeric possibilities for these C_{10} by-products, detailed investigation of this aspect of the rearrangement was transferred to the C_8 system, using octa-1,7-diyne. This was prepared by standard methods and purified by preparative g.l.c. This purified material was used for initial trials, but, as the isomerisation products were the same from the purified and crude material, the latter was used for all subsequent large scale isomerisations.

Treatment of the diyne with the same basic reagent (in a molar ratio of 1:5 of diyne to base) for 8 hrs., heating under reflux yielded an oil which had spectral characteristics very similar to those of the C_{10} diyne products. (ν_{max}^{film} 743, 709 cm.$^{-1}$; $\lambda_{max}^{c.hexane}$ 251-256 mμ. ε = 2530). Typical ethylenic absorption was also present at 3.2 - 4.9τ in the n.m.r. spectrum. Aliquots removed in the course of the reaction and examined by g.l.c. showed that equilibrium was attained after 2 hrs.

Analytical g.l.c. (capillary column) again showed that as well as the expected o-xylene and ethylbenzene (5:3 proportion), at least six other products were present (Fig. 6). On preparative g.l.c. of this complex mixture, several cuts were obtained, one of which (Cut 4) contained pure o-xylene (confirmed by g.l.c. and i.r.). The other expected product, ethylbenzene, was present in Cut 3, but the infrared

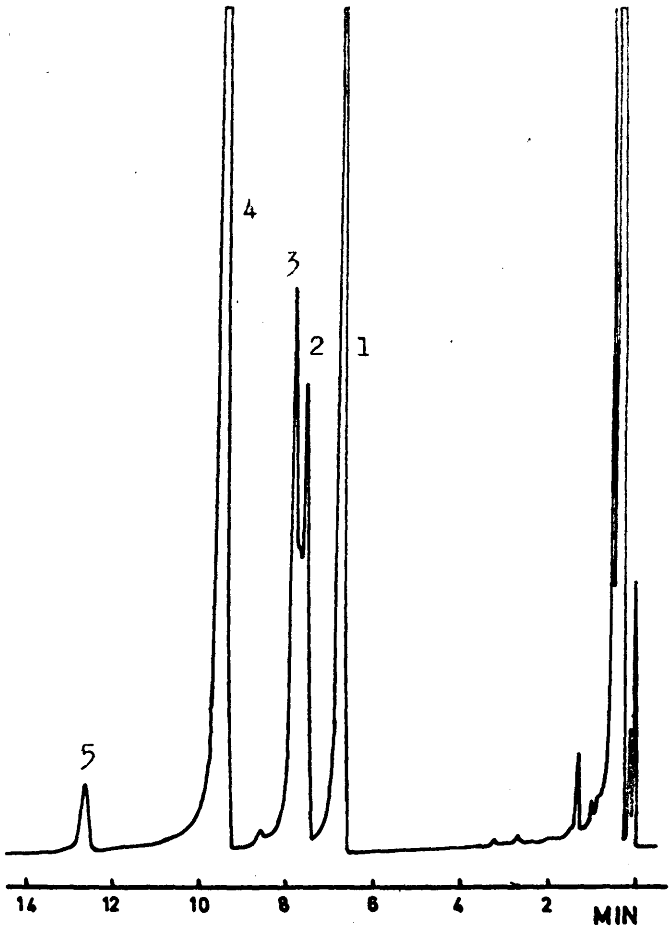


G.l.c. of the C_8 aromatic hydrocarbons (A) and Cut 3 (B) from the preparative g.l.c. of the octa-1,7-diyne isomerisation product.

<u>Conditions:</u> 20% 7,8-benzoquinoline, 2 m. x ¼" o.d., 80°,
20 p.s.i.

1. ethylbenzene.
2. <u>m</u>-xylene.
3. <u>p</u>-xylene.
4. unknown.
5. <u>o</u>-xylene.

Figure 7.

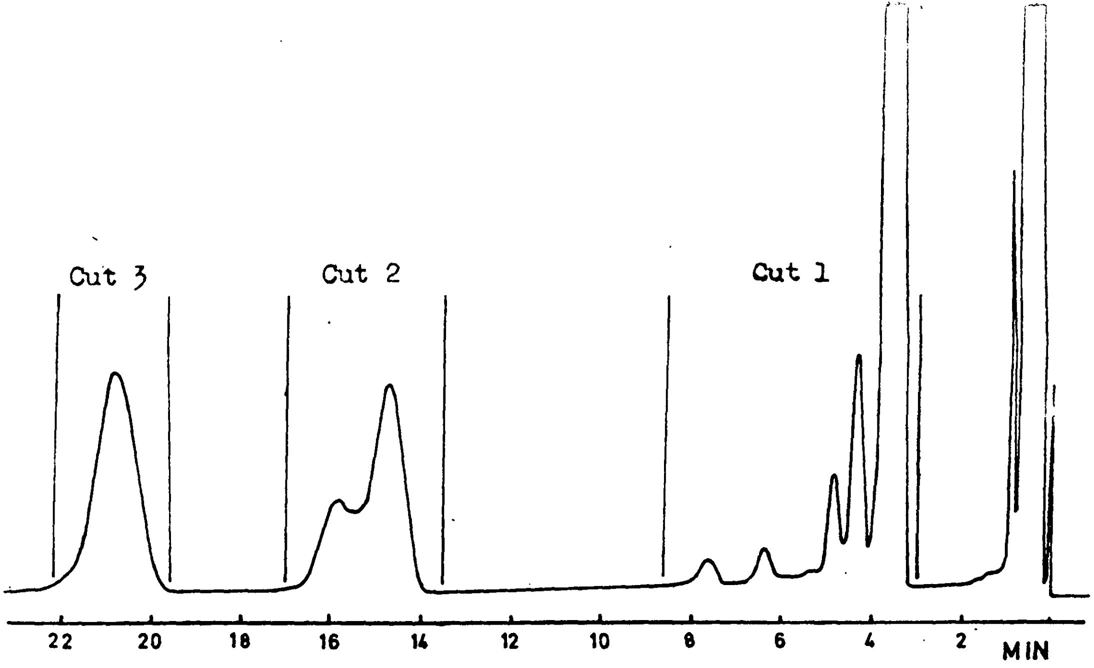


G.l.c. of the hydrogenated products from the base catalysed isomerisation of octa-1,7-diyne.

Conditions: 50 m. Ap'L' capillary, 84°, 18 p.s.i.

1. ethylbenzene
2. methylcycloheptane
3. m- plus p-xylene
4. o-xylene
5. cyclooctane

Figure 8.



Preparative g.l.c. separation of the hydrogenated product from the base catalysed isomerisation of octa-1,7-diyne.

Conditions: 20% poly(ethyleneglycol), 2 m. x ¼" o.d., 80°, 18 p.s.i.

Cut 1	ethyl acetate + C_8H_{16} isomers.
Cut 2	ethylbenzene + m-xylene + p-xylene.
Cut 3	o-xylene.

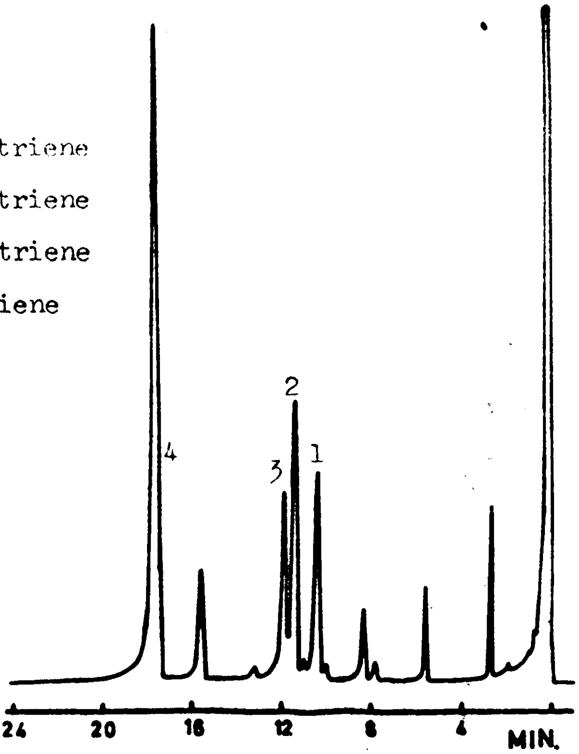
Figure 9.

spectrum of this cut indicated the presence of m- and p-xylene as well! This was proved conclusively by re-chromatography on a g.l.c. column specific for aromatic hydrocarbons (7,8-benzoquinoline, Fig. 7). Hence the aromatic hydrocarbons were present in a ratio of 5:3:2 of o-xylene: ethylbenzene : m- and p-xylene.

Additional confirmation of these other aromatics came after hydrogenation of the primary product, when the peaks due to the four isomers were found unchanged, and still in the same proportions (Fig. 8). Again, other new peaks were present, and the two main ones were isolated by preparative g.l.c. in the following way. A poly (ethyleneglycol) column was used for the initial separation of the aromatic from the saturated compounds (Fig. 9), the latter, together with ethyl acetate solvent, being rechromatographed on an A p "L" column to provide four cuts. Cuts 1 and 3 were discarded (solvent and insufficient material respectively). The material in Cut 2 was identified as methylcycloheptane by spectroscopic (i.r., n.m.r.) and g.l.c. comparison with an authentic sample. The fourth cut was also studied by n.m.r. and g.l.c., and found to be cyclooctane by comparison with an authentic sample. No n-octane could be detected amongst the hydrogenated products.

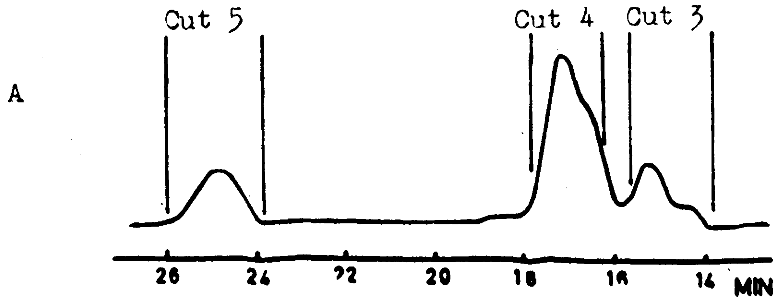
The identification of these unexpected hydrogenation products demanded that their unsaturated precursors be isolated and identified. Initial separation into aromatic and ethylenic constituents of the primary product was achieved by elution chromatography on a silver

1. 2-methylcycloheptatriene
2. 3-methylcycloheptatriene
3. 1-methylcycloheptatriene
4. Cycloocta-1,3,5-triene



G.l.c. of the unsaturated constituents from the base catalysed isomerisation of octa-1,7-diyne.

Conditions: 50 m. Ap'L'capillary, 51°, 15 p.s.i./6.0, total flow 55 ml./min.



Preparative g.l.c. separation of the above mixture.

Conditions: 20% poly(ethyleneglycol), 2 m. x $\frac{1}{4}$" o.d., 81°, 55 ml./min.

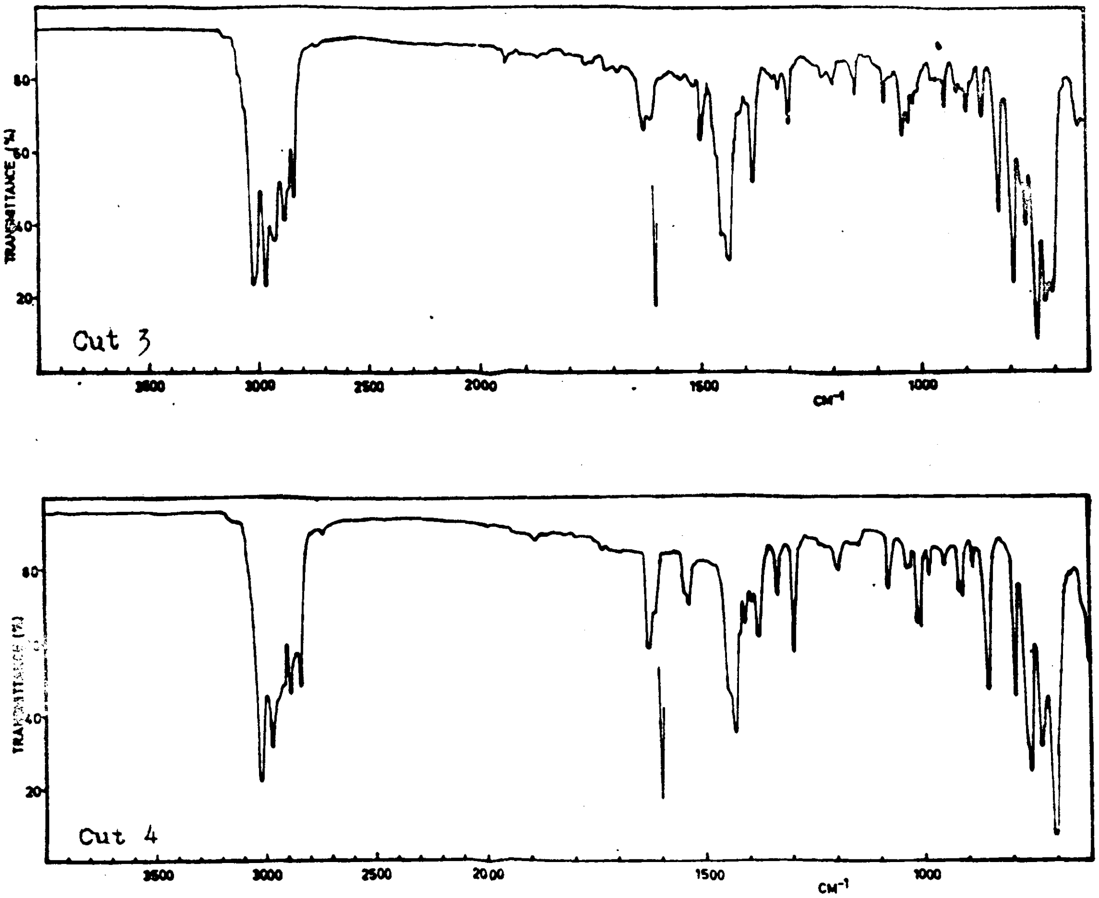
Cut 3: 1 + 2; Cut 4: 3 + 2; Cut 5: 4.

Figure 10.

nitrate/silica gel column. The fractions containing the latter compounds (Fig. 10) were carefully combined and concentrated, then subjected to preparative g.l.c., but only the last cut of the five contained a pure compound. A more efficient column in an Aerograph Autoprep again gave five cuts (Fig. 10a); Cuts 1 and 2 were discarded, Cut 5 contained a single compound, while Cuts 3 and 4, though containing several compounds in common, were obtained in sufficient quantity to identify their constituents spectroscopically.

Cut 5 had infrared and ultraviolet absorption identical to that of cycloocta-1,3,5-triene (101), and as only two groups of peaks centred at 4.23 and 7.57 τ (ratio 3 : 2) were present in the n.m.r. spectrum, this was taken as sufficient proof of its identity.

Cut 3 had $\lambda^{c.hexane}_{max}$ 269 mμ. (ε = 3,400) and absorption at ν^{film}_{max} 790, 765, 740, 720, 705 cm.$^{-1}$ in the infrared, highly suggestive of the isomeric methylcyclohepta-1,3,5-trienes (121-123). Cut 4 also had $\lambda^{c.hexane}_{max}$ 264 - 266 mμ (ε = 2750) and absorption at ν^{film}_{max} 795, 760, 735, 705 cm.$^{-1}$ in the infrared. The n.m.r. spectra of both cuts had similarities to each other and to the spectra of the isomeric methylcycloheptatrienes, (the 1-, 2-, and 3-methyl isomers only, and not the 7-methyl isomer). A close examination and comparison of their spectral properties with published data led to the conclusion that Cuts 3 and 4 were largely mixtures of 2-methylcycloheptatriene (122) [plus 3-methylcycloheptatriene (123)] and 1-methylcycloheptatriene (121)

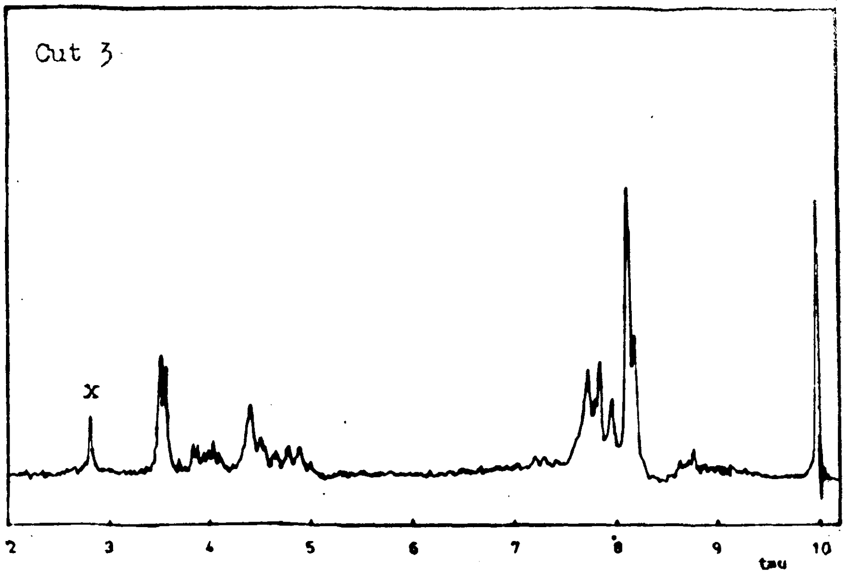


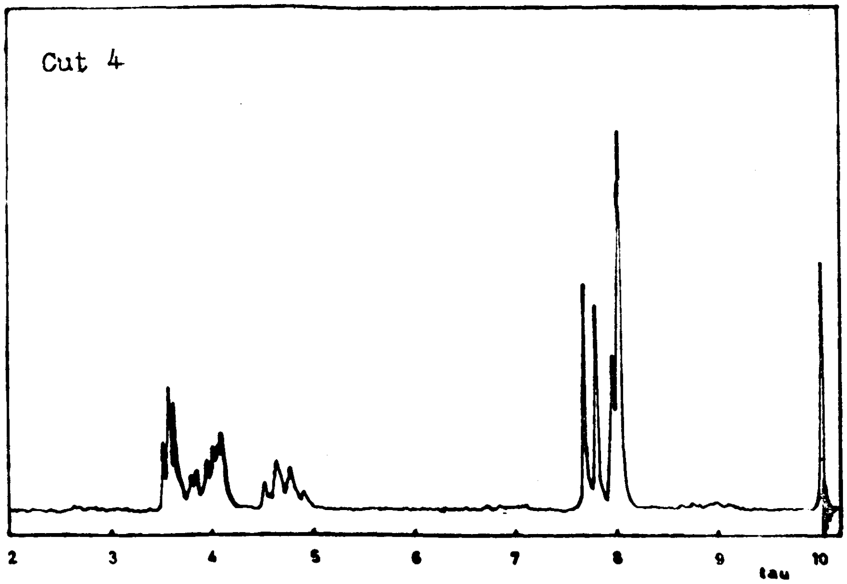
Infrared spectra (liquid film) of Cuts 3 and 4 from the preparative g.l.c. separation of the unsaturated constituents from the isomerisation of octa-1,7-diyne.

Cut 3   Mixture of 2- and 3-methylcycloheptatrienes.

Cut 4   Mixture of 1- and 3-methylcycloheptatrienes.

Figure 11.



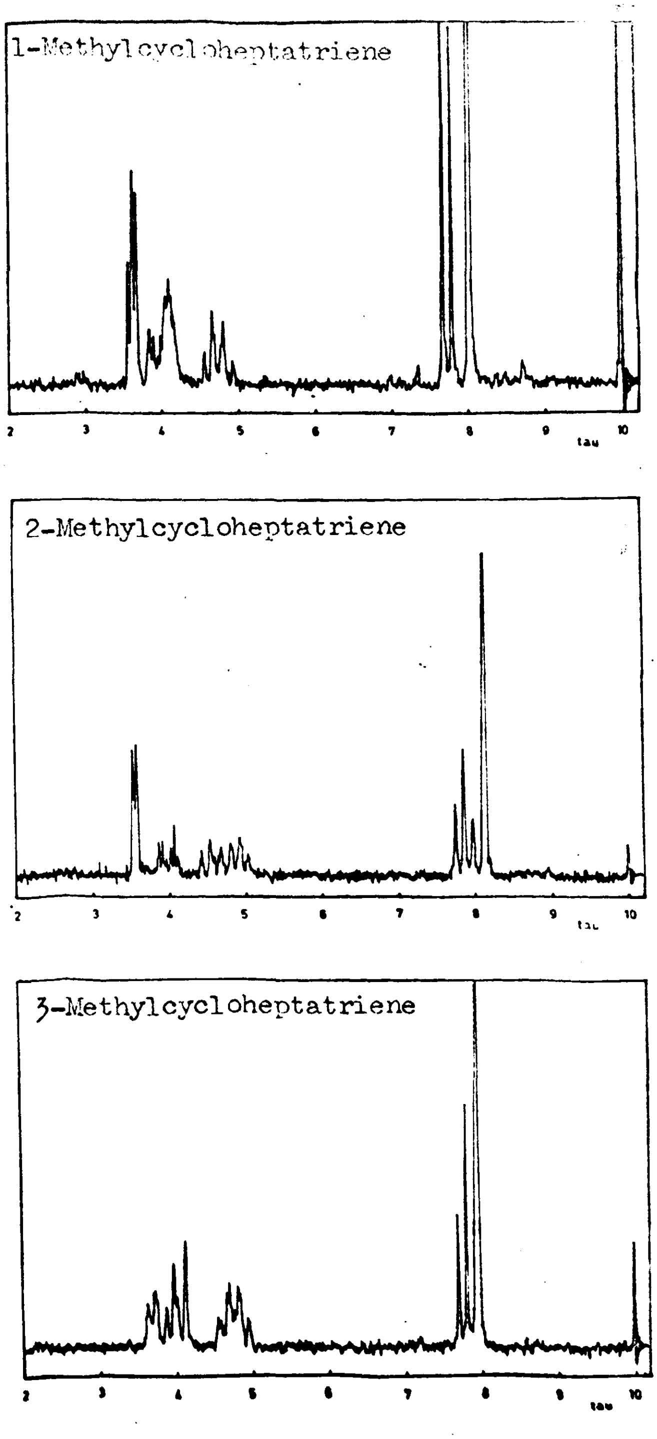


N.m.r. spectra (CCl_4) of Cuts 3 and 4 from the preparative g.l.c. separation of the unsaturated constituents from the isomerisation of octa-1,7-diyne.

Cut 3	Mixture of 2- and 3-methylcycloheptatrienes.
Cut 4	Mixture of 1- and 3-methylcycloheptatrienes.

x = impurity.

Figure 12.



N.m.r. spectra (CCl_4) of the isomeric 1-, 2-, and 3-methylcycloheptatrienes

Figure 13.

[plus the 3-methyl isomer (123) also] respectively. This spectral data is presented for comparison in tabular form (Tables II, III, IV, p. 100), and the infrared and n.m.r. spectra of the compounds under discussion are reproduced in Figs. 11, 12 and 13.

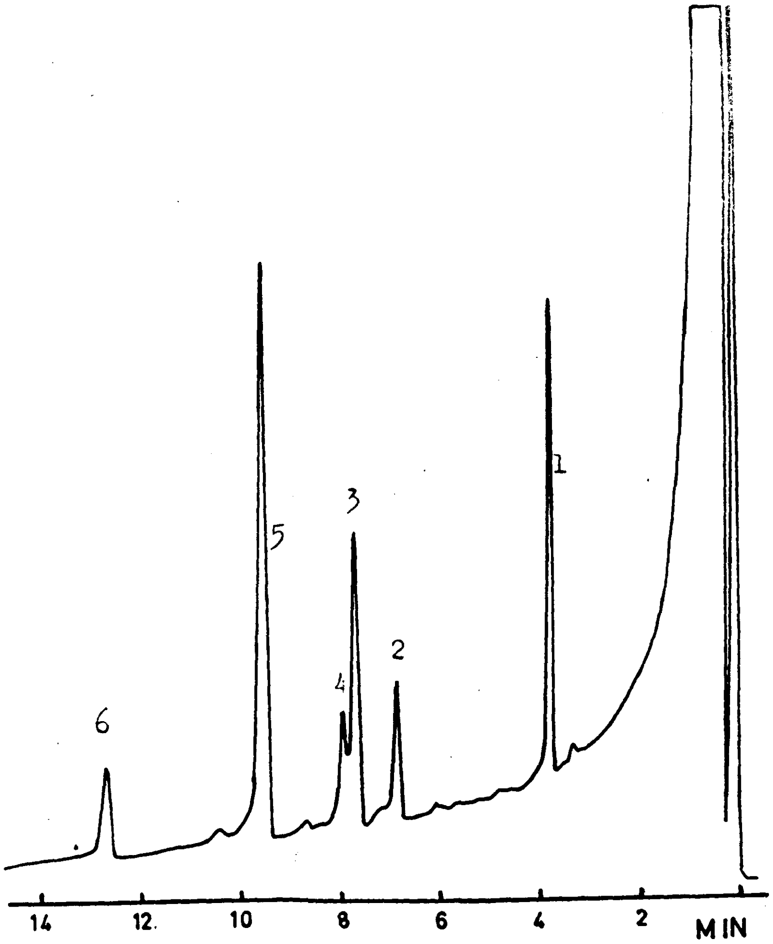
Synthesis of these isomeric C_8H_{10} hydrocarbons (p. 30) and direct spectral (i.r., u.v., n.m.r.) and g.l.c. comparison (on several columns) at a later date confirmed that Cuts 3 and 4 did indeed contain mixtures of these methylcycloheptatrienes, and that Cut 5 consisted of pure cycloocta-1,3,5-triene. (Though on standing, a second component presumed to be its valence isomer, bicyclo[4:2:0]octa-2,4-diene (102) also appeared).

Samples of Cuts 3, 4 and 5 (about 1 mg.) when hydrogenated (over palladium-charcoal in ethyl acetate) in a Clauson-Kaas apparatus gave somewhat unexpected results, for Cuts 3 and 4 yielded only ~ 50% methylcycloheptane, no starting material, and several other constituents (by g.l.c.). Cut 5 produced none of the expected cyclooctane, nor starting material, but did produce one major compound, presumed to be cyclooctene. Literature reports discovered later[110] revealed that complete hydrogenation of eight membered carbocycles is not possible under some conditions, cyclooctene being produced in most cases, and possibly a similar limitation may hold with a seven carbon ring compound. Isomerisation on the catalyst surface may have been a further complicating factor, and could not be ignored in this case as an excess of catalyst was present.

As the products isolated from the isomerisation all appeared to be end products and not genuine intermediates, attempts were made to detect these transient members. Willis, in his initial exploration of reaction conditions had remarked that weaker bases or lower reaction temperatures had resulted in incomplete conversion of starting material. On this principle, octa-1,7-diyne was heated under reflux (2 hrs.) from ambient with one molar equivalent of potassium tert-butoxide in diglyme. The infrared spectrum had, as usual, ν_{max}^{film} 745, 700 cm.$^{-1}$, but the ultraviolet spectrum showed $\lambda_{max}^{c.hexane}$ 269 (ε = 400), 280 (ε = 400), 293 (ε = 450), 306 (ε = 305), so unlike those obtained before that it warranted further investigation.

Analytical g.l.c. showed a new major component apart from the aromatic isomers, and a pure sample of it was isolated by preparative g.l.c. This was collected as a solid (colourless platelets at 0^{o}) which gave a single peak on rechromatography and had ν^{film} 1340, 1320, 1260, 1025 cm.$^{-1}$ in the infrared and only end absorption in the ultraviolet. Hydrogenation over palladium-charcoal yielded n-octane (96% of calculated uptake for four double bond equivalents).

This same compound was also found and isolated by preparative g.l.c. as a major product when octa-1,7-diyne was heated under reflux with potassium tert-butoxide in tert-butanol for 24 hrs. Its n.m.r. spectrum had peaks at 7.75 (4H) and 8.25 (6H) τ , while the mass spectrum



G.l.c. of the hydrogenated, incompletely base catalysed products from octa-1,7-diyne.

Conditions: 50 m. Ap'L' capillary, 84°, 18 p.s.i.

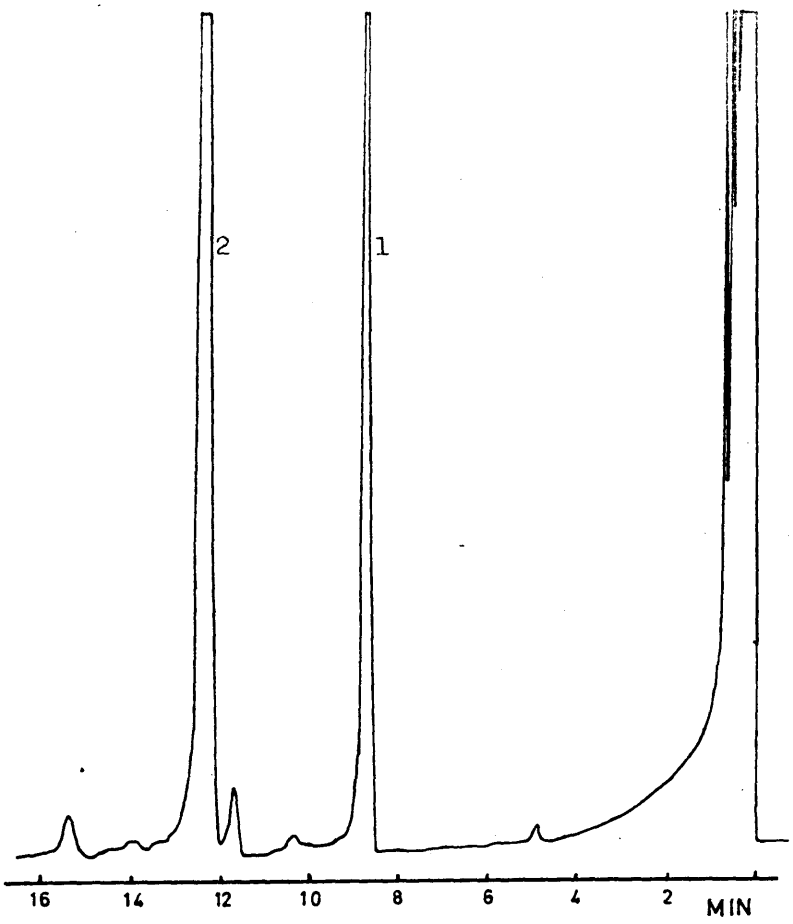
Peak	Compound	R_T (mins.)	Composition %
1	n-octane	3.7	29
2	ethylbenzene	6.8	8
3	methylcycloheptane	7.7	17
4.	m-xylene, p-xylene	7.9	7
5.	o-xylene	9.5	36
6.	cyclooctane	12.7	5

Figure 14.

had a parent ion at $^m/_e$ 106. This evidence shows this compound to be octa-2,6-diyne (124), even though the ultraviolet absorption observed originally was characteristic of the *linear* octa-1,3,5,7-tetraene (103b) (present only, of course, in very small amount as indicated by the low ε values). It must be concluded that the tetraene either rearranged on the g.l.c. column to the octa-2,6-diyne, or being present only in tiny amount together with the diyne, was overlooked completely.

That linear species were present in the reaction mixture was proved by hydrogenating a sample, and g.l.c. analysis (Fig. 14) showed that all the xylenes, ethylbenzene, cyclooctane, methylcycloheptane *and* n-octane were present. This is in sharp contrast to the fully isomerised mixture, where no n-octane had been detected after hydrogenation.

A chance observation, that the isomerisation products varied in their relative proportions depending upon whether the 1,7-diyne was added to either a hot or a cold dispersion of the base, led to the establishment of conditions for the formation of only *o*-xylene and ethylbenzene only. It was therefore argued that heating increased the proportion of potassium tert-butoxide in solution, where reaction could only occur by one mechanism, whereas at lower temperatures isomerisation could occur not only in solution, but also on the surface of undissolved solid particles. When the diyne was added to a hot solution containing less base than usual, a smaller amount of the unsaturated compounds and the *m*- and *p*-xylenes was formed. Finally, a hot dispersion of potassium



G.l.c. of the isomerisation products from octa-1,7-diyne, using a dilute, filtered solution of the base.

Conditions: 50 m. Ap'L', 75°, 18 p.s.i.

1. ethylbenzene
2. o-xylene

Figure 15.

tert-butoxide in diglyme ($\sim 2\%$ concentration) was filtered hot through sintered glass under nitrogen, to yield a pure dilute solution (~ 0.2 molar). The diyne, when added to this solution at reflux, was completely converted to o-xylene and ethylbenzene after 2 hrs. (with only traces of other compounds. Fig. 15).

This would seem to justify the assumption that at least two competing mechanisms are at play in the heterogeneous system, each yielding its own set of products. Further weight is added to this argument by the conversion of cyclooctatetraene on solid potassium tert-butoxide to mainly m- and p-xylenes along with o-xylene and ethylbenzene . This point is elaborated in the section dealing with the mechanism proposed for this isomerisation.

SECTION III

Synthesis of Hydrocarbons Isomeric with Octa-1,7-diyne

As the investigation of the base catalysed isomerisation of octa-1,7-diyne had reached the stage where most of the end products were known, and two possible intermediates had been detected, it was considered necessary to synthesise some of the likely possibilities, and subject these in turn to the isomerisation conditions. The isomeric methylcycloheptatrienes (120 - 123) were deemed possible sources for the m- and p-xylenes; cycloocta-1,3,5-triene (101) was another possibility; and it was hoped to synthesise octa-1,2,6,7-tetraene (125) as it was a likely precursor of octa-1,3,5,7-tetraene (103b).

No single method existed for preparing all the methylcycloheptatrienes (120 - 123), so two separate routes were used. The preparation of 7-methylcycloheptatriene[111] (120) is outlined in Scheme VIII. Addition of bromine to cycloheptatriene gave dibromotropilidene, which was converted by heating in vacuo into tropilium bromide (126). This, when treated with methyl magnesium iodide gave the required isomer (120) in 52% yield (purified by preparative g.l.c.).

The more laborious preparation[112] of the other three isomers is outlined in Scheme IX. Birch reduction of o-toluic acid (127) gave 1,4-dihydrotoluic acid (128), which in turn yielded 1,4-dihydro-2-methylbenzyl alcohol (129) after reduction with lithium aluminium hydride.

The p-toluenesulphonyl derivative (130) of this alcohol was solvolysed in glacial acetic acid (buffered) at 90° for 36 hrs. to give a mixture of the 1-, 2-, and 3-methylcycloheptatrienes (and the acetates arising from the alcohol). Elution chromatography separated off the hydrocarbons from the rest, which were then separated into pure compounds by preparative g.l.c. Each methylcycloheptatriene was identified spectroscopically by comparison with published data. Analytical g.l.c. of the hydrocarbon mixture prior to separation showed it to consist of 16%, 16%, and 60% of the 2-, 3-, and 1-methylcycloheptatrienes along with 8% o-xylene. This composition differs from that in the literature,[112] but this is not considered significant as later work in this thesis (p. 34) shows that these isomers can interchange under the action of heat alone.

The preparation of cycloocta-1,3,5-triene was also by a published route.[113] (Scheme X). Allylic bromination of cycloocta-1,5-diene (32) and subsequent dehydrohalogenation by base yielded the required triene. As bromination gave a series of products which could not be purified, the crude reaction mixture was treated with the base, with the result that starting cycloocta-1,5-diene had to be separated from the cyclic triene (101) by preparative g.l.c. Any cycloocta-1,3,6-triene (101a) formed by dehydrobromination of a monobromocyclooctadiene would be isomerised to the conjugated triene under these basic conditions.[114]

An attempt to circumvent the use of a crude mixture gave results and products not compatible with the literature claims. Hence allylic bromination of cycloocta-1,5-diene with two moles of N-bromosuccinimide should have given the dibromide (133a) as an oil. The compound isolated after chromatography of the product oil was a solid, and had spectral properties more in accord with (133b). An outline of its reactions and spectral characteristics is given in the Appendix (p. 146).

The preparation of the hitherto unknown octa-1,2,6,7-tetraene (125) was attempted by two routes, both unsuccessful. In the first of these,[115] (Scheme XI), attempts were made to add two moles of dibromocarbene to hexa-1,5-diene (134) by standard methods, (potassium tert-butoxide/bromoform). Very low yields of the diadduct (136) resulted, and recyclisation and addition of another mole of bromoform to the monoadduct (135) gave only slightly better yields. Worse still, it was found impossible to convert the diadduct (136) to the diallene (125) with methyl lithium as claimed in the literature: only starting material, i.e. (136), was recovered in every case.

The second route was by a very recent method,[116] for the conversion of triple bonds to allenes, and involved addition of phosphorus pentachloride to a triple bond (Scheme XII). Starting with octa-1,7-diyne it was hoped to get the phosphorane complex (137) and by hydrolysis the bis-(chlorophosphonic acid) (138). Further treatment of this compound with aqueous sodium hydroxide was to generate the terminal diallene (125).

This sequence of reactions was carried out on octa-1,7-diyne, and at the end, allenic and acetylenic absorption was observed in the infrared spectrum of the product, as well as absorption at $\lambda_{max}^{pentane}$ 208 and 212 mμ in the ultraviolet. Analytical g.l.c. showed two major components (71% and 18%) in the product, neither of which was octa-1,7-diyne. From this information it was assumed that the major component was octa-1,2-diene-7-yne (139) and the other possibly octa-1,3-diene-7-yne (140). Both these compounds could have been formed from the mono-addition product with subsequent hydrolysis giving the allene and this isomerising to the diene. There was insufficient material to purify and characterise each one properly.

TABLE V

Isomerisation conditions and products of C_8H_{10} hydrocarbons and related species.

Starting Material	Reaction Conditions			Products (% composition)
	Reagent	Temp.	Time	
o-xylene	KO^{t}Bu/diglyme 2:1 ratio	160°	3-4 hrs.	100% starting material.
ethylbenzene	KO^{t}Bu/diglyme 2:1 ratio	160°	3-4 hrs.	100% starting material.
cycloocta-1,5-diene	KO^{t}Bu/diglyme 2:1 ratio	160°	3-4 hrs.	cycloocta-1,5-diene 38%; cycloocta-1,3-diene 60%; others 2%.
cycloocta-1,5-diene	KOH/diglyme	160°	3-4 hrs.	cycloocta-1,5-diene 60%; cycloocta-1,3-diene 38%; others 2%.
cycloocta-1,5-diene	KO^{t}Bu/^{t}BuOH	80°	3-4 hrs.	100% starting material.
cyclohepta-1,3,5-triene	KO^{t}Bu/diglyme 2:1 ratio	160°	3-4 hrs.	100% starting material.
methylcyclohepta-1,3,5-trienes	KO^{t}Bu/diglyme 2:1 ratio	160°	3-4 hrs.	Equilibrium mixture of each other. TABLE VI.
methylcyclohepta-1,3,5-trienes	none	160°	3-4 hrs.	Equilibrium mixture of each other. TABLE VII.
cycloocta-1,3,5-triene	KO^{t}Bu/diglyme 2:1 ratio	160°	3-4 hrs	cycloocta-1,3,5-triene 52%; ethylbenzene 10%; bicyclo[4:2:0]-octa-2,4-diene 28%; others 10%.
octa-1,2-diene-7-yne	KO^{t}Bu/diglyme 2:1 ratio	160°	8 hrs.	o-xylene 57%; m-xylene 9%; p-xylene 4%; ethylbenzene 30%; others 6%.
octa-1,2-diene-7-yne	none	160°	8 hrs.	o-xylene 7%; m-xylene 23%; p-xylene 9%; ethylbenzene 4%; starting products 51%; others 6%.
octa-1,7-diyne	none	160°	8 hrs.	100% starting material.

SECTION IV

Base Catalysed Isomerisation of C_8H_{10} Hydrocarbons and Related Species.

After these C_8H_{10} hydrocarbons had been prepared, they were subjected to the same reaction conditions as had been used for the isomerisation of octa-1,7-diyne. The results of the isomerisations on them and related compounds are summarised in Table V as well as Tables VI and VII (p.116). The products were examined by infrared in most cases and identified and estimated by g.l.c. The results may be summarised as follows:

(i) Neither m- nor p-xylene were produced by any of the following:- o-xylene; ethylbenzene, cycloocta-1,3,5-triene (101) or any of the isomeric methylcycloheptatrienes (120 - 123).

(ii) Cycloocta-1,5-diene (32) was readily converted to cycloocta-1,3-diene [(175) 80%] by the standard reagent; similar treatment of cycloocta-1,3,5-triene (101) yielded ethylbenzene (10%), bicyclo[4:2:0]octa-2,4-diene[(102) 28%] and starting material.

(iii) Neither cycloheptatriene nor the methylcycloheptatrienes (120 - 123) produced any aromatic compounds, either by treatment with base or by simply heating under reflux. With base, all the methylcycloheptatrienes formed one equilibrium mixture, irrespective of the starting compound (Table VI). Heating without base produced equilibrium mixtures, but these depended upon the starting isomer - probably because true equilibrium was not achieved as rapidly as with base (Table VII).

(iv) The crude allene-yne, octa-1,2-diene-7-yne (139), was isomerised completely. The products were o-xylene (51%), ethylbenzene (30%), m-xylene (9%), p-xylene (4%), and other minor products (6%).

(v) When octa-1,7-diyne was heated under reflux without base, no isomerisation occurred.

(vi) When octa-1,2-diene-7-yne (139) was likewise heated without base, the products contained not only the two components (139 and 140) from the starting material (38% and 13% respectively), but also o-xylene (7%), ethylbenzene (4%), m-xylene (23%) and p-xylene (9%), as well as minor products (6%). This result is in striking contrast to that produced by base isomerisations and to the thermal stability shown by octa-1,7-diyne.

These results (and their implications) described in this section, are discussed fully in the following section. The results are interpreted and included in the proposed mechanism for the overall reaction.

SECTION V

The Mechanism of Base Catalysed Isomerisation of the Diynes.

The migration of triple and double bonds has been known for a long time, for as long ago as 1888 Fovorskii[117] described the isomerisation of but-1-yne to but-2-yne with alcoholic potassium hydroxide, and showed that the allene buta-1,2-diene was an intermediate. More recently,[118] the analogous rearrangement of pentyne (141) (with the same reagent) was shown to exist as an equilibrium mixture of pent-1-yne (141), the allene (142), and pent-2-yne (143). The mechanism shown in Scheme XIII was proposed to explain this, but it also allowed for the formation of a conjugated diene (144). Jacobs, who proposed this, did not find any diene, but later work by many authors has shown that dienes can be formed, though only in certain favourable cases.[98,99.]

Much work has been done on the migration of triple bonds along alkyl chains, or their isomerisation to allenes, and only a few relevant examples will be quoted. In general, terminal acetylenes preferentially migrate into the chain (as in the pentyne example), and further rearrangement to an allene or diene only occurs in special cases where these are the preferred forms.[119] For instance, Normant and Mentione[120] prepared (146) from (145), and the researches of Moore[121,122] have shown that in the case of cyclic acetylenes, e.g. cyclonona-yne (147), base treatment produces the preferred cyclonona-1,2-diene (148). There is less strain with the latter compound (only three consecutive collinear groups as compared with four for the acetylene), and as a consequence an appreciable energy difference between the two. In larger rings this becomes less for then conditions are approximately as in n-alkynes. Hubert and Dale[99] have shown that treatment of macrocyclic alkadiynes (C_{12} - C_{20}) with base, even under mild conditions, causes extensive triple bond migration. With the exception of the smallest ring (C_{12}), the intermediate allenic compounds are only present in small amounts, and equilibrium is achieved between the various positional isomers (the distribution corresponding to that demanded by conformational requirements).

This situation is well illustrated by the formation of octa-2,6-diyne (124) from octa-1,7-diyne on treatment with potassium tert-butoxide in tert-butanol (as found in the course of this work). From the rapid - and presumably quantitative - rearrangement of the terminal diyne it is assumed that steric requirements are also important for linear molecules. Consideration of models of these diynes, (147) and (148), shows that for octa-1,7-diyne there are four methylene groups together in the centre of the molecule (with the CH_2 groups appropriately staggered as in any alkyl chain). In (148) there are only two adjacent methylenes, and it is obvious that for <u>any</u> chain length of alkadiyne, migration of each terminal triple bond inwards will decrease by one the number of interacting CH_2 groups with consequent decrease of Pitzer strain. By this simple argument, the other isomer, octa-3,5-diyne (149) should also try to achieve the most energetically favoured form, and in this case the triple bonds should migrate away from each other for the same reason. Furthermore, in the case of this conjugated diyne there are six consecutive methylene groups, and it appears that as few as possible are preferred for maximum stability in straight chain compounds.

The further rearrangement of triple bonds to dienes is also well known, though again there has to be an additional gain in stability for it to occur. Thus rearrangement and migration (or vice versa) may lead to a more stable conjugated system as in the formation[122] of (151) from (150). (In this case it is impossible for the second triple bond to rearrange). Similar migration, though of double bonds, has been achieved by Weedon et al., who in a series of communications[123,124,125] have shown that base catalysed migration of double bonds in unsaturated acids can be extensive (152 → 153) and cause molecular change.

The rearrangement of triple bonds exclusively to dienes has been used extensively by Sondheimer,[126] who used it to make cyclic polyene-ynes from the parent poly-ynes, [e.g. (49) to (154)]. From these studies it again became evident that rearrangement in these cyclic compounds had to conform to the permitted stereochemistry. When this reaction was attempted on unsuitable compounds, rearrangement (to aromatic systems) or decomposition resulted. Similar results were obtained by Hubert and Dale[127] who succeeded in following the migration of the double bonds spectroscopically. Again, they formed either an equilibrium mixture (with one preferred isomer) or, under more forcing conditions, they aromatised, [e.g. (155) to (156) to (157)].

A simple example,[128] but one which illustrates all the possible isomerisations of a triple bond, is the rearrangement of nona-2,7-diyne-1,9-dicarboxylic acid (158). Here, base isomerisation by one route causes the formation of homophthalic acid (159), while by the other route the base actually participates to form a derivative (160) of the starting compound. The full sequence of triple bond → allene → diene → further rearranged product is utilised in explaining the end products, (Scheme XIV). Hence in the present work, the formation of octa-1,2-diene-7-yne (139) and octa-1,3-diene-7-yne (140) from the same compound (albeit by a circuitous route) is quite logical. As there is no driving force for the formation of the diene, the allene-yne (139) should be the preponderant structure.

These reactions illustrate the ease and widespread occurrence of this isomerisation, both in acyclic and cyclic systems, with both liable to the same limitations. The experimental data would seem to support Willis' original hypothesis that in the long chain diacetylenes there is a migration of the triple bonds inwards prior to aromatisation. One of his other claims, however, does not appear to be correct (that polyenes cannot aromatise) for the triple bonds have to isomerise to allenes or dienes before aromatisation can take place - as illustrated in the examples already quoted. (The stereochemistry of the available double bond systems is, however, all-important).

In fact, there are many cyclisation reactions of polyenes known, though most occur at higher temperatures or upon irradiation. Of these, the Diels Alder type is perhaps best known, and is illustrated by the pyrolytic aromatisation of limonene (161) to m-xylene (162)[129] (Scheme XV, 161→162), and the cyclisation of elaeostearic acid derivatives[130] (163→164). (The simplest example of an internal Diels Alder reaction is described by Alder,[131] and is the isomerisation of cis-hexatriene (165) to cyclohexadiene (166) at 400°).

A similar reaction[132] exists in the conversion of (167) to (168), again by pyrolysis, though it cannot be formulated as a simple Diels Alder. It is a cyclisation reaction, similar to the cyclisation[133] of (169) to (170), though it is probable that the triple bond rearranges prior to cyclisation. A related reaction, much used in explaining the aromatisation of cyclic compounds, is the conversion of (171) to toluene (172), which occurs spontaneously at room temperature.[134].

Many reactions related to the Diels Alder, but initiated by irradiation and involving only two double bonds, are also known. Closest[135] to the previously discussed compounds is the equilibrium between (173) and (174), and the conversion of cycloocta-1,3-diene (175) to (176), its bicyclic valence bond isomer.[136] The term "valence bond isomerisation" as illustrated[88] by the reversible transformation of cycloocta-1,3,5-triene (101) into bicyclo[4:2:0]octa-2,4-diene (102), describes a rearrangement that proceeds without the migration of atoms or groups of atoms. The structural change consists solely of a "reorganisation" of the σ and π electrons within the framework of the molecule, accompanied by corresponding changes in atomic distances and bond angles. [This term was first introduced by Grob and Schiess,[137] to include all the "Cope rearrangement" isomerisations, and is excellently reviewed by Vogel[138] .]

Valence tautomerism is most frequently encountered as ring opening or closing, as these reactions can proceed in either direction. For instance,[104] (114) can be induced to form the polycyclic structure (115), but this in turn cleaves readily to two molecules of phenanthrene (177). In a similar fashion,[91,139,140] (80; X = Br) and (106) can ring open to their corresponding acyclic derivatives (178) and (107), (though the latter may be a mixture), while the octatetraene (103) has been very recently reported[89] as going in the opposite direction to (101).

A reaction which is mechanistically even more relevant to those in this thesis, is the base catalysed rearrangement[38] and subsequent dimerisation of <u>cis</u>-octa-4-ene-1,7-diyne (108) to the dimers (180) and (181), [probably via the intermediates (179) and (46)]. Similar intermediates may be postulated for the reactions of cyclic diynes, (in medium ring compounds formation of the allene would be facile), with subsequent transannular bond formation to give the precursors necessary for aromatisation. Several of these reactions have been already mentioned in the introduction (the section dealing with the aromatisation of macrocyclic polyynes) so these examples will not be further elaborated. One notable example not mentioned before is the formation[141] of biphenylene (183) in 25% yield from the highly strained cyclododeca-1,3,7,9-tetrayne (182).

One point common to all these examples, and investigated by Willis, is that none of the compounds which aromatise has less than seven carbon atoms. Willis tried various conditions in the hope of aromatising hexa-1,5-diyne (119; n = 2) but neither he nor Sondheimer[142] ever succeeded. This is a strong pointer to the mechanistic requirements for aromatisation, and with this in mind a scheme is prepased below for the formation of mono- and o-disubstituted aromatics.

No matter where the acetylene function is placed in a molecule, either linear or cyclic, its facile migration under base catalysis can be taken as proved by the examples already quoted. In a linear molecule, terminal acetylenes will migrate inwards, (via allene or diene formation), and in a conjugated diyne migration away from each other will be energetically favoured. In the latter system, reaction and aromatisation should be faster, for fewer migrations will be necessary before the correct sequence of unsaturated linkages is attained. In cyclic systems, ring size will dictate the preferred state, whether allenic, acetylenic or polyenic, and the ease with which aromatisation can occur.

A basic catalyst is necessary - unless the reaction is pyrolytic -

for this type of reaction. Thermal rearrangement of the acetylene to the allene or diene does not seem to occur, at least with octa-1,7-diyne. Hence, base catalysed isomerisation to the allene, followed by further migration until the reactive centres are within a seven or eight carbon chain must occur. Anything shorter, and it is impossible for them to react; anything longer, then reaction may not take place or will yield only macrocyclics. Thereafter, if the allene-diene, or any of its equivalents, is formed for any length of time, cyclisation can occur in the manner depicted in Scheme XVI. (* See p. 49).

By route A of the scheme, the allene-diene can be transformed into the mono-substituted aromatic by a Diels Alder reaction; by route B, the o-disubstituted aromatic should result. Obviously, the longer the chain length of the starting diyne, the more likely it is that the o-disubstituted isomer will result, for migration of both active centres would be expected, and a terminal allene or diene would not be expected to exist for a period sufficient for reaction. Also, the asymmetrically o-disubstituted isomer (where possible) should become predominant with increasing chain length, because, for statistical reasons, it is unlikely that both active centres will migrate at the same rate towards or away from each other. In shorter molecules, e.g. the octadiynes, there is insufficient scope for statistical discrimination, and the symmetrical isomer is predominant. However, in the products from both the decadiynes, the asymmetrical isomer is, as expected, predominant, with the monosubstituted isomer least of the three. [If only one group migrated, then in all cases the (o-methyl) disubstituted isomer, via route B, should result]. The final rearrangement of the cyclic triene (with one double bond exo to the six membered ring) can proceed either by a base catalysed allylic shift, or by a thermal rearrangement as in the conversion of (171) to toluene.

This mechanism is adequate for the formation of two isomers only, in a very dilute basic medium. This mechanism, however, cannot be invoked for the formation of the m- and p-xylenes nor the other cyclic unsaturated isomers. One theory held until negated by experimental trial, was that [in a manner similar to the known[143] methyl migration of other alkyl benzenes, where the alkyl residue is C_4 or higher] ethylbenzene or o-xylene could rearrange in strongly basic solution. This was not the case.

It was also possible that the unsaturated, non-aromatic components of the reaction mixture somehow contributed to the production of these other isomers. Initial experiments showed that the basic system normally used was the most efficient in causing conversion of the trial compound, cycloocta-1,5-diene (32) to cycloocta-1,3-diene (175). Other systems tried were inferior in causing double bond migrations. Although this basic system was used with the various methylcyclohepta-1,3,5-triene isomers (120 - 123), none of them could be aromatised to any of the aromatic products under these experimental conditions. Instead equilibrium mixtures were formed of all the possible forms, in proportion to the relative stability of each isomer. The formation of a mixture of the 1-, 2-, and 3-methyl isomers from the 7-methyl isomer (120) [which can be synthesised in two easy stages] constitutes the simplest synthesis yet of these isomers.

Cycloocta-1,3,5-triene was known[88] to form its valence isomer, bicyclo[4:2:0]octa-2,4-diene (102) readily on heating in the absence of base. Treatment of cycloocta-1,3,5-triene with base gave a product containing ethylbenzene in addition to the starting material and its valence isomer (102). This is not too difficult to explain, for the yield was low, and this means that the ethylbenzene was probably formed from the bicyclic form as shown in Scheme XVII. Again no other aromatic compounds could be detected.

In a likewise manner (as mentioned on p. 35), treatment of a crude mixture of octa-1,2-diene-7-yne (139) and octa-1,3-diene-7-yne (140) with base resulted in the usual products, with the m- and p-xylenes forming only 13% of the total product. Hence this also is not an intermediate for the formation of these structurally rearranged aromatics. A new mechanistic route for their formation had therefore to be proposed, one which must include the formation and rearrangement of intermediates containing cyclopropane rings.

Prototropic rearrangement of double bonds within cyclic and acyclic systems is well authenticated. Tracer studies have shown that the migration of atoms in the manner shown by two examples, cycloocta-1,3,5-triene (Scheme XVIII) and indene (Scheme XIX) are of widespread occurrence.[133] However, in the apparently similar C_9 series, the equilibrium between (184), (104), and (185) is well established, more akin to the related interconversion of (186) with (187), and (188) with (189).[133] In each case, a cyclopropane ring may be taken as equivalent to a double bond, and prototropic rearrangement causes interconversion of these species.

The most famous case, and one which is still causing controversy, is the cycloheptatriene - norcaradiene (190) equilibrium. The reactions of these compounds are such that either structure could be the participant in some cases, but recent work has shown that the cycloheptatriene seems to be predominant.[144] This does not clarify the issue, for structure (191), (obtained from cyclopentadiene) is converted only at high temperatures to (192) and not cycloheptadiene as would be expected by comparison of the products (194) and (196) from the analogous reactions of the cycloheptadiene and cyclooctadiene derivatives (193) and (195). Again, anomalous results are obtained from the thermal pyrolysis of the cyclohexadiene derivative[90] (197), acyclic products such as (198) being formed.

This situation is complicated even further, for work in the terpene field has provided practically identical, but conflicting pairs of reactions. Dehydrobromination of (6) and (8), (already quoted in the introduction[7, 8]), yields two completely different products, one a cycloheptadiene (4), the other the aromatic p-cymene (10) !! A similar pair of reactions exists in the preparation of oxepin (42), which is more stable as the seven membered ring[35] rather than the bicyclo (41), and the reaction of benzene with dicyanocarbene,[36] which produces the bicyclic compound (43), and is converted at 160° to the aromatic derivative (44)! Out of this melange of results, only one point emerges clearly - that there is a mechanistic carte blanche and each case must be treated on its own merits.

For a variety of reasons, embodied in the examples quoted, the formation of the aromatic and cyclic unsaturated compounds from octa-1,7-diyne is thought to be best represented by Schemes XX, XXI, and XXII.

Assuming formation of the allene-diene (199) by the route already discussed, followed by an internal Diels Alder reaction which simultaneously generates a cyclopropane ring, leads to the formation of (200). As there are various allylic protons which could be abstracted by a nucleophile for further rearrangement, each will be considered separately.

Further prototropic rearrangement by route C would produce o-xylene, and the fact that it could arise by two different mechanisms (Scheme XVI as well) may account for its being the major product. Route D would lead to the formation of the intermediate (201), which could either be converted to m-xylene as shown, or it could undergo further rearrangement, as illustrated fully in Scheme XXI (discussed below). Route E would be expected to produce 2-methylcycloheptatriene (122), but as base treatment of any methylcycloheptatriene isomer forms an equilibrium mixture, this will rearrange further and produce the other isomers. No further isomerisation of the methylcycloheptatrienes is expected.

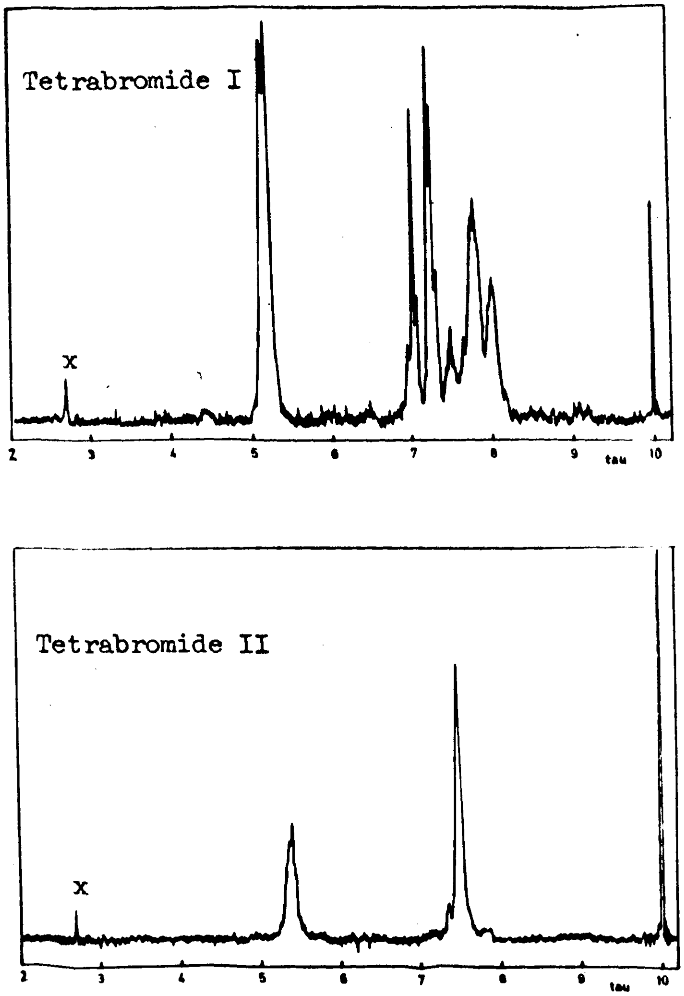
As mentioned, (201) can rearrange in two ways, the first yielding m-xylene, the second, [Scheme XXI, which has an analogy in the steroid field[145] (203) to (204)] would form (202), which could be converted in turn to p-xylene by route H, or regenerate compound (201) and produce more m-xylene as shown in route J. The fact that there is always an approximately 3:1 ratio of m-xylene to p-xylene would tend to support this mechanism. Compound (202) could also arise directly from (200) as shown by route G. This appears feasible from a consideration of molecular models, but no analogies have been found for it in the literature.

The last of the unsaturated compounds, cycloocta-1,3,5-triene, could be formed by either route K or L as shown in Scheme XXII. The former route involves an internal Diels Alder of compound (199), formation of the bicyclic valence isomers, and rearrangement of these to the triene. On the other hand, a very recent literature report[89] claims the formation of (101) directly from the tetraene (103a), and as this type of molecule had been detected spectroscopically in the course of these studies, it seems that it could rearrange directly to the cycloocta-1,3,5-triene, without the intermediacy of the bicyclic forms.

These mechanisms provide an explanation of the products formed by base catalysis of octa-1,7-diyne or octa-1,2-diene-7-yne. However, the latter, when heated without base, also aromatised to a considerable extent, but the m- and p-xylenes were the major aromatic products (octa-1,7-diyne could not be thermally isomerised). No reason can be found for this, except that obviously the mechanisms in Schemes XXI, XXII must be dominant, rather than that outlined in Schemo XVI.

* A recent communication[81] provides proof for the preferential formation of the cis-allylic anion form of an olefin during base catalysed isomerisation in a strongly basic solution. Variations in the rate of isomerisation are dependent on the base employed, particularly the cation. Similarly it is found that U-shaped pentadienyl anions are more stable than other planar forms, although the corresponding transoid dienes are more stable than the cisoid dienes.

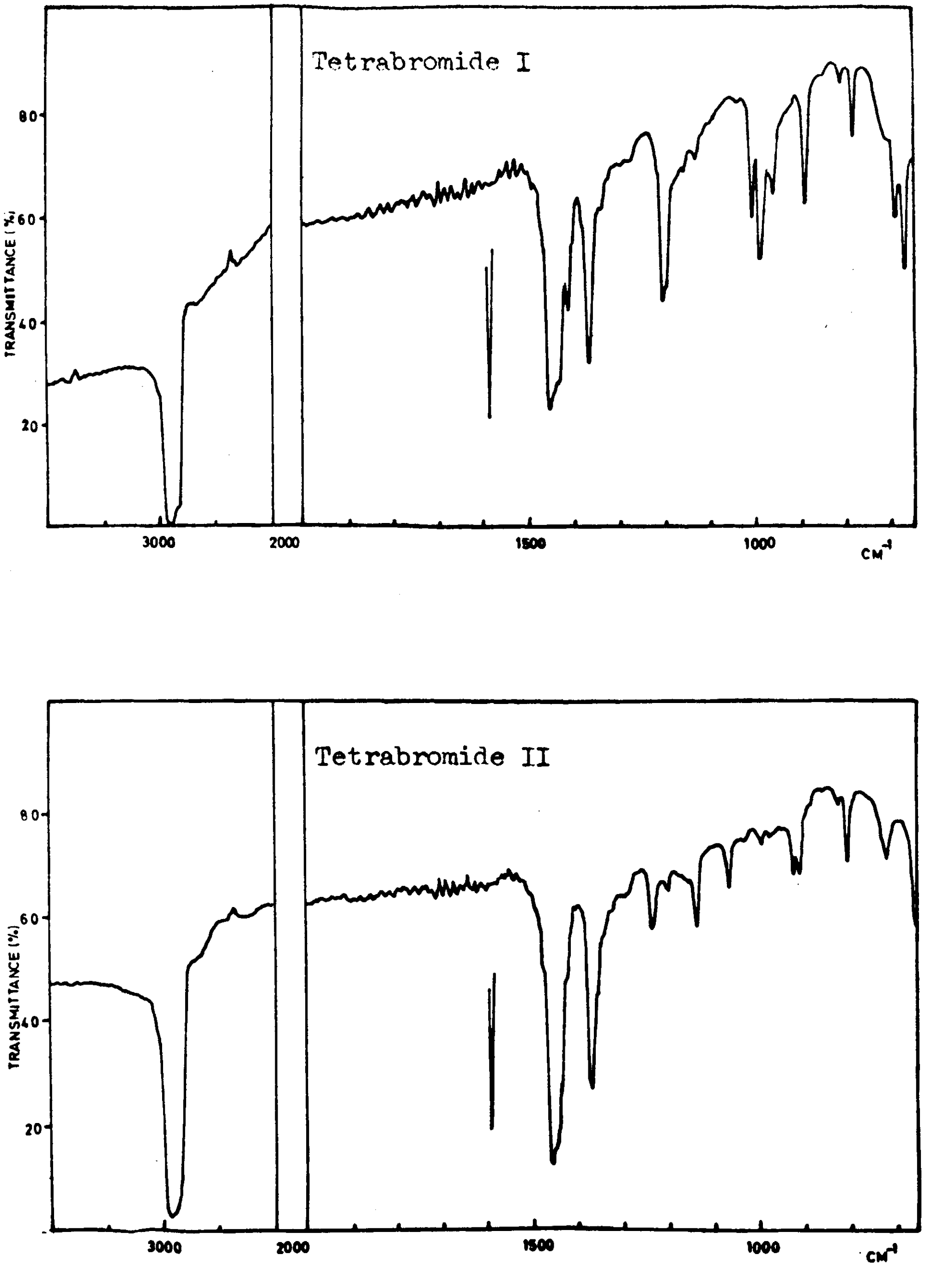
Hence this observation lends weight to the mechanism proposed in this thesis, insofar that an energetic preference has been shown to exist for the formation of cisoid ionic forms, and thus cyclisation will be so much more facile.



N.m.r. spectra (CDCl$_3$) of the isomeric 1,2,5,6-tetrabromocyclooctanes.

x = CHCl$_3$.

Figure 16.



Infrared spectra (nujol mulls) of the isomeric 1,2,5,6-tetrabromocyclooctanes.

Figure 17.

SECTION VI

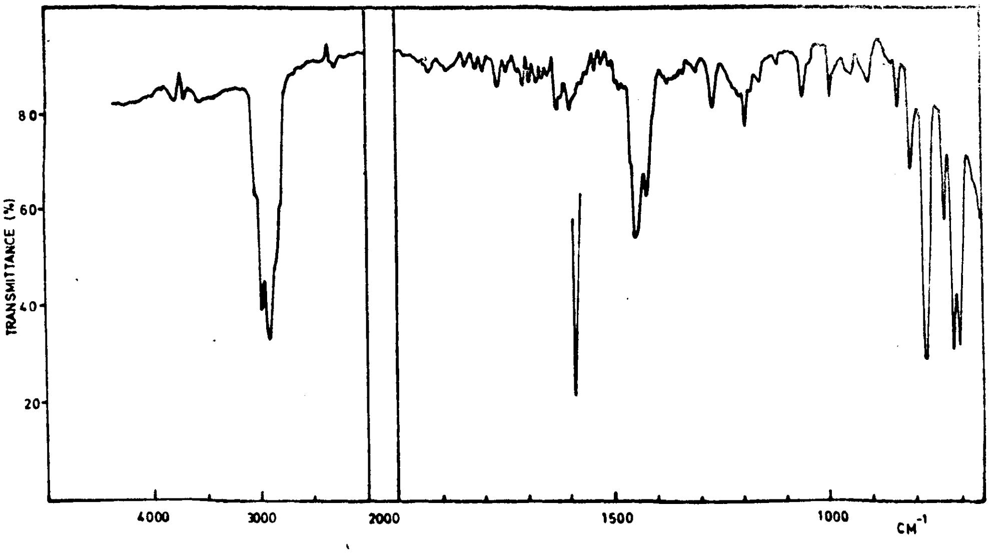
Preparation and Dehydrobromination of the Tetrabromocyclooctanes

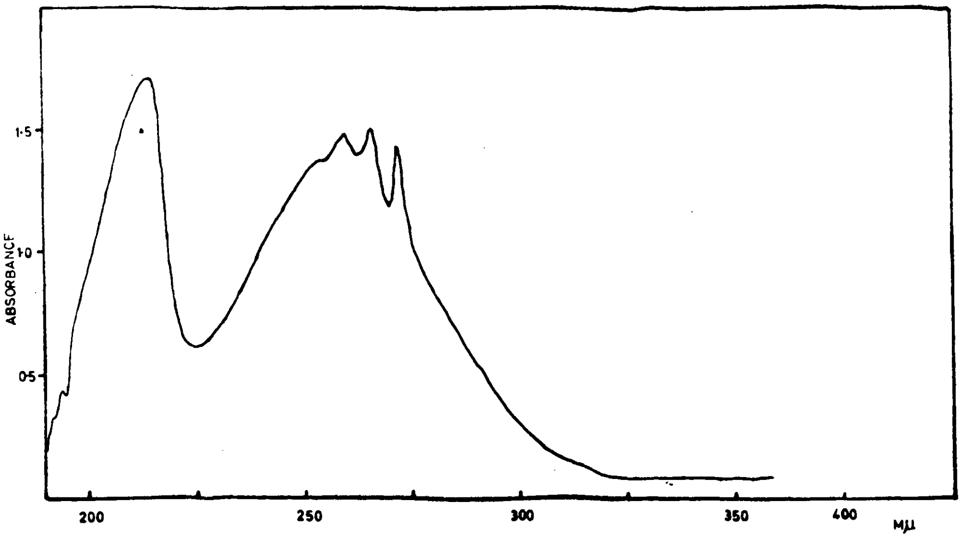
As was stated briefly in the introduction, Willis succeeded in preparing benzocyclobutene by dehydrobrominating tetrabromocyclooctane. Of the other compounds formed concurrently with benzocyclobutene, styrene and cyclooctatetraene were identified by Willis.[43] As other compounds were also known to be present, a repetition of this work was undertaken with the intention of identifying them, and in the process perhaps elucidating their mode of formation - as was done with the octa-1,7-diyne isomerisation.

Bromination of cycloocta-1,5-diene gave a much smaller yield of colourless crystals than reported by Willis. (Bromination with bromine/carbon tetrachloride gave a better yield). Moreover, published literature data[146] corroborated t.l.c. evidence that the product consisted of two isomers and not one as claimed by Willis. Indeed, comparison (t.l.c., i.r., n.m.r. and m.p.) of freshly prepared material with a sample of Willis' showed both to consist of the same two isomers. These isomers were separable on a silica column, and were obtained as colourless crystals of m.p. 135° and 138° respectively (a mixture of the isomers had m.p. 100 - 110°).

Furthermore, both the n.m.r. and infrared spectra were sufficiently different (Figs. 16, 17) for some deductions to be made about their probable structure. As both analysed for $C_8H_{12}Br_4$ and gave cycloocta-1,5-diene on debromination with zinc, it seems certain that they are both 1,2,5,6-tetrabromocyclooctanes. Assuming trans addition of bromine to the double bonds, and excluding any possible transannular mechanism, only two configurational isomers can exist. These are (205) and (206). The former has the pairs of bromine atoms anti to each other, while the latter has them syn. The anti isomer, (205), would have all its bromines pseudo-equatorial [as in the most likely conformation (207)], while the syn isomer (206) would have at best two axial and two equatorial [as in (208)].

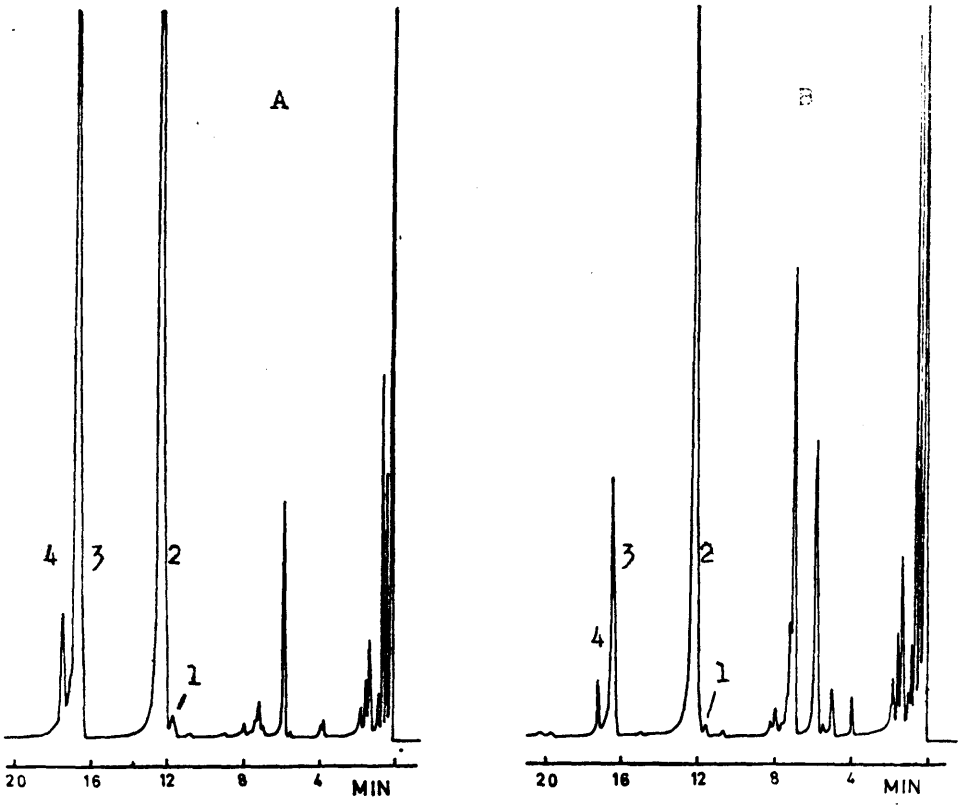
As stated before, the infrared spectra of these two isomers (Nujol mull; Fig. 17) display differences which persist in the solution spectra (CS_2). Studies are in progress to determine whether any significant correlations can be made from the absorption spectra of these isomers at temperatures other than ambient. Some useful deductions can, however, be made from the n.m.r. spectra run at ambient temperature (Fig. 16). The spectrum of Tetrabromide I consists of sharp peaks in three groups, while the spectrum of Tetrabromide II displays only two broad peaks (with only indications of further splitting). These types of spectra are characteristic of fixed and flexible conformations in each case. Hence at ambient, the first isomer is in a relatively rigid conformation (possibly all equatorial bromines), while the second probably consists of an equilibrium mixture of several conformers.





Infrared (liquid film) and ultraviolet (cyclohexane solution) spectra of the product from the dehydrobromination of the tetrabromocyclooctane isomers.

Figure 18.

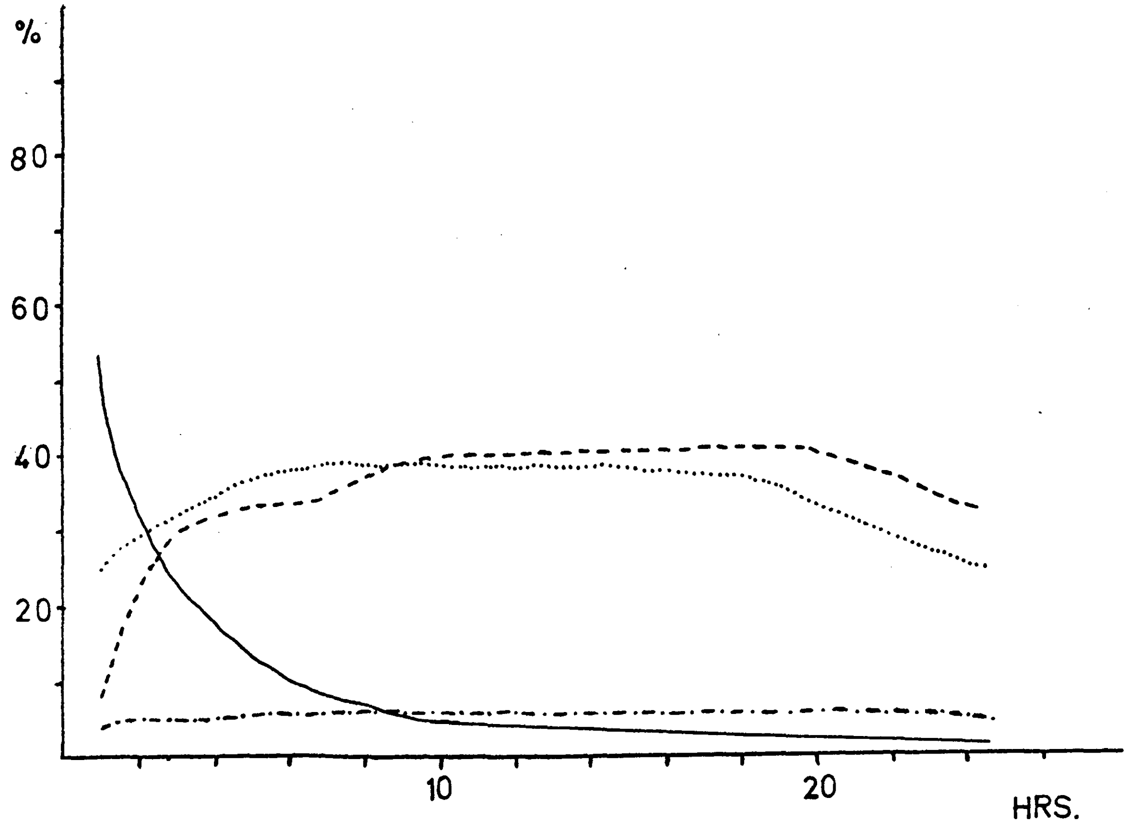


G.l.c. traces of the products from the dehydrobromination of the tetrabromocyclooctane isomers (A) and the isomerisation of cyclooctatetraene (B).

Conditions: 50 m. poly(ethyleneglycol) capillary, 50°, 20 p.s.i./6.3, total flow 70 ml./min.

1. cyclooctatetraene.
2. cycloocta-1,3,5-triene.
3. benzocyclobutene.
4. styrene.

Figure 19.



Dehydrobromination of the mixture of tetrabromocyclooctane isomers - variation in composition of the mixture of products.

———	cyclooctatetraene
·········	cycloocta-1,3,5-triene
- - - - - -	benzocyclobutene
–·–·–·	styrene

Figure 20.

Again, studies of the spectra of these isomers run at higher and lower temperatures, should show whether this is the correct interpretation of these features.

The identity of each Tetrabromide seemed so interesting that an X-ray investigation (by Dr. W. Oberhansli) has been made of Tetrabromide II, and preliminary results (R factor of 20%) have shown it to have one pair of bromine atoms equatorial, and the other pair axially orientated, as in (208), in the crystalline state. Hence, on the basis of the mechanism of addition of bromine atoms to double bonds, the other Tetrabromide (I), should possess the configuration illustrated by (207).

The next stage, Willis' dehydrobromination of the tetrabromocyclooctane, was attempted after the above physical and chemical data had shown that both isomers possessed eight membered rings and were not rearranged skeletally. This dehydrobromination was effected by heating a mixture of them (8 hrs.) with the usual agent (potassium tert-butoxide, 3 molar excess). The product had infrared and ultraviolet spectral properties (Fig. 18) identical to those reported by Willis for his product. Prominent peaks in the infrared could be associated with olefinic cis double bonds, (ν^{film} 1640, 1610, 710 cm.$^{-1}$), and with the o-disubstitution pattern of benzocyclobutene (ν^{film} 790, 725 cm.$^{-1}$). The ultraviolet spectrum had absorption at $\lambda_{\text{max}}^{\text{c.hexane}}$ 260, 266, 272 mμ. (indicative of benzocyclobutene), superimposed upon a broader absorption over this range (Fig. 18).

TABLE VIII

Base catalysed dehydrobromination of tetrabromo cyclooctanes and related species - Products and Conditions.

Starting material	Reaction Conditions			Products (% composition)				
	Reagent	Temp. °C	Time hrs.	benzocyclobutene	styrene	cyclooctatetraene	cycloocta-1,3,5-triene	others
Tetrabromocyclooctane (mixture)	KO^{t}Bu/diglyme 7:1 ratio	130	8	32%	7%	1%	42%	18%
Tetrabromocyclooctane I	KO^{t}Bu/diglyme 7:1 ratio	130	10	57%	17%	4%	19%	3%
Tetrabromocyclooctane II	KO^{t}Bu/diglyme 7:1 ratio	130	10	52%	12%	0%	31%	5%
Tetrabromocyclooctane (mixture)	KO^{t}Bu/DMSO 5:1 ratio	20-70	30	4%	26%	66%	0%	4%
Tetrabromocyclooctane (mixture)	KO^{t}Bu/DMSO 5:1 ratio	80-90	24	19%	6%	26%	0%	49%
Tetrabromocyclooctane (mixture)	KO^{t}Bu/diglyme filtered	160	8	37%	35%	0%	24%	4%
5,7-dibromocycloocta-1,3-diene	KO^{t}Bu/diglyme 8:1 ratio	160	10	44%	3%	9%	32%	12%

Analytical g.l.c. (Fig. 19a) of the product on a variety of columns confirmed the presence of benzocyclobutene (32%), and showed styrene (7%), cyclooctatetraene (1%) and a major unknown (42%) to be present also. As the total yield of products was 40%, the actual yield of benzocyclobutene was only 13%, in contrast to Willis' estimated yield of 23% and 20% by infrared spectroscopy and chemical degradation to phthalic anhydride.

A study of the variation in composition over 24hrs. during a reaction was made by withdrawing aliquots at regular intervals, examining their contents by analytical g.l.c., and plotting graphically the composition versus time (Fig. 20). From this it is obvious that reaction is very rapid, equilibrium is reached in 3 hrs. and little change occurs after 7 hrs. Initially, a high proportion of the reaction mixture consists of cyclooctatetraene; this means that dehydrobromination must be very rapid to build up such a high concentration. Thereafter the cyclooctatetraene concentration decreases steadily, while the other constituents (especially the other major one later identified as cycloocta-1,3,5-triene) increase at a similarly steady rate. The concentration of benzocyclobutene, once formed, stays at a constant level, whereas cycloocta-1,3,5-triene starts to decrease after ~17 hrs., probably due to decomposition. The styrene (as well as other minor products) is formed at the same rate, but again it decreases slowly during the course of reaction.

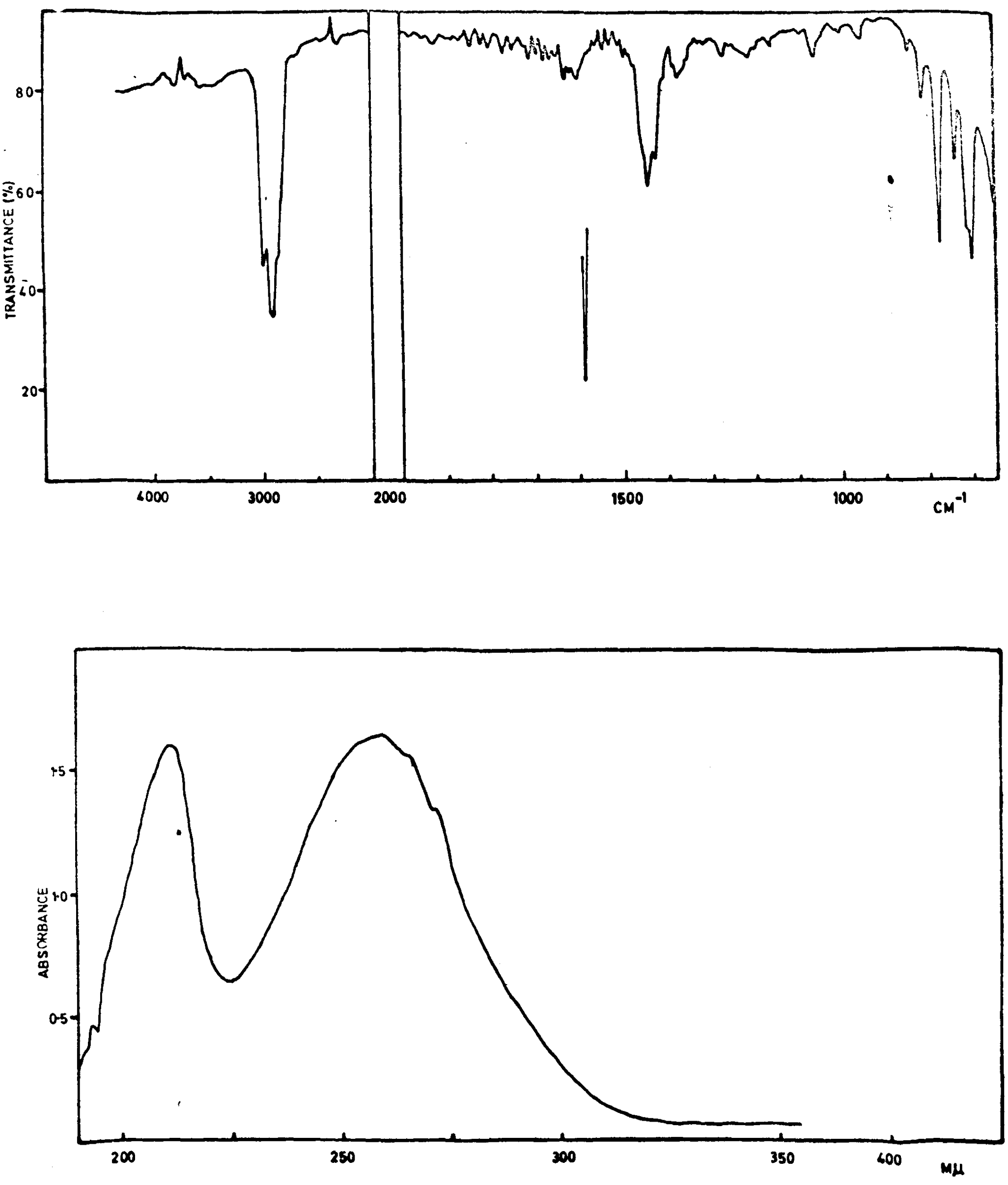
As both Tetrabromides I and II were available pure, it was of interest to see whether their structural differences bore any relation to product composition. Accordingly, dehydrobromination with the same agent (3 molar excess, 10 hrs. at 160°) yielded the following results - which are included in Table VIII. In both cases the quantity of benzocyclobutene and styrene is greater than obtained before from the mixture of I and II, (although the yields are 30% and 50% respectively as compared to 40% for the mixture). The simultaneous decrease of the major unknown compound (identified later as cycloocta-1,3,5-triene) could be due to the longer reaction time and its resultant removal through decomposition. (The lower yield from I, and the smaller quantity of cycloocta-1,3,5-triene in the product mixture, supports this hypothesis, though decomposition could also occur during the extraction process). Hence it must be concluded that there is no significant difference in composition between the end products derived from either tetrabromide. This and the fact that the same isomers are obtained from each tetrabromide, suggests that the intermediates in each case are similar or interconvertible, or that the conformation of each tetrabromide prior to dehydrobromination is the same.

As a filtered solution of the base had been employed successfully to produce only o-xylene and ethylbenzene from octa-1,7-diyne, a similar simplification of product was hoped for with the tetrabromides. Accordingly a solution of the base in diglyme was filtered through sintered glass under nitrogen, titrated to estimate the amount of base in solution, and an aliquot of this (sufficient to provide a 6:1 molar ratio of base to tetrabromide) was employed for the dehydrobromination. However, though the quantity of cycloocta-1,3,5-triene was diminished (Table VIII; 24%) it was not eliminated, though benzocyclobutene (37%) and styrene (35%) between them accounted for all the rest.

Another interesting result was obtained when 5,7-dibromocycloocta-1,3-diene (133b) was heated under reflux with the base (1:8 molar ratio) to produce benzocyclobutene (44%), styrene (3%), cyclooctatetraene (9%) and cycloocta-1,3,5-triene (32%) - comparable with the yields from the tetrabromides. Though this is not direct evidence for the participation of this partly dehydrobrominated tetrabromocyclooctane in the dehydrobromination reaction, it does permit this structural type to be postulated as an intermediate. This point - and a discussion of the relative stabilities of dibromocyclooctadienes - is presented more fully in the section on the mechanism of dehydrobromination and isomerisation.

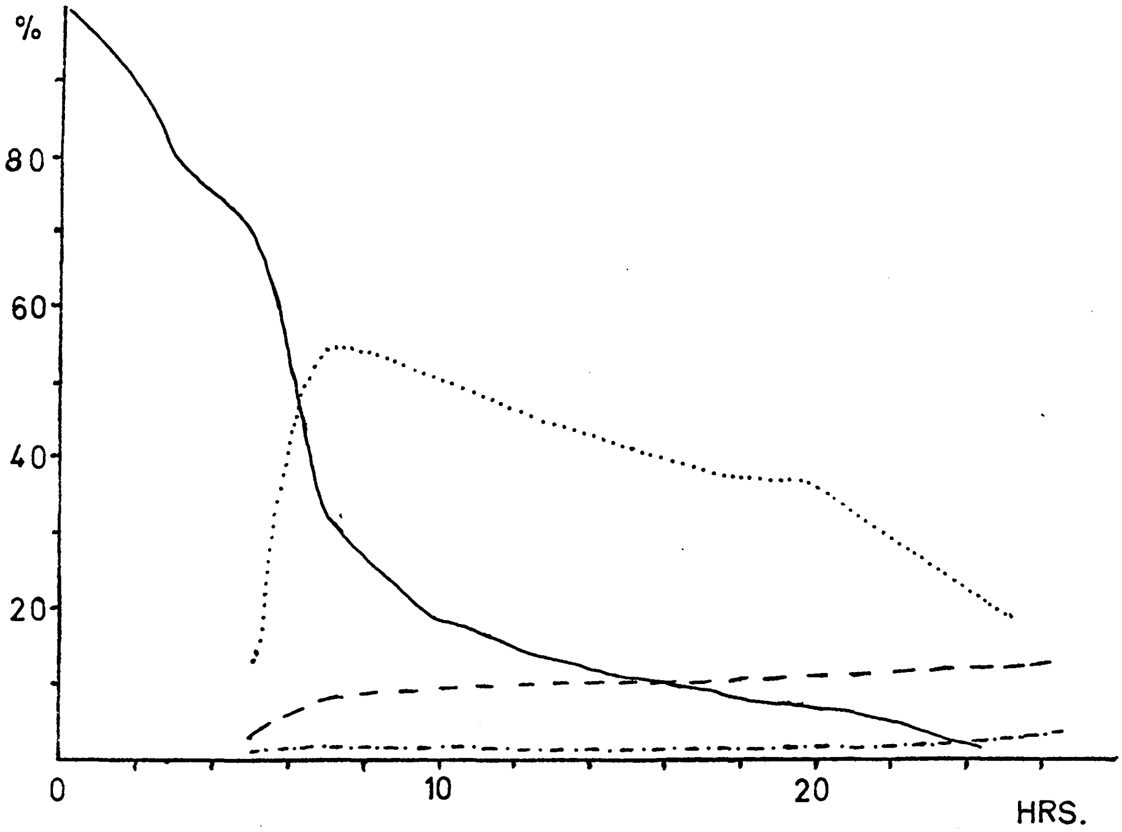
A very recent report[66] described the dehydrobromination of the tetrabromocyclooctanes with potassium tert-butoxide in dimethylsulphoxide (DMSO) to produce only styrene (22%) and cyclooctatetraene (78%). This work has been repeated in the present study, using similar conditions (the authors do not provide full details). Heating of the tetrabromides in DMSO with potassium tert-butoxide (1:5 molar ratio) at

20° for 24 hrs. and at 70° for a further 6 hrs. yielded a bromine free product, composed of cyclooctatetraene (66%), styrene (26%), and benzocyclobutene (4%), but no cycloocta-1,3,5-triene. Repetition of this reaction, but heating at 80-90° for 24 hrs., yielded a product containing cyclooctatetraene (26%), styrene (6%), benzocyclobutene (19%) and a host of other products (all with shorter R_T on g.l.c.). Hence, benzocyclobutene *is* produced, though the amount is dependent upon reaction temperature. It is not likely that dehydrobromination should be *slower* at higher temperatures, so the lower yield of cyclooctatetraene and styrene may again be due to either further reduction, or decomposition, rather than a fundamental difference in the mechanism.



Infrared (liquid film) and ultraviolet (cyclohexane solution) spectra of the product from the isomerisation of cyclooctatetraene.

Figure 21.



Isomerisation of cyclooctatetraene - variation in composition of the mixture of products.

——— cyclooctatetraene
·········· cycloocta-1,3,5-triene
- - - - benzocyclobutene
–·–·–· styrene

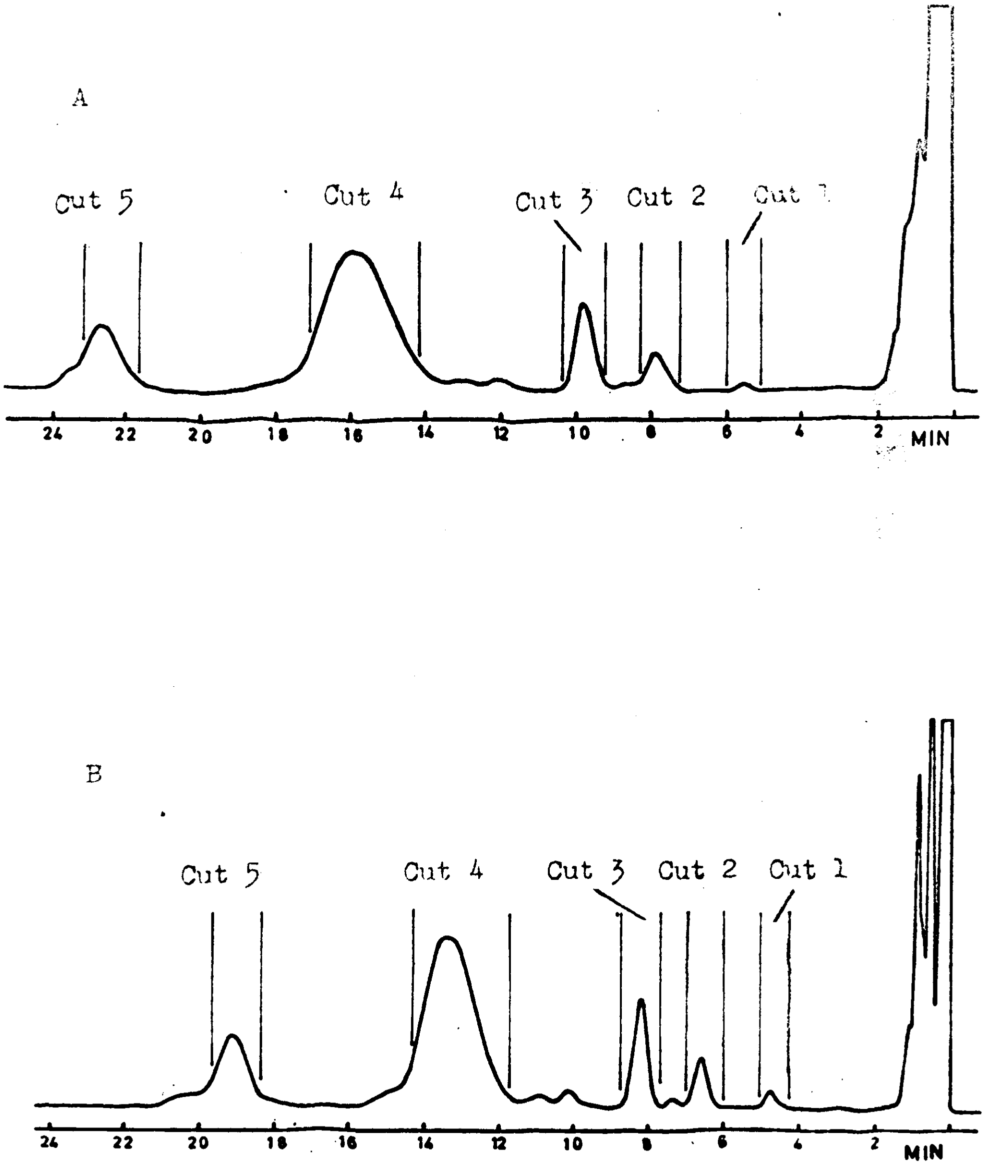
Figure 22.

SECTION VII

Isomerisation of Cycloocta-1,3,5,7-tetraene.

Previous work by Willis had shown that cyclooctatetraene (a probable intermediate in the dehydrobromination of the Tetrabromocyclooctanes) could be induced to rearrange by base treatment to an identical series of products (under conditions similar to those in the dehydrobromination). As in the dehydrobromination, the reaction mixture was complex, and Willis was able to identify only two of the products (benzocyclobutene and styrene). He reported that the products from both reactions were the same, though the components were present in different proportions (g.l.c.). Accordingly, further studies were conducted to identify their products and observe the effects of different reaction conditions.

Cyclooctatetraene, when heated under reflux (8 hrs at 130°) with a 1:4 molar ratio of potassium tert-butoxide in diglyme gave an oil in about 40% yield. This had the same spectral characteristics as did the product from the dehydrobromination of tetrabromocyclooctane: (ν_{max}^{film} 790, 750, 725, 710 $cm.^{-1}$; $\lambda_{max}^{c.hexane}$ 259, 266, 272 mμ; Fig. 21, cf. Fig. 18) . As before, analytical g.l.c. (Fig. 19b) confirmed the presence of benzocyclobutene (9%), styrene (2%), cyclooctatetraene (1%) and the major unknown (37%; cycloocta-1,3,5-triene). The remainder of the mixture consisted of materials with shorter retention times, presumed



Preparative g.l.c. separation of the products from the isomerisation of cyclooctatetraene, after 8 hrs. (A), and 24 hrs. (B) respectively.

<u>Conditions:</u> 25% 'Cyano 'P', 15' x $\frac{3}{8}$" o.d.

A. 115°, 150 ml./min.

B. 120°, 160 ml./min.

Figure 23.

to be reduced products.

A time study (Fig. 22) of the reaction over a period of 24 hrs. was effected in the same way as before, (i.e. withdrawal of aliquots and examination by g.l.c.). Trends similar to those observed in the dehydrobromination study were noted. Thus the quantity of cyclooctatetraene decreased steadily throughout the reaction, while the other constituents increased in proportion. A steady state was established fairly rapidly, and as before, all the unstable constituents started to decrease after about 8 hrs., again probably through decomposition. The quantity of benzocyclobutene, once formed, stayed constant. The "time lag" before cycloocta-1,3,5-triene appears is probably due to an initially lower reaction temperature as compared to the dehydrobromination reaction temperature (due to difficulties in reproducing identical reaction temperatures).

Analytical g.l.c. confirmed that the products from both the dehydrobromination and direct isomerisation of cyclooctatetraene were very similar (Figs. 19a, 19b), though the latter contained more secondary products. For this reason, these were the products that were subjected to preparative g.l.c. in an attempt to identify the secondary constituents. Preparative g.l.c. of a reaction product obtained in the usual manner (8 hrs. reflux at 130°) yielded five cuts (Fig. 23a), each of which was rechromatographed, to check for purity. Cuts 5 and 3 contained one component each; Cut 1 was in insufficient amount to be detected; Cut 2 was a mixture of at least two compounds, while Cut 4 showed a new peak, with shorter retention time, as well as the main compound. This second component could not have been present originally in that cut; the explanation must be that it is formed by thermal isomerisation of the main component on rechromatography. This explanation seemed quite satisfactory once the identity of Cut 4 had been established.

When collecting the cuts, no attempt was made to collect the peaks due to cyclooctatetraene or styrene, as they were small and tended to decompose extensively prior to collection. Benzocyclobutene (as expected) constituted Cut 5 and its identity was confirmed by spectroscopic comparison (i.r., u.v., n.m.r.) with an authentic sample. Cut 4 was also collected in sufficient amount to enable determination of its infrared, ultraviolet and n.m.r. spectra. From these, it was unhesitatingly identified as cycloocta-1,3,5-triene. (The appearance of a peak with shorter R_T on rechromatography can be ascribed to the generation of bicyclo[4:2:0]octa-2,4-diene, (102), its valence isomer). Comparison of g.l.c. characteristics and spectral data left by Willis, confirmed the fact that this was his major unknown, for which he suggested a bicyclic[4:2:0] structure.

None of the other three cuts were identified. Cut 1 was insufficient for any spectral measurements; Cut 2, a mixture of at least two compounds had λ_{max} 218, 248 mμ in the ultraviolet. Cut 3 had spectral characteristics (i.r., u.v., n.m.r.), which <u>resembled</u> those of 2-methylcycloheptatriene (122), but could not be assigned to any known compound.

This isomerisation reaction was repeated to obtain more material; this time heating was continued for 24 hrs., after which the products were subjected to preparative g.l.c. (which again gave five cuts: Fig. 23b). Analytical g.l.c. of Cuts 1-3 showed that Cut 1 contained three compounds; Cut 2 only one, while Cut 3 either decomposed or isomerised, for two peaks appeared with shorter R_T than the original cut had.

Cut 5 was, as before, shown (i.r.) to be benzocyclobutene. The identity of Cut 4 was not checked, but Cut 3 had an infrared spectrum identical with that of ethylbenzene, and no ultraviolet absorption could be detected at the concentration used. This assignment could not be substantiated through lack of an n.m.r. spectrum, and as the g.l.c. of this sample was anomalous, its identity cannot be taken as proved.

The infrared and ultraviolet spectra of Cut 2 were identical to those of Cut 3 in the previous separation, though slight differences were apparent in their n.m.r. spectra. The mass spectrum of this component also showed a parent ion at $^m/e$ 108, corresponding to C_8H_{12} - equivalent to a doubly reduced cyclooctatetraene. This compound could not be identified further.

Cut 1, though a mixture of three components, had an ultraviolet spectrum similar to Cut 2 of the previous separation, but although its infrared and n.m.r. spectra were obtained, the structures could not be

TABLE IX

Isomerisation conditions and products of cycloocta-1,3,5,7-tetraene and related compounds.

Starting Material	Reagent	Reaction conditions Temp. (°C)	Time (hrs.)	Products (% composition) benzocyclobutene	styrene	cyclooctatetraene	cycloocta-1,3,5-triene	others
cyclooctatetraene	KO^{t}Bu/diglyme 4:1 ratio	150	8	9%	2%	1%	37%	51%
cyclooctatetraene	1:1 ratio	160	10	13%	2%	0%	39%	46%
cyclooctatetraene	KOH/diglyme 4:5 ratio	160	8	13%	1%	53%	28%	5%
cyclooctatetraene	4:5 ratio	160	24	20%	7%	13%	49%	9%
cyclooctatetraene	KO^{t}Bu/diglyme filtered 1:1	160	2	11%	1%	61%	23%	4%
cyclooctatetraene	filtered 2:1	160	8	25%	3%	13%	48%	11%
cyclooctatetraene	KO^{t}Bu/diglyme radical inhibitor	160	8	11%	3%	29%	7%	50%
cyclooctatetraene	solid KO^{t}Bu	100	4	o-xylene 10%; m-xylene 7%; p-xylene 5%; ethylbenzene 50%; others [illegible]%.				
cyclooctatetraene	KO^{t}Bu/DMSO	75	24	No products or starting material isolated.				
cyclooctatetraene	none	160	8	100% starting material.				
benzocyclobutene	KO^{t}Bu/diglyme or heat alone		8	100% starting material				
styrene	KO^{t}Bu/diglyme or heat alone		8	100% starting material.				

identified.

These 'out of sequence' cuts during preparative g.l.c. can be explained by the rationale outlined on p.128 , i.e. Cuts 4 and 5 correspond, but in each case these are preceded in actual fact by four compounds, of which only three could be collected (this was confirmed by analytical g.l.c.). This confirms Willis' observation that the reaction period does affect the nature and properties of the end products, especially as these seem to be either reduced derivatives of cyclooctatetraene or isomers thereof.

Simultaneously with the work on the characterisation of the products from the isomerisation of cyclooctatetraene, a series of experiments was carried out with a variety of reagents and reaction conditions. These are described in the following passages, and the results are summarised in Table IX.

(i) When cyclooctatetraene was heated under reflux (with various proportions of potassium tert-butoxide in diglyme for 10 hrs.) isomerisation to the usual products occurred each time. However, when phenothiazine (a free radical scavenger) was added, the quantity of cycloocta-1,3,5-triene formed was much reduced. (This result is discussed further in the mechanistic section).

(ii) When a weaker base was employed (potassium hydroxide in diglyme) the extent of conversion to the usual products depended very much upon reaction time, longer periods of reflux causing more extensive conversion.

(iii) A filtered solution of potassium tert-butoxide in diglyme, to which was added cyclooctatetraene (molar ratio 1:1 or 2:1), was also effective but conversion was much less rapid.

(iv) No isomerisation occurred when either potassium tert-butoxide in butanol, or potassium hydroxide on alumina, or solid potassium hydroxide were used as catalysts.

(v) Cyclooctatetraene, when heated in contact with solid potassium tert-butoxide (about 150°) was completely isomerised to a mixture of the isomeric xylenes (22% total), and ethylbenzene (50%) as determined by g.l.c. and infrared spectroscopy. A series of peaks with shorter R_T values was also seen in the g.l.c. trace. These were presumed to be further reduction products of cyclooctatetraene. The isolation of material tentatively identified as ethylbenzene from the isomerisation of cyclooctatetraene with a suspension of potassium tert-butoxide in diglyme now becomes more credible. (p. 60).

(vi) Cyclooctatetraene, benzocyclobutene, or styrene failed to react on heating (8 hrs. at 160°) without base in diglyme. Benzocyclobutene or styrene similarly heated alone under reflux for the same time, also failed to react.

Since benzocyclobutene had been prepared from tetrabromocyclooctane by heating with potassium tert-butoxide in DMSO (p. 56), it was hoped to prepare it in a similar manner from cyclooctatetraene. Cyclooctatetraene in a solution of DMSO containing potassium tert-butoxide (1:2 molar ratio) was heated at ~ 75° for 24 hrs. Extraction of the reaction mixture in the usual manner yielded no isomerisation products, nor even any starting material. Although the reaction was repeated, and the extraction technique modified, no starting material or product could be detected. The reason for this is unknown - combination of the cyclooctatetraene with the DMSO or complete decomposition may be the answer.

SECTION VIII

The Mechanism of Base Catalysed Dehydrobromination and Isomerisation of the C_8 cyclics.

The X-ray structural analysis had shown that the Tetrabromocyclooctane II has structure (206), best represented by (208), in which two bromines are axial, and two are equatorial. Assuming similar trans addition of bromine to cycloocta-1,5-diene, then Tetrabromide I must be (205), represented by (207), with all four bromines equatorial. The n.m.r. spectra showed that even at ambient temperature, structure (207) was relatively rigid, and structure (208) flexible. At higher temperatures it is to be expected that both structures would become more flexible, and this has some significance when considering the mechanism of their dehydrobromination.

Willis has already considered the conditions for bimolecular 1,2-elimination, where, as in all cases, the participating species have to be trans-anti-trans. In the cyclooctane molecule, as in others, trans addition of bromine to the cis cycloalkane leads to a situation where the α hydrogen and β bromine will be mutually cis, and cannot attain the necessary trans diaxial conformation. Because of this, β,γ, elimination will be compulsory, and it would be expected that the rate of dehydrobromination would be dependent upon the ease with which this elimination could occur.

As the C_8 ring is comparatively flexible, there should be no difficulty in each bromine, regardless of its configuration, attaining the required conformation for β, γ elimination. This appears to be confirmed by a study of the molecular models of each isomer. Hence, postulating a four stage dehydrobromination as in Scheme XXIII, (209) would be the first intermediate formed. Thereafter, if the second molecule of hydrogen bromide eliminated involved the loss of the other bromine of that pair, (133) would result. From a study of its molecular model, it appears to be rather strained, and as a result further elimination should be rapid to give (210). At this stage, further dehydrobromination could give cyclooctatetraene, or by analogy with cycloocta-1,3,5-triene, other products could be obtained by the formation of the bicyclic structures (211a) and (211b).

If (211a) is formed, then dehydrobromination can only occur to give (109), as no other hydrogen is <u>trans</u> to the bromine. If (211b) results, then either (109) or (212) can be formed, because either hydrogen could be eliminated with the bromine. Further rearrangement of intermediates (109) and (212) would yield styrene and benzocyclobutene. There may be two reasons for the greater yield of the latter. Stabilisation on achieving an aromatic system will be considerable, but as the formation of benzocyclobutene does not involve carbon-carbon bond cleavage, this particular conversion will be energetically favoured. The other reason is that (211b) may be formed in preponderant amount, and hence formation of (212) would be more likely than (109).

One point that requires to be dwelt upon further is the probable formation of structures (133a, c, d, or b). The formation of structure (133) has already been commented upon, but neither (133a) nor (133c) seems likely from work done in the course of this thesis (Appendix), or from the literature,[147] where all attempts to prepare (133c) by allylic bromination of cycloocta-1,3-diene have been unsuccessful. Neither of these dibromides is thermally stable, let alone resistant to base, and they would be expected to form (210) spontaneously, or by further rearrangement to form (133d), then (133b). The latter could happen by an initial allylic rearrangement of one of the bromine atoms (133a ⟶ 133d), followed by migration of the double bond into conjugation with the other, to give (133b). That this sort of rearrangement does take place, even thermally, is borne out by the marked lack of success in obtaining one product from the allylic bromination of cycloocta-1,5-diene (p. 107), and the isolation from the reaction mixture of a compound with a structure corresponding to (133b). The other interesting point is that the dehydrobromination of (133b) yielded a mixture of hydrocarbons very similar in composition to that obtained from the dehydrobromination of the tetrabromide. Hence the dibromide (133b) is a possible intermediate in the dehydrobromination of the tetrabromide.

The reason that cyclooctatetraene is not suggested as the sole intermediate in Scheme XXIII for the formation of benzocyclobutene and styrene, is that these compounds are not the major products from the base catalysed isomerisation of cyclooctatetraene. Hence in the dehydrobromination reaction there must be an alternative route for their formation, probably via (211) as shown. (The formation of a large amount of cycloocta-1,3,5-triene instead of cyclooctatetraene will be discussed at a later stage).

It is difficult to rationalise the higher yield (35% of product) of styrene formed when a filtered solution of base is used. It may be due partly to the higher reaction temperature, or the fact that a smaller quantity of base was present, thereby forming less cycloocta-1,3,5-triene.

Yet another different result is obtained when a solution of potassium tert-butoxide in dimethylsulphoxide (DMSO) is used. A recent literature report[66] stated that the sole products were cyclooctatetraene and styrene. When this reaction was repeated in these laboratories, benzocyclobutene was also found, in an amount dependent upon the reaction temperature. It is logical to suppose that the main reaction is straightforward dehydrobromination at lower temperatures, and that rearrangement to benzocyclobutene only occurs at higher temperatures. What is inexplicable, is the complete lack of cycloocta-1,3,5-triene, which is formed under every other reaction condition. The nature of the nucleophilic species must be such that it is either too weak to form the octatetraenyl dianion (213), which may be a necessary precursor for formation of the triene, or that the presence of the sulphur compound acts as an inhibitor to its formation. The formation of styrene rather than benzocyclobutene is in accord with related reactions in the literature,[113,64] where halogenated cyclopolyenes have been converted to β-halostyrene rather than the corresponding benzocyclobutene derivative (p. 11). This must be due to an energetic preference, for with the exception of Willis' results and its preparation from tetrabromocyclooctane,[66] benzocyclobutene has never been synthesised directly from cyclooctatetraene or any halogenated precursor with an eight membered ring.

The occurrence of cyclooctatetraene in the reaction mixture from the dehydrobromination of tetrabromocyclooctane suggested that it could be an intermediate in the formation of styrene and benzocyclobutene, though possibly not the main one in the dehydrobromination. A study of the vast amount of research carried out on cyclooctatetraene in recent years provides a ready explanation for the formation of styrene, benzocyclobutene and cycloocta-1,3,5-triene.

The preferred conformation of cyclooctatetraene is now fully established as a 'tub' (79a), and the generally accepted mode of base catalysed prototropic rearrangement cannot apply in such a rigid non-planar system. It must be converted into a more or less planar structure which will permit unhindered movement of electrons. As the energy to do this would be appreciable, some compensating factor, such as the production of a highly resonance stabilised aromatic system must be involved. The addition of two electrons to cyclooctatetraene would give it ten π electrons, and allow it to comply with Huckel's (4n + 2) π electrons rule for pseudo-aromaticity, so the formation of the cyclooctatetraenyl dianion (213) should be facile under the appropriate conditions. This species has been proposed by Katz et al., and its spectral characteristics, as well as its quantum mechanical assessment, are in accord with theory.[148,149,150,151,152,153] Furthermore, it has been shown that in the presence of alkali metals,(in tetrahydrofuran), an equilibrium between the structures (79a), (213) and (214) (a radical anion) is set up, with the equilibrium as shown. Further work has also shown that there is a difference of 2.4 Kcal. in free energy between cyclooctatetraene and the dianion, with the former being favoured.[154]

This dianion formation with alkali metals has been utilised to prepare cyclooctatriene derivatives, such as the diacid (215), by addition of carbon dioxide to the dianion[155] (213). Experiments using tracer techniques[156] have shown that both (216) and (217) are formed from the dianion on addition of deuterium oxide, so that initially an equilibrium must exist between these forms, before (217) is converted to the conjugated isomer (216).

A related mechanism can be postulated for the formation of cycloocta-1,3,5-triene from cyclooctatetraene with base. Reaction of cyclooctatetraene with potassium tert-butoxide could yield the dipotassium salt of the dianion, and generate two tert-butoxide radicals, which could either react in some further way, or become inactivated and take no further part in the reaction (Scheme XXIV). An attempt was made to detect these tert-butyloxy radicals by electron spin resonance spectroscopy, but this was unsuccessful. Though so far no direct analogies have been found in the literature for this, under comparable reaction conditions, these factors should not be held to invalidate this argument without further experimental trial.

The dipotassium salt of the dianion is thought to remain as such for the duration of the reaction, and will form either of the cyclooctatrienes on addition of water to the reaction mixture during the extraction process [though the 1,3,6 isomer (101a) will be converted by aqueous base to the conjugated 1,3,5 isomer (101)]. This same mechanism will account for the formation of cycloocta-1,3,5-triene, again via cyclooctatetraene, during the dehydrobromination of the Tetrabromocyclooctanes. [A related reaction has been observed with the cyclononatetraenyl ion (218), which gave cyclononatetraene (219), indene (221), and the dihydroindene (220)].

Some sort of related mechanism must also be postulated for the formation of further reduction products. These may arise by free radical reduction of any free cyclooctatetraene in the reaction mixture, in a manner analogous to the reduction by hydrazine hydrate and oxygen of cyclododeca-1,5,9-trienes to dienes, olefins, or even cyclododecane.[158] Another possible mechanism, related to the reduction of conjugated polyenes with sodamide in liquid ammonia, is also feasible. In this case, the potassium tert-butoxide would need to produce electrons which could become solvated in the diglyme (which has a high dielectric constant) or alternatively the electrons associated with the cyclooctatetraenyl dianion may be the reactive species. If either type was formed, then subsequent reduction of cyclooctatetraene would be quite likely.

The results of many investigations have helped to clarify the reactions of cyclooctatetraene, in particular the fact that it appeared to react via the isomer (109) in some cases, in a fashion similar to the valence tautomerism of cycloocta-1,3,5-triene. (Its other isomer (46) has also been proved as a participant in several reactions, examples of which are quoted in the Introduction, p.13). With the actual preparation of this compound,[97] which has a half life of 14 mins. at 0°, it may be said with certainty that (109) can exist in equilibrium with cyclooctatetraene. Hence, cyclooctatetraene can form either (212) or (109), which in turn can form benzocyclobutene or styrene (Scheme XXIII). The simple applicability of this mechanism to both the dehydrobromination of tetrabromocyclooctane and the direct isomerisation of cyclooctatetraene, is immediately obvious.

Various other reaction conditions and compounds were tried with a view to proving this mechanism. As expected, neither benzocyclobutene nor styrene could be isomerised to anything else. Cyclooctatetraene under most reaction conditions produced the same relative proportions of products (Table XI); the best yields of benzocyclobutene and styrene were obtained with a weaker base (potassium hydroxide) or a filtered solution of potassium tert-butoxide in diglyme - in a 2:1 ratio (much less than usual). Hence excess base does seem to create a greater number of side products, and more cycloocta-1,3,5-triene. The proportion of side products, thought to be mostly further reduction products (some proof was obtained for this), was as high as 50% of the total at times, so that much further work needs to be done before this becomes a practical synthesis of benzocyclobutene.

Puzzling results remain as before. Addition of cyclooctatetraene to hot solid potassium tert-butoxide resulted in isomerisation, 72% of the products consisting of C_8H_{10} aromatic compounds, mainly ethylbenzene (50%) and the isomeric xylenes! The remainder consisted of further reduction compounds, without any benzocyclobutene or styrene. As cyclo-octa-1,3,5-triene has been converted in small yield to ethylbenzene, it must be assumed that the tetraene gives cycloocta-1,3,5-triene, which is in turn rearranged to the aromatics or reduced to the other minor products. The reason for these being the preponderant products in this case is not evident.

The remaining problem resulted from the attempted isomerisation of cyclooctatetraene with potassium tert-butoxide in DMSO, when no products or starting material could be extracted from the reaction mixture! This is also a mechanistic mystery, though it is hoped someone will be inspired to try and elucidate this some time.

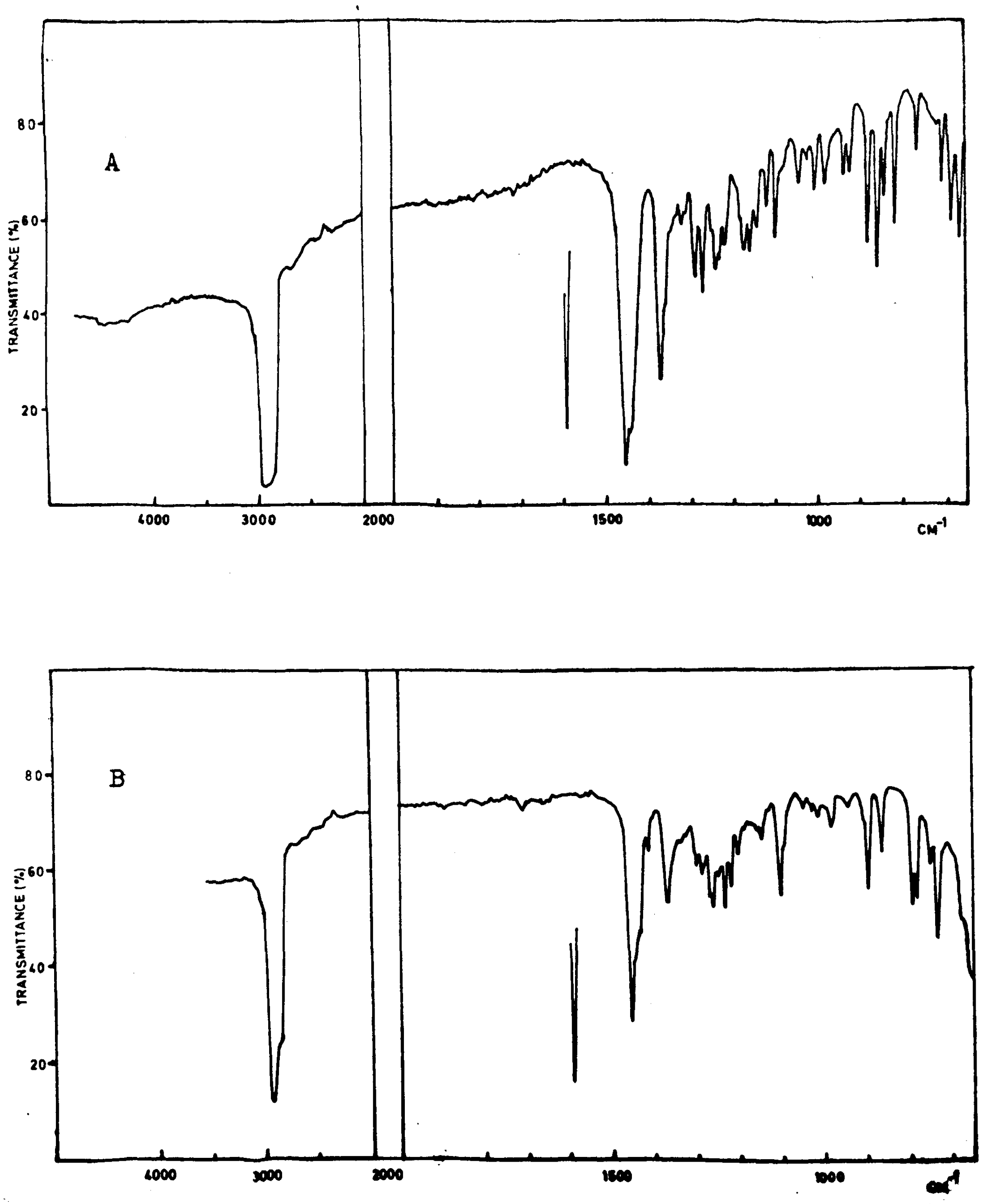
SECTION IX

Preparation, Dehydrobromination, and Isomerisation of C_{12} and C_{14} Cyclic Compounds

As the direct preparation of C_{12} carbocycles is now a commercial process, producing the isomeric cis,trans,trans- and trans,trans,trans-cyclododeca-1,5,9-trienes [(116) and (117)] on the ton scale (by trimerisation of butadiene over e.g. titanium tetrachloride/diethylaluminium chloride[159]), these isomers form very useful starting materials for the synthesis and isomerisation of cyclic C_{12} polyenes.

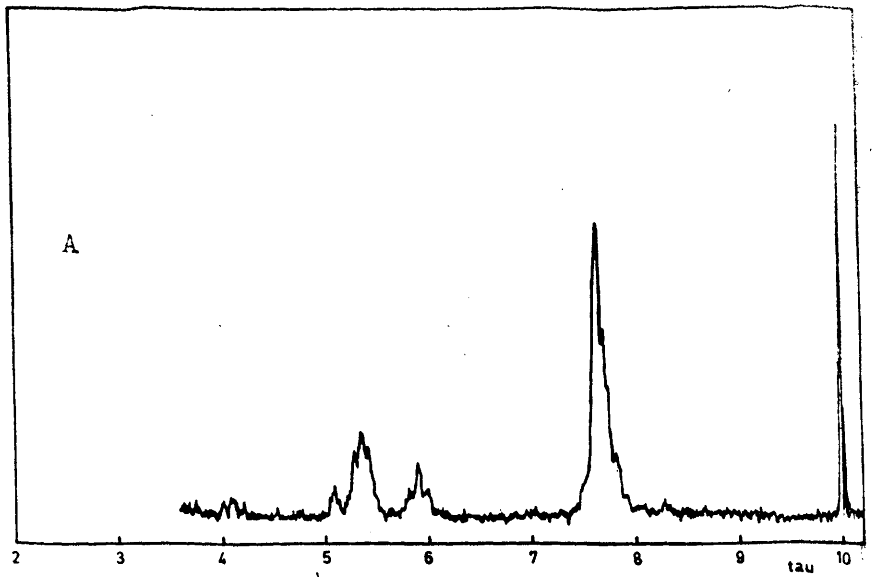
The cis,trans,trans isomer [(116), henceforth called c,t,t.] was available in small quantities (100% pure by g.l.c.) from Aldrich Chemical Co.; material obtained from Koch-Light was less pure (~98%) and this was used for reactions on a large scale. The trans,trans,trans isomer [(117), henceforth shortened to t,t,t.] was obtained from Cities Service Research and Development Co., but required further purification (fractional crystallisation from pentane gave ~99% pure material). The spectral properties (i.r.; n.m.r.) of both isomers corresponded with their structural assignment.

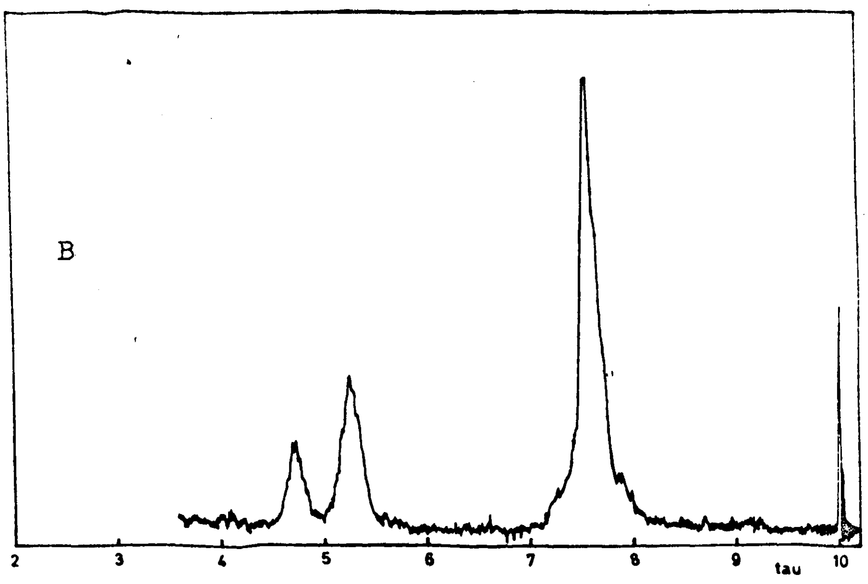
The preparation of a double bond equivalent of cyclododeca-1,5,9-triyne (224), by dehydrobromination of the 1,2,5,6,9,10-hexabromocyclododecane isomers was undertaken in a manner analogous to the preparation of a cycloocta-1,5-diyne double bond equivalent (by dehydro-



Infrared spectra (nujol mulls) of the hexabromo derivatives from c, t, t-cyclododeca-1,5,9-triene (A), and t, t, t-cyclododeca-1,5,9-triene (B).

Figure 24.





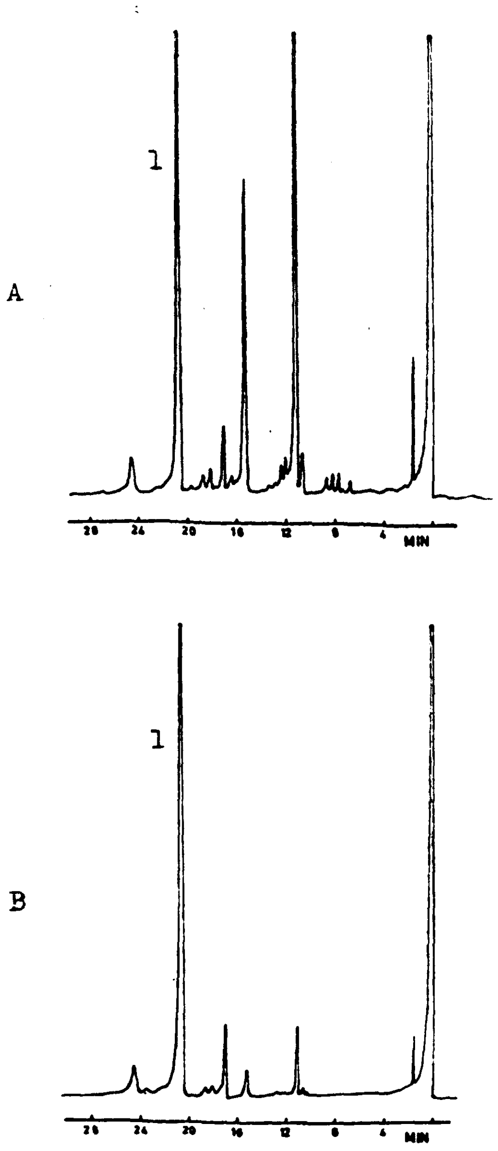
N.m.r. spectra (pyridine solution) of the hexabromo derivatives of c,t,t-cyclododeca-1,5,9-triene (A), and t,t,t,-cyclododeca-1,5,9-triene (B).

Figure 24.

bromination of 1,2,5,6-tetrabromocyclooctane). Initial attempts by McCrae[47] to brominate the c,t,t. directly gave only intractable gums, so pyridinium bromide perbromide (cf. p. 119) was used instead. A repetition of this work in the present studies yielded solid hexabromo derivatives of c,t,t. and t,t,t. by either method. The method with pyridinium bromide perbromide gave better yields than even a modified version of the direct bromination method.[160] The physical properties of both solid hexabromides [represented by (222) and (223)] corresponded with published data,[161] and the spectral characteristics of the hexabromide from the c,t,t. isomer (222) corresponded with those obtained by McCrae.

The spectral properties (i.r., n.m.r.) of the two hexabromide isomers, though similar, were not identical [cf. the two tetrabromocyclooctane isomers (205) and (206)], but further analysis of the spectral characteristics was not possible - apart from identifying expected absorptions. (Fig. 24a and b).

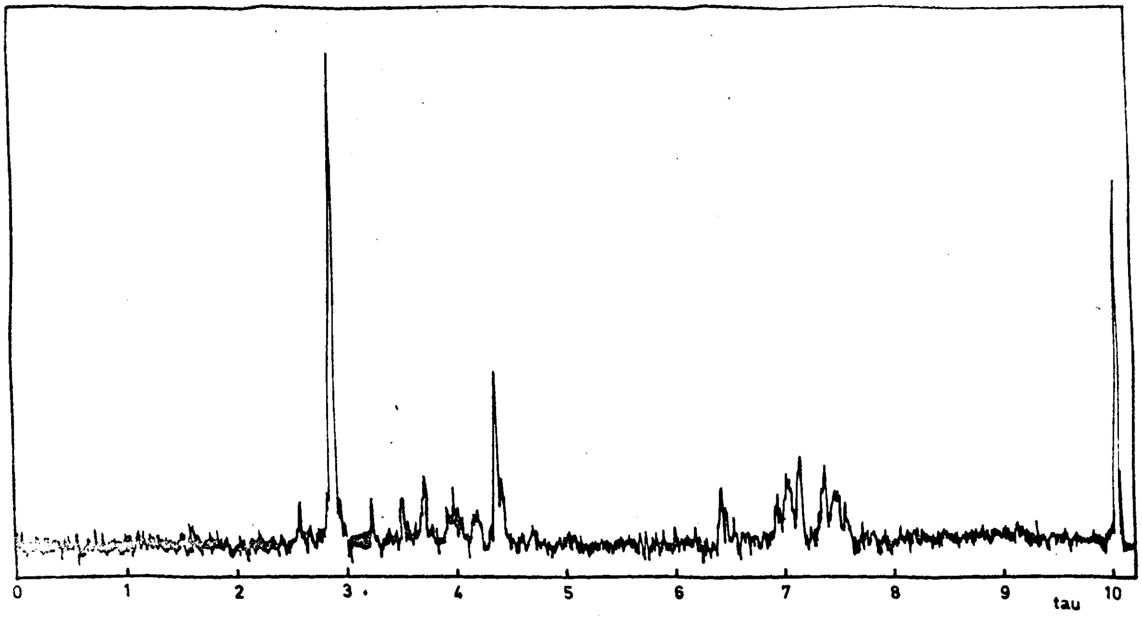
Attempts made by Alexander[162] and McCrae[47] to dehydrobrominate hexabromocyclododecane had shown that the best reagent was potassium tert-butoxide in diglyme, and accordingly this was used in this instance as well. The bromine-free oils obtained after extraction of the reaction mixtures from the dehydrobromination (heating at 130° for 14 hrs.) of the hexabromides of either c,t,t. or t,t,t. had similar spectral characteristics; several prominent bands could be attributed to either aromatic or olefinic chromophores (ν^{film} 1640, 1490, 770, 730,



G.l.c. traces of the products from the dehydrobromination of the hexabromides from c,t,t-cyclododecatriene (A), and t,t,t-cyclododecatriene (B).

1. 1,2-benzocycloocta-1,3,5-triene.

Figure 25.



N.m.r. of 1,2-benzocycloocta-1,3,5-triene (CCl_4 solution).

Figure 26.

690 cm.$^{-1}$; for both products which had λ_{max} 240 mμ and λ_{max} 264 mμ respectively). Analytical g.l.c. showed that the constituents of each product were the same, but present in different proportions (Fig. 25). This may be due to slightly different reaction conditions, for when the dehydrobromination of the hexabromide (222) was repeated on a larger scale, the composition of the product was very similar to that from the dehydrobromination of hexabromide (223).

As the most stable compound in the dehydrobromination product appeared to be the third major constituent (with longest R_T), so the isolation of this compound was undertaken. After initial chromatography of the reaction products, over silica gel, this compound was obtained in a pure state by preparative g.l.c. Its spectral properties (i.r., u.v.) were identical to those obtained by McCrae[47] for his product 'A'. The infrared spectrum showed bands characteristic of o-disubstituted aromatic compounds (ν^{film} 1495, 755 cm.$^{-1}$) as well as multiple bands in the region 800-650 cm.$^{-1}$ of which several could be ascribed to cis double bonds. The ultraviolet spectrum had λ_{max} 264 mμ., typical of aromatic chromophores, but the intensity (ε = 6,450) was far higher than normally found for aromatic nuclei, so that a double bond at least must be in conjugation with the aromatic ring. The n.m.r. spectrum (Fig. 26), had absorptions typical of aromatic, ethylenic and allylic or benzylic protons in the ratio 1:1:1. This data, coupled with a molecular weight of 156 (by mass spectrometry), equivalent to $C_{12}H_{12}$, is sufficient to confirm the identity of this compound as 1,2-benzocycloocta-1,3,5-triene (225a) as proposed by McCrae, and not the other possible isomers (225b and c). (The other structural degradations carried out by McCrae[47] also confirm this assignment). Furthermore, hydrogenation (over 10% palladium/charcoal) of this compound, and g.l.c. comparison of the product with a sample of 1,2-benzocyclooct-1-ene [(226), prepared by another route, p. 80] showed them to be the same.

Dehydrobromination of both hexabromides with potassium tert-butoxide in DMSO gave 1,2-benzocycloocta-1,3,5-triene (225a) as the major product in each case (31% and 79% respectively, as determined by g.l.c.), but a series of compounds with longer R_T (on g.l.c.) than any obtained before was also present. These may be either polyunsaturated C_{12} carbocycles or other aromatic species such as substituted azulenes (227) or naphthalenes (228). This view is substantiated somewhat by the detection of weak absorption in the ultraviolet at $\lambda_{max.}^{hexane}$ 310, 330, 345 mμ, as well as absorption at $\lambda_{max.}^{hexane}$ 245 mμ.

To substantiate the results of these dehydrobrominations it was desired to carry out a similar reaction on a cyclododecadiyne equivalent - or in this case its precursor - such as a tetrabromocyclododecane. Reduction of the cyclododecatrienes to dienes and subsequent bromination would give the required starting material. A recent publication[158] had described the reduction of c,t,t. (116) to *cis*-cyclododecene (231) with hydrazine hydrate/oxygen, catalysed by copper sulphate. This reduction proceeds step-wise, *cis,trans*-cyclododeca-1,5-diene (229) being formed initially, then preferentially reduced further to *cis*-cyclododecene (231), though complete reduction to cyclododecane (233) could also occur.

This reduction was tried on both t,t,t. and c,t,t., and the reactions followed by withdrawing aliquots which were examined by g.l.c. With the former, reduction was rapid, and after 26 hrs. the reaction mixture contained cyclododecane [(233), 61%], *trans*-cyclododecene [(230), 20%], and starting material (8%). The fourth compound present (11%) was assumed to be the *trans,trans*-cyclododeca-1,5-diene (232). This diene formed as much as 29% of the mixture after 4 hrs., but thereafter the quantity decreased steadily as the reaction time increased.

C,t,t. (116) was reduced more slowly, although reaction conditions were identical. Thus, after 6 hrs., the reaction mixture contained *cis*-cyclododecene [(231), 19%], the starting material (27%), and a compound taken to be the *cis,trans*-cyclododeca-1,5-diene [(229), 54%].

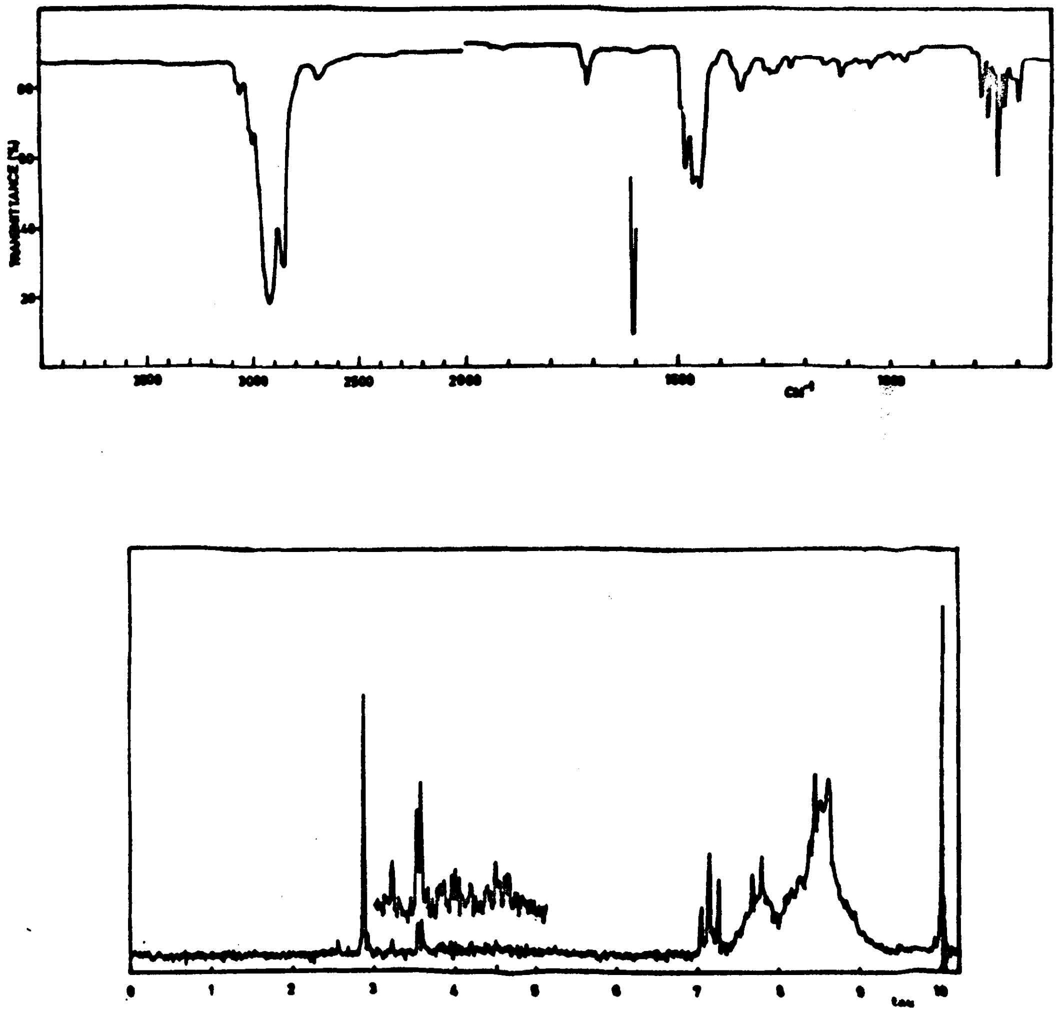
Hence, as this isomer (116) yielded more of the required diene, a larger quantity was reduced under similar conditions over 30 hrs. to give a mixture of *cis*-cyclododecene (29%), starting triene (22%), and the required *cis,trans*-cyclododeca-1,5-diene (49%). [Again, the course of the reaction was followed by withdrawing aliquots and analysing by g.l.c. the proportions of the reduced compounds.]

Bromination of this mixture containing ~50% of the diene (229) with bromine/acetic acid yielded a brown gum upon extraction, which showed two main spots on t.l.c. analysis. (The hexabromide derived from the bromination of c,t,t. in the mixture, precipitated out during the reaction, and was filtered off prior to extraction). The 1,2-dibromocyclododecane (234) derived from the cis-cyclododecene (231) present in the mixture (one of the two major constituents of the extract) was separated from the rest of the mixture by chromatography, and purified by distillation. Analysis, and the spectral characteristics of this material confirmed the structure assigned to it.

Although the other major bromination product was purified further by chromatography and preparative t.l.c., at best only a low melting gum could be obtained. The spectral characteristics of this material (which consisted of two close running spots on t.l.c.) were similar to those of the dibromo- and hexabromocyclododecanes (i.r., n.m.r.), and its R_f value was intermediate to these two compounds on t.l.c. A good elemental analysis could not be obtained due to the difficulties in purification. The mass spectrum showed no parent ion, but ions at $^m/e$ 401, 403, 405, and 407, (1:3:3:1 ratio), due to P - Br, were clearly visible. Further fragmentation ions confirmed the presence of four bromine atoms originally. Thus this material can be said to consist of two 1,2,5,6-tetrabromocyclododecane isomers [represented by (235)] derived from the cis,trans-cyclododeca-1,5-diene (229). Lack of time precluded a possible separation of these isomers, and hence it is impossible to say what their relative configurations are, for this problem can only be solved by X-ray analysis.

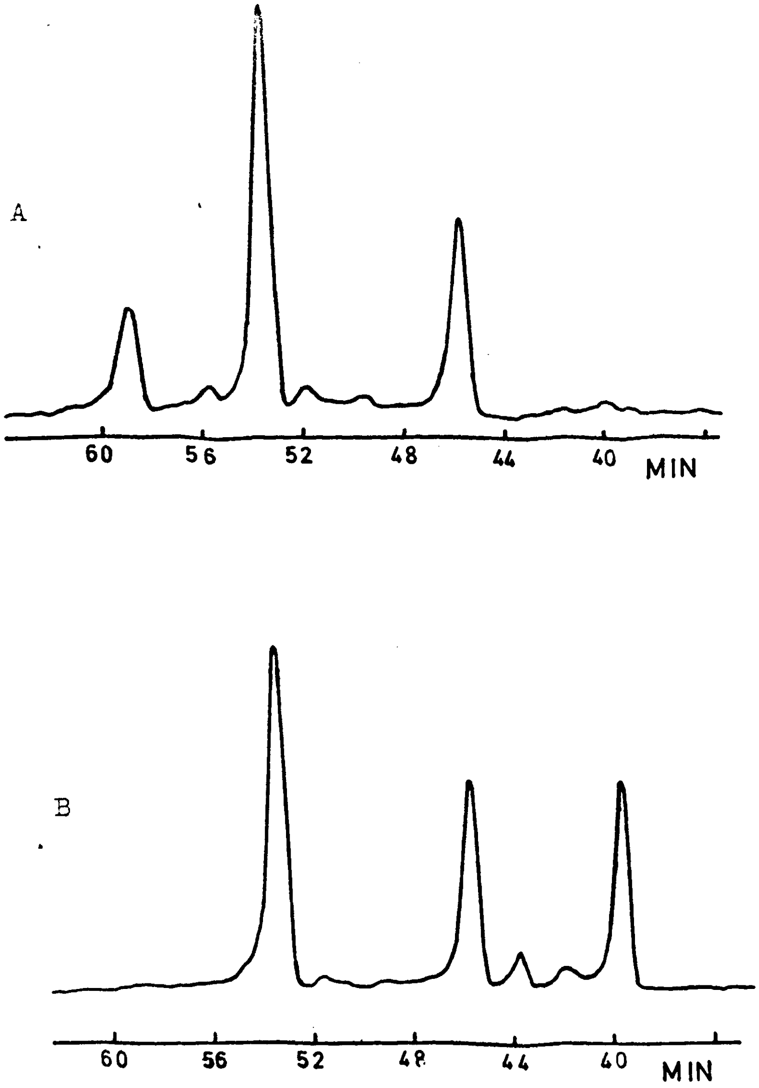
Dehydrobromination of this mixture of tetrabromocyclododecanes with potassium tert-butoxide in diglyme (1:8 molar ratio of tetrabromide to base; heated at 130° for 16 hrs.) gave, after extraction, a product which was shown by analytical g.l.c. to contain only one compound. This material, a clear oil after distillation, had physical properties very similar to those quoted in the literature for 1,2-benzocyclooct-1-ene (226), and the spectral characteristics were similar to those obtained by McCrae[47] for his product 'B', which was the hydrogenated 1,2-benzocycloocta-1,3,5-triene. Furthermore, g.l.c. comparison of this product with the hydrogenated 1,2-benzocycloocta-1,3,5-triene obtained previously in these studies (p. 77), showed them to be the same compound. Hence it may be said with certainty that the product from the dehydrobromination and subsequent isomerisation of tetrabromocyclododecane is 1,2-benzocyclooct-1-ene (226).

A related isomerisation of cyclotetradeca-1,8-diyne (53, m = n = 5) with the same basic reagent as reported by Hubert and Dale[46] was also investigated. The cyclotetradeca-1,8-diyne was prepared (as described by these authors) in 40% yield from nona-1,8-diyne (119, n = 5) and 1,5-dibromopentane. This cyclic diyne was heated under reflux (14 hrs.) with potassium tert-butoxide (1:6 molar ratio of diyne to base) in diglyme. The product obtained after extraction was a yellow oil, which showed absorption in the infrared and ultraviolet characteristic of aromatic and ethylenic chromophores [Fig. 27; ν^{film} 1660, 1495, 770, 750, 735,



Infrared (liquid film) and n.m.r. (CCl_4 solution) spectra of the product from the base catalysed isomerisation of cyclotetradeca-1,8-diyne.

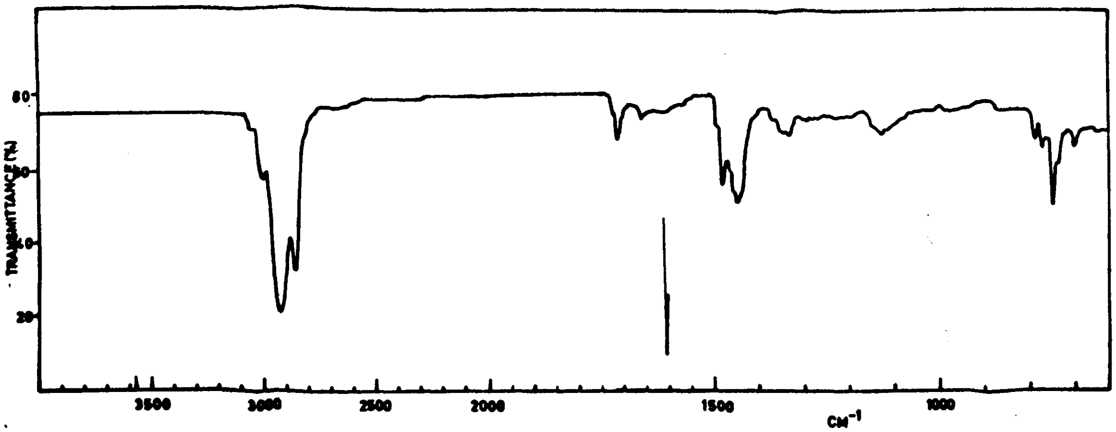
Figure 27.



G.l.c. traces of the primary (A), and hydrogenated (B) products from the base catalysed isomerisation of cyclotetradeca-1,8-diyne.

<u>Conditions:</u> 50 m. Ap'L' capillary, 160°, 20 p.s.i./5.3, total flow 45 ml./min.

Figure 28.



Infrared (liquid film) and n.m.r. (CCl_4 solution) spectra of the hydrogenated product from the base catalysed isomerisation of cyclotetradeca-1,8-diyne.

Figure 29.

700 cm.$^{-1}$; $\lambda_{max.}^{hexane}$ 250, 274 mμ. (ε = 2,150 and 1,750) . The n.m.r. spectrum also showed the presence of aromatic, ethylenic, and allylic protons (Fig. 27). Analytical g.l.c. (Fig. 28) showed two major components (25% and 53%) as well as some of the starting diyne (14%).

Hydrogenation of this mixture (over 10% palladium/charcoal) gave an oil, which was shown by g.l.c. to consist of three main components (25%, 25%, 43%), of which the last two had retention times identical with those of two of the compounds in the original mixture. Comparison with cyclotetradecane showed that the first peak in the hydrogenated mixture was due to this compound (Fig. 28). The spectra (i.r.; u.v.; n.m.r.) of this hydrogenated product showed absorptions which could be ascribed to aromatic material . [Fig. 29; ν^{film} 1495, 770, 745, 735, 700 cm.$^{-1}$; $\lambda_{max.}^{hexane}$ 266, 274 mμ. (ε = 280, 290); no absorption in the n.m.r. at 3.2-4.7τ due to ethylenic protons . Thus the compounds remaining after hydrogenation can only be aromatic or cyclic isomers (and cyclotetra:decane), of which 1,2-benzocyclodec-1-ene (236) is the most likely by analogy with previous work. The identity of the other consituent can only be guessed at; possible structures could be (243) or (244) or some bicyclic [7:5:0] compound.

SECTION X

Mechanism of Dehydrobromination and Isomerisation of Cyclic C_{12} and C_{14} Compounds

The dehydrobromination of the hexabromocyclododecanes [(222) and (223) derived from (116) and (117)] must be considered as proceeding by the same mechanism as in the dehydrobromination of the tetrabromocyclooctanes (p. 64). Without an X-ray structural determination of these compounds [(222) and (223)] it is impossible to assign definitely any one preferred conformation or configuration. The n.m.r. spectra (Fig. 24) of the hexabromides indicate apparent flexibility of the molecules; all that can be deduced from a study of their molecular models is that trans-anti-trans conformations can be adopted by the bromine atoms relative to the protons, so again β, γ elimination of hydrogen bromide should be facile. Thus it would be expected, that as α, β elimination seems less likely, so cyclododeca-1,5,9-triyne (224) would not be formed, and instead the cyclododeca-1,3,5,7,9,11-hexaene (238) - the so-called C_{12} annulene - should be formed instead. This particular annulene has never been isolated, and Sondheimer's study[163] of other annulene homologues has shown that this system would be too strained to exist for any length of time, so further rearrangement must be expected.

It is difficult to predict the mechanism of this rearrangement. Isolation of 1,2-benzocycloocta-1,3,5-triene (225a) shows that transannular ring closure must occur, but it is impossible to say at what stage of the dehydrobromination sequence this occurs. Transannular ring closure could take place with a partly dehydrobrominated species, in a manner similar to that outlined in Scheme XXIII [i.e. (210) to (211)] for the C_8 compounds. As there is no evidence at the moment as to the extent to which this could occur, only rearrangement of the fully dehydrobrominated species will be considered. (Scheme XXV).

As it does not seem feasible for dehydrobromination to yield a cyclic triyne [such as (224), or possibly the less strained tri-allene (237)], so the only compound possible initially must be the annulene (238). This, when represented as (238a) can be envisaged to undergo transannular ring closure to give structure (239), a bicyclic [6:4:0] system. Further base catalysed allylic shifts can then occur to give (239a) which should readily rearrange to give the aromatic compound (225a), which is 1,2-benzocycloocta-1,3,5-triene.

The experimental evidence (and analogy with previous systems) does seem to support this mechanism. The other two major peaks seen on g.l.c. analysis of the reaction mixture may in fact be compounds (239) or (239a), for repetition of the dehydrobromination at a slightly higher temperature, caused a marked decrease in their amounts. This would indicate that they had been transformed into the aromatic compound, for the amount of this in the reaction mixture increased proportionally. Experimental results also obtained by Hubert and Dale[127] indicate that this is the structure to be expected, for in the formation of compound (157) from (155), structure (156) was the favoured intermediate with all the double bonds in the macrocyclic part of the molecule conjugated with one another and with the benzene ring. This makes structures (225 b and c) unlikely on theoretical grounds, quite apart from the fact that they were not identified amongst the reaction products. It is impossible to say whether the products [i.e. possibly substituted azulenes and naphthalenes (227), (228)] in the reaction mixture from the dehydrobromination in DMSO are formed by this same mechanism (or formed at all) until they are positively identified.

The preparation of 1,2-benzocyclooct-1-ene (226) from tetrabromocyclododecane (235) can be explained by a rationale similar to that for the formation of 1,2-benzocycloocta-1,3,5-triene (225a) from the hexabromides [(222) and (223)], and this is outlined in Scheme XXVI. The route and mechanism is identical to that outlined in Scheme XXV for the hexabromide dehydrobromination, except that in this case only four double bonds instead of six can be formed. Hence the product is 1,2-benzocyclooct-1-ene, though it is interesting to note that the aromatic compound is preferred to the C_{12} carbocycle with the four double bonds placed in the most sterically favoured positions (which is presumably first formed). A C_{12} cyclic diyne (53, m = n = 4) has also been aromatised by Hubert and Dale[46] (under forcing conditions), and it is evident that the starting material is of relatively little importance in determining the nature of the final products. So long as there are the same number of double bonds in the intermediate mono-cyclic polyene, the same aromatic isomers will be formed when the same basic catalyst is employed in these reactions.

A report by Hubert and Dale,[99] that the aromatisation of cyclotetradeca-1,8-diyne (53, m = n = 5) with base gave bi- and tri-cyclic compounds (as well as aromatic compounds under more forcing conditions[46]), was deemed worth investigating, considering the results obtained with the C_8 and C_{12} cyclic compounds. This diyne gave, after base isomerisation, a product whose spectral characteristics were compatible with structure (236), i.e. 1,2-benzocyclodec-1-ene. However, as there were three major components (one of them starting diyne), only one could be aromatic, while the other was unknown. After hydrogenation, cyclotetradecane and two other compounds were seen (by g.l.c.) so it is highly probable that there are bicyclic compounds other than the 1,2-benzocyclodec-1-ene being formed. These may be, as suggested by Hubert and Dale,[99] either bicyclic [7:5:0] compounds (analogous to the formation of cycloheptatrienes from the linear octa-1,7-diyne) or m- and p-cyclophane compounds, such as (243) and (244). Hence it is possible that in larger macrocyclic diynes, the same mechanisms can operate as for the isomerisation of octa-1,7-diyne. This reaction could then be applied to the preparation, in two stages, of m- and p-cyclophanes from the appropriate macrocyclic diyne.

EXPERIMENTAL

General

Unless otherwise stated, the following experimental conditions apply throughout.

Quantitative infrared (i.r.) spectra were obtained with a Unicam SP 130 grating spectrophotometer, (accuracy ± 1 cm.$^{-1}$), and survey spectra with either Perkin Elmer 137, 237 or Unicam SP 200 (accuracy ± 10 cm.$^{-1}$). All survey spectra are corrected to the 1603 cm.$^{-1}$ band of polystyrene; only absorption characteristic of main functional groups is quoted. The letters (vs), (s), (m), (w), after quoted frequencies denote very strong, strong, medium or weak intensity.

Ultraviolet (u.v.) spectra were measured on either a Unicam SP 500 (manual), 800 (automatic) or Perkin Elmer 137 U.V.

Early nuclear magnetic resonance spectra, (n.m.r.), were recorded (in carbon tetrachloride unless otherwise stated) on an Associated Electrical Industries model RS2 (60 megacycles), while later spectra were run on a Perkin Elmer RS10, 60 megacycles instrument. Tetramethylsilane was used as the internal standard throughout.

Mass spectra were obtained with an Associated Electrical Industries MS 9 instrument, either 'hot-box' or 'probe' samples as indicated.

Gas liquid chromatographic analyses were conducted on a variety of instruments and columns. Operating conditions, columns and detectors are quoted where necessary; retention times (R_T, in minutes) were calculated from the solvent front (pentane usually); all quantitative work was done with a flame ionisation detector, using peak area or peak heights (as indicated). Except for a few known compounds (as indicated), no corrections were made for differences in detector response. Pye Argon Chromatographs (equipped with a closed injection system and flash preheater) and a Perkin Elmer 451 Fractometer were used for analytical isothermal runs; a Perkin Elmer F 11 and a Wilken's Aerograph 204 (dual columns, dual flame ionisation detectors) for temperature programmed work, and the Fractometer or a Wilken's Autoprep 700 for preparative work.

Alumina (neutral) of activity determined by the method of Brockmann[164] was used; silica gel was normally ex B.D.H. unless indicated otherwise. Silver nitrate on silica gel was prepared by two methods:-[165]

(a) Silica gel (50 g.) was slurried in distilled water (200 ml.) containing silver nitrate (25 g.) for several minutes, filtered and partially dried by suction. The remainder of the water was removed under reduced pressure and gentle heating (less than 75°); at all times the material was shielded from light. Titration or weighing of the product showed that silver nitrate comprised 10% wt./wt. using the above proportions.

(b) Silica gel was slurried with the required weight of silver nitrate as before. Water was removed completely by the freeze drying method. In this case, the actual amount of silver nitrate used determines the percentage composition.

Thin layer chromatography (t.l.c.) was done on Kieselgel G (E. Merck AG.) prepared according to Stahl,[166] of standard thickness. Eluents and sprays are indicated in each case.

Melting points were taken on a Kofler hot-stage and are uncorrected. Refractive indices were obtained on a standard Abbe refractometer.

Unless indicated otherwise, magnesium sulphate was used as drying agent throughout.

SECTION I

Preparation and Isomerisation of Decadiynes.

Deca-1,9-diyne[43,167] (119, n = 6)

To a suspension of sodium acetylide[168] (from 11 g. sodium) in liquid ammonia (600 ml.) was added with stirring (over 1 hr.) a solution of 1,6-dibromohexane (25.9 g.) in ether (40 ml.). The mixture was stirred vigorously for a further hour, then left standing overnight. Ether (200 ml.) was added to the suspension, followed by solid ammonium chloride (20 g.) with rapid stirring. This, and the addition of aqueous ammonium chloride decomposed any remaining acetylide, and evaporated off the bulk of the ammonia. After decanting the organic layer, the aqueous solution was extracted with ether, and the combined ethereal extracts washed with dilute sulphuric acid (2 N), saturated sodium bicarbonate solution, water, and then dried, concentrated, and fractionally distilled. Fractions of similar b.p. and refractive index were combined to yield 5.8 g. (46%) of deca-1,9-diyne. b.p. 74-76°/16-17 mm. ; n_D^{20} 1.4496. (Lit.[167] b.p. 78-30°/29 mm. ; n_D^{20} 1.4528); ν_{max}^{film} 3250 (vs), 2100 (m) cm.$^{-1}$

1,4-Dichlorobut-2-yne[169]

Thionyl chloride (50 ml.) was added slowly, with stirring, over 6 hrs. to but-2-yne-1,4-diol (25 g.) in dry pyridine (65 ml), the temperature not being allowed to rise above 20°. The thick, dark paste so formed, was allowed to come to room temperature towards the end, stirred for a further 2 hrs. then left overnight. The resulting solid mass was decomposed by the addition of crushed ice (150 g.), extracted with ether, the extracts washed with saturated sodium carbonate, and then dried, concentrated, and fractionally distilled. Fractions of similar b.p. and refractive index were combined to yield 15.2 g. (36%) of 1,4-dichlorobut-2-yne: b.p. 60-61°/10 mm.; n_D^{20} 1.5048. (Lit.[169] b.p. 68°/17 mm.; n_D^{20} 1.5072); ν_{max}^{film} 3,400 (w), 1260 (m), 1160 (m), 700 (vs) $cm.^{-1}$

Deca-4,6-diyne[170]

1,4-Dichlorobut-2-yne (10 g.) was added slowly, with stirring, to a suspension of sodamide (from 7.7 g. sodium) in liquid ammonia (500 ml.), followed by n-propylbromide (22.12 g.) over 5 minutes. This mixture was stirred with cooling (solid carbon dioxide-methanol) for 45 minutes, then for 1 hr. without external cooling, followed by stirring with intermittent cooling for a further 2 hrs. Ether (200 mls.) was added, followed by solid ammonium chloride (20 g.). Any remaining acetylides were decomposed by the cautious addition of an iced solution of ammonium chloride (~ 150 ml.), and the mixture was left to stand overnight. The organic layer was decanted, and the aqueous solution extracted with ether. These ethereal extracts were combined, washed with 2N sulphuric acid, saturated sodium bicarbonate, water, dried, concentrated, and fractionally distilled. Fractions of similar b.p. and refractive index were combined to give 5.3 g. (32%) of deca-4,6-diyne: b.p. 37-39°/0-3 mm.; n_D^{20} 1.4911 (Lit.[170] b.p. < 60°/0.01 mm., 76°/2 mm.). ν_{max}^{film} 2150 (w), 1330 (m), 1310 (m), 1270 (m) $cm.^{-1}$; $\lambda_{max.}^{MeOH}$ 225 mμ. (ε = 615).

Base Catalysed Aromatisation of Diynes

The General Method

The basic medium was prepared just before use, as an opalescent dispersion, by refluxing freshly prepared potassium tert-butoxide (previously heated at ~ 160° under reduced pressure until sublimation started) in approximately ten times its weight of diglyme (dried by distillation from sodium). The diyne and this reagent (in the required ratio) were then heated under reflux for the requisite length of time under nitrogen. On cooling, the reaction mixture was diluted with water, extracted with pentane, and the extracts washed repeatedly, dried, and concentrated to give the liquid hydrocarbons. Except for initial experiments, distillation of the products was not attempted, owing to the losses occasioned through polymerisation.

The Isomerisation of Deca-1,9-diyne (119, n = 6).

The purity of both deca-1,9-diyne and deca-4,6-diyne was checked by analytical g.l.c. prior to use (10% Ap'L', 4' x ¼" o.d., 100°, 50 ml./min.; purity 100% for both; R_T, deca-1,9-diyne = 7.88 mins., deca-4,6-diyne = 23.25 mins.).

Heating of the diyne (2 g.) with the above basic system (in a molar ratio of 1:7) for 18 hrs. at 160° gave 1.9 g. (95%) of a yellow oil after extraction. This had $\lambda_{\max}^{\text{c.hexane}}$ 265 mμ. (ε = 1900) Fig. 3 ; $\nu_{\max}^{\text{film}}$ 740 (s), 710 (m) cm.$^{-1}$, no trace of ethynyl in the i.r. (Fig. 1); n.m.r. 2.94 (singlet), 3.5-3.6 (mult.), 4.0-4.1 (doublet), 4.5-4.8 (mult.), 7.3-7.8 (mult.), 8.7-9.0 (mult.)τ. g.l.c. data, Table I, p. 21.

The Isomerisation of Deca-4,6-diyne.

Treatment of the diyne with the same basic system as above (1:7 molar ratio) for 12 hrs. at 160° gave 1.5 g. (75%) of product: $\nu_{\max}^{\text{film}}$ 740 (m), 710 (s) cm.$^{-1}$; no trace of ethynyl in the i.r.; $\lambda_{\max.}^{\text{c.hexane}}$ 265 mμ. (ε = 2,800); n.m.r. 2.95-2.98 (mult.), 3.5-3.6 (mult.), 3.8-4.1 (mult.), 4.5-4.8 (mult.), 7.3-8.2 (mult.), 8.7-9.2 (mult.)τ. (Fig. 2a) g.l.c. data, Table I, p. 21 .

Hydrogenation of the Decadiyne Primary Isomerisation Products.

Hydrogenation in ethyl acetate over palladium/charcoal (10%) of either of the isomerisation mixtures gave similar material - as determined by spectroscopy (i.r., u.v.) and analytical g.l.c. (Table I); $\nu_{\max.}^{\text{film}}$ 740 (s) cm.$^{-1}$ for both samples (see Fig. 3); $\lambda_{\max.}^{\text{c.hexane}}$ 257, 264, 272 mμ. ($\varepsilon \simeq$ 100) and $\lambda_{\max.}^{\text{c.hexane}}$ 257, 264, 272 mμ. ($\varepsilon \simeq$ 50) for the mixtures derived from the 1,9- and 4,6- isomers respectively. No absorption from ethylenic protons in the n.m.r. spectrum for either product (Fig. 2).

Analytical g.l.c. of Primary and Hydrogenated Isomerisation Products of the Decadiynes (Table I).

The three expected isomers in the mixtures (o-n-propylmethylbenzene, o-diethylbenzene, and n-butylbenzene) were identified by comparison of their R_T values and by co-chromatography with authentic samples. Several columns were tried for optimum resolution, the best results being achieved with a poly(ethyleneglycol) capillary column (Figs. 4a and b).

The percentage composition (to the nearest whole number) was calculated from the peak heights of the components of the mixtures, and is not corrected for variations in detector response.

The optimum conditions used were:- 50 m. poly(ethyleneglycol) capillary, temp. 50°, 18 p.s.i./6.0 = total flow 55 ml./min. Flame ionisation detector, 300 v., x 256, Filter 2.

Time study of Deca-4,6-diyne Isomerisation.

Treatment of deca-4,6-diyne under the same conditions as described previously was followed by withdrawing aliquots (1 ml.) from the reaction at regular intervals over 25 hrs. These were worked up by the usual method and their contents examined by g.l.c. (50 m. Ap'L' capillary, 103°, 20.75 p.s.i./7.1 = total flow 90 ml./min.; Fig. 5).

This study showed that isomerisation takes place very rapidly; even after 1 hr. the composition of the mixture was practically the same as after 25 hrs. Some further decomposition or isomerisation did seem to take place towards the end as evidenced by the appearance of further peaks. The composition remained the same throughout the first ten hours, e.g. the proportions of n-butylbenzene, o-diethylbenzene and o-n-propyltoluene were 9.7% (10.1%), 16.8% (16.1%) and 42.5% (38.3%) after 2 hrs. and 10 hrs. (in brackets).

SECTION II

Isomerisation of Octa-1,7-diyne

Octa-1,7-diyne (119, n = 4) - General

This material, prepared by standard methods,[43, 171] was obtained from R. G. Willis and I. D. Campbell, and showed several components by g.l.c. It was accordingly purified by preparative g.l.c. (Perkin Elmer 451, 1" x 90 cms. column, 20% poly(propylene)glycol, 90°, 10 p.s.i. (nitrogen), R_T 20 mins.) to give 100% pure material. This was used for initial trials, but as the isomerisation products were the same from the purified and crude diyne, the latter was used for all large scale isomerisations. (The impurities did not interfere with g.l.c. analysis). ν_{max}^{film} 3300 (s), 2100 (m), $cm.^{-1}$

Isomerisation of Octa-1,7-diyne - Standard Procedure.

The diyne (2 g.) was heated under reflux (8 hrs.) with the basic system (potassium tert-butoxide, from 3.8 g. potassium, in the ratio 1:5) under nitrogen, to give after extraction, 0.35 g. (35%) of a yellow oil; ν^{film} 1652 (w), 1624 (w), 1605 (w), 1498 (s), 743 (s), 709 (s), 698 (s) cm^{-1}; $\lambda_{max}^{c.hexane}$ 251-256 mμ. (ε = 2,530); n.m.r. 2.45 - 2.9 (mult.), 3.2-3.7 (mult.), 4.1-4.9 (mult.), 7.2-7.8 (mult), 8.0-8.2 (mult.), 8.7-9.1 (mult.) τ. Aliquots removed in the course of the reaction, and examined by g.l.c. (conditions as below) showed that equilibrium was attained after 2 hrs.

Isomerisation of Octa-1,7-diyne: Analysis of the Product.

Analytical g.l.c. (Fig. 6; 50 m. Ap"L" capillary, 81°, 17 p.s.i./5:8s, total flow 52 ml./min.) showed that eight components were present. The two main components were identified by R_T values and co-chromatography as o-xylene and ethylbenzene in a proportion of 5:3 (by direct area comparison), and comprising about 60% of the total reaction products.

Preparative g.l.c. [[redacted], 20% poly(ethyleneglycol), 2 m. x ¼" o.d., 85°, 20 p.s.i. (helium)] furnished several cuts, one of which was pure o-xylene (single peak on analytical g.l.c.); ν_{max}^{film} 3060 (s), 3020 (s), 1605 (w), 1500 (s), 1390 (m), 745 (vs) cm.$^{-1}$; identical with published data.[172] The presence of the m- and p-xylenes, as well as ethylbenzene, in an earlier fraction was proved by i.r. and analytical g.l.c.; ν^{film} 3050 (m), 3020 (s), 1605 (w), 1500 (m), 1380 (w), 795 (s), 770 (s), 740 (s), 715 (s), 700 (vs) cm.$^{-1}$; (lit.[172] ethylbenzene 790 (vw), 772 (w), 697 (vs) cm.$^{-1}$; m-xylene 770 (vs), 695 (s) cm.$^{-1}$; p-xylene 795 (vs) cm.$^{-1}$). G.l.c. (20%, 7,8-benzoquinoline, 2 m. x ¼" o.d., 80°, 65 ml./min.) showed four components present with retention times of 17.88, 19.12, 20.38, 21.8 mins, respectively. Ethylbenzene, m-xylene, and p-xylene had retention times of 17.8, 19.0, and 20.3 min. respectively under identical conditions (Fig. 7). The material in the other cuts was insufficient to permit identification.

Isomerisation of Octa-1,7-diyne; Analysis of the Hydrogenated Product.

Hydrogenation of the isomerisation mixture (over 10% palladium/charcoal in ethyl acetate) yielded a mixture of saturated and aromatic compounds, as shown by analytical g.l.c. (Fig. 8; 50 m. Ap'L' capillary, 84^{o}, 18 p.s.i. inlet pressure). These were separated by preparative g.l.c. in the following manner. A poly(ethyleneglycol) column (20%, 2m. x $\frac{1}{4}$" o.d., 85^{o}, 18 p.s.i. helium) was used for the initial separation of the aromatic from the saturated compounds (Fig. 9); the latter (together with ethyl acetate solvent) were then rechromatographed on an Ap'L' column (20%, 2 m. x $\frac{1}{4}$" o.d., 85^{o}, 18 p.s.i.) to give four main cuts. The first was ethyl acetate, and the second was identified as methylcycloheptane; ν_{max}^{film} 2945 (s), 2914 (vs), 2853 (s), 1460 (m), 1448 (m), 1377 (w), 1366 (w), 1352 (w), 1048 (vw), 966 (vw), 814 (w) $cm.^{-1}$ A synthetic sample had an identical spectrum. The n.m.r. spectra of the isolated cut and authentic methylcycloheptane were identical, having absorptions at 8.0, 8.44, 8.75, 9.1 τ. Analytical g.l.c. (50 m. Ap'L' capillary, 84^{o}, total flow 55 ml./min) showed this compound by co-chromatography and R_T to be identical with methylcycloheptane.

The third cut, containing two compounds was in an amount insufficient for identification. The fourth cut was identified as cyclooctane; one signal in the n.m.r. spectrum at 8.46 τ identical with authentic material and identical R_T with cyclooctane by g.l.c. (same conditions as above). No n-octane could be detected by g.l.c.

Isomerisation of Octa-1,7-diyne: The Olefinic Constituents of the Primary Product.

(i) The reaction products (3 g.) from the base catalysed isomerisation of octa-1,7-diyne (10 g.) were chromatographed on a 10% silver nitrate/silica gel column (40 g.) using pentane and diethyl ether as eluants (5 ml. fractions). The ultraviolet spectra of initial fractions were aromatic in character, and the appropriate fractions (20-29) were combined; later fractions (33-50) had more diffuse spectra consistent with diene chromophores, and these in turn were combined, and after careful concentration, subjected to preparative g.l.c.

(ii) Utilising a poly(ethyleneglycol) column (20%, 2 m. x ¼" o.d., 81°, 55 ml./min.) five cuts were taken (Fig. 10, 10a). The first two consisted of solvent and trace materials, and were discarded. Cuts 3 and 4 contained several components in common, and will be considered later. The fifth cut was obtained pure, and identified spectroscopically as cycloocta-1,3,5-triene (101); ν_{max}^{film} 3010 (vs), 2935 (vs), 2895 (m), 843 (m), 815 (m), 775 (vs), 742 (m), 702 (vs), 647 (vs) cm.$^{-1}$, identical with a published spectrum;[172] $\lambda_{max}^{c.hexane}$ 263 mμ (ε = 3,000). [Lit.[87] λ_{max} 265 mμ (ε = 3,600)].

A more efficient column [2% poly(ethyleneglycol) 600, 12' x [illegible]" o.d., 70°, 180 ml./min.] installed in an Aerograph Autoprep instrument yielded a more convenient separation. Again Cuts 1 and 2 were discarded, but Cuts 3 and 4, as well as 5, were better separated, the last being obtained in an amount sufficient for an n.m.r. spectrum; this had absorption at 4.16, 4.3, 7.57 τ (all broad singlets), identical with that of a synthetic sample of cycloocta-1,3,5-triene (p.109).

Cuts 3 and 4 were obtained in sufficient quantity to be identified by their spectral characteristics as mixtures of mainly 2-methylcyclohepta-1,3,5-triene (122), [plus 3-methylcyclohepta-1,3,5-triene (123)], and 1-methylcyclohepta-1,3,5-triene (121), [plus 3-methylcyclohepta-1,3,5-triene] respectively. These three isomers, as well as the 7-methylcyclohepta-1,3,5-triene (120) were synthesised by a published route[112,111] (see p. 30), and a comparison of their spectral characteristics and those of Cuts 3 and 4 follows in tabular form; their i.r. and n.m.r. spectra are illustrated in Figs. 11, 12, 13 (p. 26).

Comparison of these fractions by analytical g.l.c. (20% Cyano 'P', 4' x ¼" o.d., 50°, 38 ml/min.) with synthetic materials showed that Cut 3 contained four components, the two major ones being 2- and 3-methylcyclohepta-1,3,5-triene respectively. Cut 4 contained the 3- and 1-methyl isomers (major), while Cut 5 contained only cycloocta-1,3,5-triene.

(iii) A small amount (~1 mg.) from each cut was dissolved in either carbon tetrachloride or ethyl acetate and hydrogenated in a Clauson-Kaas apparatus over an excess of palladium on charcoal (10%). The products were analysed by g.l.c. (50 m. Ap'L' capillary, 76°, 45 ml./min. total

TABLE II

Infrared Spectral Data for the Isomeric Methylcyclohepta-1,3,5-trienes and Cuts 3 and 4 from Preparative g.l.c. of Isomerised Octa-1,7-diyne

Cut 3	Cut 4	1-Methyl (121)	2-Methyl (122)	3-Methyl (123)	7-Methyl (120)
	3200 vs				
3022		3026	3028	3026	
			3012	2992	3014
2970	2965	2970	2970	2980	2962
2925			2944	2942	2930
		2911		2920	
2880	2885	2886	2882	2884	2874
2835	2840	2838	2836	2840	2852
	1650				
1625	1620	1633		1627	
1610				1604	
1500	1535	1540	1550	1550	
1380	1375	1380	1378	1375	1377
	1360				
1298	1295			1295	1290
1145	1190				
1080	1080				1059
1040					
1025	1010			1015	1016
942	915				
	855	854		858	
825			822		
790	795	795	790		
765	760	769		760	
740	735		737	737	742
720			719		
705	705	708		705	707
					671

Values quoted are ν^{film} in cm.$^{-1}$

Cuts 3 and 4 run on PE 237, all others on Unicam SP 130.

TABLE III

Ultraviolet Data for the Isomeric Methylcyclohepta-1,3,5-trienes and Cuts 3 and 4 from Preparative g.l.c. of Isomerised Octa-1,7-diyne

Cut 3	Cut 4	1-Methyl[112] (121)	2-Methyl[112] (122)	3-Methyl[112] (123)	7-Methyl[111] (120)
259 $\varepsilon = 2200$	264-266 $\varepsilon = 2750$	269 $\varepsilon = 3400$	258 $\varepsilon = 2600$	260 $\varepsilon = 3800$	258 $\varepsilon = 3310$

Values for 1-, 2-, and 3-methyl isomers are $\lambda^{\text{EtOH}}_{\text{max}}$; all others are $\lambda^{\text{c.hexane}}_{\text{max}}$.

TABLE IV

Proton Magnetic Resonance Data for the Isomeric Methylcyclohepta-1,3,5-trienes and Cuts 3 and 4 from Preparative g.l.c. of Isomerised Octa-1,7-diyne

Cut 3	Cut 4	1-Methyl (121)	2-Methyl (122)	3-Methyl (123)	7-Methyl (120)
3.53 doublet	3.55 triplet	3.6 triplet	3.55 doublet	3.6 doublet	3.4 triplet
3.95 mult.	3.95 mult.	3.98 mult.	3.98 mult.	4.01 triplet	3.93 doublet
4.75 mult.	4.7 quartet	4.74 quartet	4.72 mult.	4.75 mult.	4.97 quartet
7.86 triplet	7.7 doublet	7.75 doublet	7.85 triplet	7.75 mult.	8.4 mult.
8.16 doublet	8.0 doublet	8.05 singlet	8.15 singlet	7.96 triplet	8.65 doublet

All samples run in carbon tetrachloride with T.M.S. as internal reference. Mid-points only of multiplets are quoted (τ).

flow. Peak heights used to calculate percentage composition).

Cuts 3 and 4 produced in each case ~ 50% of methylcycloheptane, no starting material, and several other peaks.

Cut 5 did not contain any cyclooctane, nor any starting material, but did have one major component, presumed to be cyclooctene.

Literature reports reveal that complete hydrogenation of eight membered unsaturated carbocycles is not possible under some conditions, cyclooctene being the major product in most cases. Possibly a similar limitation may apply to the hydrogenation of the seven carbon ring compounds. Isomerisation on the catalyst surface may be a further complicating factor, especially when an excess of catalyst is present.

Isomerisation of Octa-1,7-diyne: Identification of Transitory Intermediates.

(i) The diyne (5 g.), was heated under reflux (2 hrs.) from cold with the base (potassium tert-butoxide from 1.85 g. potassium in a 1:1 molar ratio) in diglyme (500 ml.) under nitrogen. The product was isolated as before, and had ν^{film} 3000 (s), 2940 (vs), 2880 (s), 1970 (w), 1920 (w), 1720 (w), 1650 (w), 1620 (m), 1490 (s), 1450 (s), 1380 (m), 790 (m), 775 (m), 745 (vs), 700 (s) cm.$^{-1}$; $\lambda_{\text{max}}^{\text{c.hexane}}$ 269 (ε = 400), 280 (ε = 400), 293 (ε = 450), 306 (ε = 305) $m\mu$. [Lit.[142] for octa-1,3,5,7-tetraene (103b); $\lambda_{\text{max}}^{\text{iso-octane}}$ 267, 278, 290, 304 $m\mu$. (ε = several thousand - immeasurable accurately due to decomposition)].

Analytical g.l.c. (50 m. Ap'L' capillary, 80°, 18 p.s.i.) showed one major component (R_T relative to ethylbenzene 1.23) apart from the aromatic hydrocarbons. Preparative g.l.c. [20% poly(ethyleneglycol), 2 m. x $\frac{1}{4}$" o.d., 96°, 18 p.s.i.] yielded five cuts, the last consisting of this major product. This was collected as a solid (colourless platelets at 0°) which gave a single peak on re-chromatography. $^{\text{film}}$ 2922 (s), 2858 (m), 1435 (m), 1340 (w), 1320 (w), 1260 (m), 1025 (w) cm.$^{-1}$; end absorption only in the ultraviolet.

Hydrogenation over palladium/charcoal (10%; 96% of calculated uptake for four double bond equivalents) yielded *n*-octane (identified by g.l.c.). These properties, as well as its correspondence to the compound isolated in section (ii), show this intermediate to be octa-2,6-diyne (124).

(ii) Octa-1,7-diyne was heated under reflux in a solution of potassium tert-butoxide in tert-butanol (1.5 molar; 4:1 ratio of base to diyne) for 24 hrs. under nitrogen.[122] Analytical g.l.c. [50 m. poly(ethylene:glycol) capillary, 50°, 20 p.s.i./6.5, total flow = 75 ml./min.] showed the mixture to have the following composition after 10 hrs. reflux. (A number of minor peaks were present also).

R_T (mins.)	% Composition *	Compound
7.36	8	ethylbenzene
7.92	7	*p*-xylene
8.16	14	*m*-xylene
11.0	26	*o*-xylene
30.6	43	unknown.

* Calculated from peak heights.

Preparative g.l.c. [25% poly(ethyleneglycol) 600, 12' x $\frac{3}{8}$", 125°, 140 ml./min.] again yielded several cuts, the last of which was the unknown, identified as octa-2,6-diyne (124), colourless platelets at 0°, i.r. and end absorption in the u.v. identical with that given above under (i). A mass spectrum had the parent peak at $^m/_e$ 106, i.e. C_8H_{10}; n.m.r. absorption showed signals at 7.75 (singlet, 4H), and 8.25 (singlet, 6H) τ. No octatetraene (103b) or allene could be detected spectroscopically.

(iii) Hydrogenation over palladium/charcoal (10%) in ethyl acetate of the product obtained by method (i), followed by examination of this material by analytical g.l.c. (50 m. Ap'L' capillary, 84°, 18 p.s.i.) demonstrated the presence of all three xylenes, ethylbenzene, n-octane, cyclooctane and methylcycloheptane in the proportions as indicated in Fig. 14 (p. 28).

<u>Isomerisation of Octa-1,7-diyne; Filtered Solution of Base.</u>

A hot dispersion of potassium tert-butoxide in diglyme (~ 2% concentration) was carefully filtered through a sintered glass filter under nitrogen. The resulting dilute solution (~ 0.2 molar concentration, by titration) to which the diyne was added, gave complete conversion to o-xylene and ethylbenzene after 2 hrs. reflux (with only traces of other components, Fig. 15) as shown by analytical g.l.c. (50 m. Ap'L' capillary, 75°, 18 p.s.i.)

SECTION III

Synthesis of Hydrocarbons Isomeric with Octa-1,7-diyne.

7-Methylcyclohepta-1,3,5-triene (120)[111,173]

(i) Bromine (40 g.) in carbon tetrachloride (125 ml.) was added with stirring over 3½ hrs. to a solution of cyclohepta-1,3,5-triene (ex Shell, 23 g.) in 200 ml. of carbon tetrachloride at 0°. The dibromotropilidene complex obtained on removal of the solvent, was heated in vacuo for 72 hrs. (55-60°/15-20 mm.). The solid greenish-yellow cake was ground in a mortar under carbon tetrachloride, filtered off, washed, and dried in vacuo at room temperature. The crude product (38 g. 90%), m.p. ~140° dec. [lit.[173] 163-165 dec.] was shaken vigorously with absolute ethanol (350 ml., added at reflux) till solution was complete. The resulting dark solution was set aside at -50° for several hours, filtered rapidly, and the solid washed with cold absolute ethanol (at -50°; 50 ml.) to give a dark solid (25 g.; m.p. ~140° dec.). Removal of solvent of crystallisation by heating under vacuum resulted in yellow crystals of tropylium bromide [(126) same indefinite melting point]: ν_{max}^{nujol} 1250 (m), 1210 (m), 1040 (m), 980 (m), 670 (s), 650 (s) cm.$^{-1}$; λ_{max}^{EtOH} 243-248, 205-215 mμ. (ε = 1,130, 1,660).

(ii) The crude tropylium bromide (126), 4 g. was added over 30 mins. to a solution of methylmagnesium iodide in ether (75 ml.; from 0.8 g.

magnesium and 47 g. methyl iodide). This mixture was stirred for 1 hr. at 20°, then refluxed for a further 30 mins. Excess Grignard reagent was decomposed with ice, the mixture extracted with ether, and the extracts washed, dried, and concentrated to yield 1.3 g. (52%) of a brown oil. This was purified by preparative g.l.c. (25% Cyano 'P' column, 15' x $\frac{3}{8}$", 75°, 190 ml./min.) to give pure 7-methylcyclohepta-1,3,5-triene (120). The spectral characteristics (i.r., u.v., n.m.r.; Tables II, III, IV) were in agreement with values quoted in the literature.

<u>1-, 2-, and 3-Methylcyclohepta-1,3,5-trienes.[112,174] [(121), (122), (123)]</u>

(i) Birch reduction of <u>o</u>-toluic acid [(127), 25 g.] with methanol and sodium/liquid ammonia yielded 1,4-dihydrotoluic acid [(128), 23 g.; 90%] m.p. 74-76° from pentane, (lit.[174] 74-76°); $\nu_{\max}^{\text{nujol}}$ 1720 (vs), 890 (vs), 690 (m) cm.^{-1}

(ii) Lithium aluminium hydride reduction of the dihydrotoluic acid (16 g.) in ether gave 1,4-dihydro-2-methylbenzyl alcohol (129) as an oil (15 g.; 92%), n_D^{20} 1.5024 (lit.[112] n_D^{20} 1.5053), which was purified by distillation (b.p. 109°/26 mm.); $\nu_{\max}^{\text{film}}$ 3400 (vs), 1040 (vs), 890 (s), 690 (s) cm.^{-1}

(iii) The p-toluenesulphonyl derivative (130) of this alcohol was obtained in 62% yield (by the action of p-toluenesulphonyl chloride in dry pyridine for 44 hrs. at 0-5°), m.p. 42-43° from ethanol (lit.[112] 42-43°); $\nu_{\max}^{\text{nujol}}$ 1360 (vs), 1180 (vs), 1170 (vs), 890 (s), 690 (s) cm.^{-1}

(iv) Solvolysis of this tosylate [(130), 6 g.] in glacial acetic acid (7 g. ; sodium dihydrogen orthophosphate as buffer) at 90° for 36 hrs. yielded 4.7 g. of a mixture of the required methylcycloheptatrienes and of the acetates arising from the alcohol. This mixture was separated into its hydrocarbon and ester fractions by chromatography (alumina, Grade II) with n-pentane as eluant. Preparative g.l.c. (25% Cyano 'P', 15' x $\frac{3}{8}$", 75°, 180 ml./min.) of the hydrocarbon fraction yielded the pure 1-, 2-, and 3-methylcyclohepta-1,3,5-trienes, identified by a comparison of their spectral properties (Tables II, III, IV) with published data.[112,123].

Analytical g.l.c. on three different columns [50 m. poly(ethylene-glycol) capillary; 20% silver nitrate/tri(ethyleneglycol); 20% Cyano 'P'] of the hydrocarbon mixture prior to separation, showed it to consist of 16%, 16%, and 60% of the 2-, 3-, and 1-methyl isomers, as well as 8% o-xylene. These values differ from the literature findings,[112] but later work in this thesis, (p. 117), shows that these isomers can readily interchange under the action of heat alone.

Attempted Preparation of Monobromocycloocta-1,5-dienes[113] [(131),(132)]

Cycloocta-1,5-diene [(32), ex Cities Service; 47 g., 0.44 mole], N-bromosuccinimide (53 g., 0.3 mole) and benzoyl peroxide (2 g.) in carbon tetrachloride (250 ml.), were heated under reflux for 3 hrs. to yield a yellow oil (after removal of the precipitated succinimide by filtration, and concentration of the solution). Distillation of this oil, even under reduced pressure, caused gross decomposition and was discontinued; (recovered 11.1 g., 10% yield); ν^{film} 1630 (w), 760 (s), 710 (s) cm.$^{-1}$ Chromatography over silica gel resulted in decomposition, but use of neutral alumina (Grade I or II) gave a small amount of colourless needles, m.p. 119-125°, (found to be dibromide, p. 109) in later fractions. The oil obtained from earlier fractions seemed to consist of isomerisation products. No further purification was attempted.

Preparation of Dibromocyclooctadienes[113] [(133a), (133b)]

A bromination method identical to that described above was used, except that a 2:1 molar ratio of N-bromosuccinimide to cycloocta-1,5-diene was employed. Thin layer chromatography (silica; petrol; iodine spray) showed two main spots as well as a minor one. (A single product could never be obtained, despite variations in the reaction conditions). The oil obtained was chromatographed over alumina (Woelm, neutral, Grade II, pentane as eluant) to yield a solid, m.p. 122.5-123.5° sub., (lit.[113] 124-125°), in the later fractions. This, unlike the oil in earlier fractions, was a single compound, and corresponded to the spot with the lowest R_f in the t.l.c. of the reaction mixture.

This solid had $\nu^{\text{KBr}}_{\text{max}}$ 1645 (w), 1150 (s), 840 (s), 783 (s), 753 (s), 719 (m), 708 (s), 578 (s) cm.$^{-1}$; $\lambda^{\text{c.hexane}}_{\text{max}}$ 224 mμ.(ε = 3400);

the n.m.r. showed multiplets centred at 4.3, 5.4, 6.4, 7.2 τ in the ratio 2:1:1:1. The mass spectrum had a parent triplet at $^m/e$ 264, 266, 268, (1:2:1 ratio), arising from the presence of two bromine atoms in the molecule. Found: C 36.3; H 3.8 : $C_8H_{10}Br_2$ requires C 36.1; H 3.8. For a discussion of the probable structure (133b) and reactions of this compound see the Appendix (p. 146).

Preparation of Cycloocta-1,3,5-triene[113] (101)

The oily product from the attempted preparation of mono-bromocycloocta-1,5-diene was heated under reflux (3 hrs.) with potassium tert-butoxide in tert-butanol. The reaction mixture was cooled, water was added, this mixture was extracted with ether, and the extracts dried and concentrated to give a yellow oil. (Potassium hydroxide in triethylene glycol, heated under reflux for 1 hr. was equally effective). Chromatography of this over alumina (Grade I) with pentane as eluant gave a colourless oil; ν^{film} 1640 (w), 1630 (w), 1210 (w), 1000 (w), 820 (m), 800 (m), 770 (m), 735 (m), 700 (vs) $cm.^{-1}$ Analytical g.l.c. [25% poly(ethyleneglycol), 12" x ¼", 80°, 45 ml./min.] revealed one minor and two major components. The two major components were obtained pure by preparative g.l.c. [25% poly(ethyleneglycol), 12' x ⅜", 75°, 80 ml./min.]; cycloocta-1,5-diene was eluted first and identified by its i.r. spectrum. The later compound was shown to be cycloocta-1,3,5-triene by its spectral properties; ν^{film}_{max} 850 (w), 820 (m), 780 (s), 740 (m), 705 (vs), 650 (vs) cm.$^{-1}$, identical with published data.[172].

Preparation of 1,2-Bis(2,2-dibromocyclopropyl)ethane.[115,175] (136)

Trial attempts to generate dihalocarbenes from sodium trichloro-;acetate[176] or phenylmercury tribromomethane[177,178] failed, so bromoform/potassium tert-butoxide in pentane was used (as outlined by Skattebol[115]).

(i) Redistilled bromoform (68.2 g.; 0.25 mole) was added to a stirr hexa-1,5-diene [(134), 8.2 g.; 0.1 mole, ex Lights, checked by i.r. and hexa- g.l.c.] in dry pentane at 0-5° over 6 hrs. Stirring was continued for g.l.c.] in dry pentane at 0-5° over 6 hrs. Stirring was continued for a further 18 hrs., during which the temperature was allowed to rise to ambient. Water was then added, the solution extracted with ether, and the extracts washed, dried and concentrated to yield 58.7 g. of an oil (containing some bromoform). Purification was attempted by two methods.

Firstly, repeated fractional distillation of this oil (29 g.) yielded a fraction (3.8 g.) which gave only a single spot on t.l.c. (silica; petrol; iodine spray), b.p. 86-88°/14 mm.; n_D^{20} 1.5175, (lit.[179] b.p. 78-80°/12 mm.; n_D^{20} 1.5180). This oil had ν^{film} 1640 (m), 1110 (m), 1045 (m), 995 (m), 920 (s), 690 (s) cm.$^{-1}$ and the n.m.r. showed multiplets centred at 4.1, 4.93, 7.7, 8.38, 8.8 τ (ratio of 1:2:2:4:1). These spectral properties were identical with reported values.[179].

A mass spectrum showed parent peaks at $^m/e$ 210, 212, 214 (1:2:1

ratio) corresponding to $C_4H_4Br_2$. This is obviously a fragmentation product of the original molecule, and ions corresponding to fragments of the alkyl chain were also observed. These spectral features and physical properties permit this material to be identified as the mono-addition product 1,1-dibromo-2(but-3-enyl)cyclopropane (135) obtained by Skattebol[179].

Chromatography of the distillate residues (1.5 g.) on alumina (Grade II, 50 g.) with pentane as eluant (5 ml. fractions) yielded a further 0.35 g. of the mono-adduct (135), and 0.6 g. of a solid, m.p. 68-69.5° (lit.[179] 68-70°), which had ν^{film} 1220 (m), 1210 (m), 1120 (s), 1050 (s), 1015 (s), 930 (w), 760 (w), 690 (vs) cm.^{-1} The n.m.r. had multiplets centred at 8.25, 8.75 τ (ratio 4:1) identical with quoted values.[179] The mass spectrum showed parent ions at approximately $^m/e$ 422, 424, 426, 428, 430 (ratio 1:4:6:4:1) due to $C_8H_{10}Br_4$. The quintuplet (and the ratio of these peaks) indicates the presence of four bromine atoms in that molecule. This product would therefore appear to be the diadduct 1,2-bis(2,2-dibromocyclopropyl) ethane (136).

Secondly, a pentane solution of the crude oily product (30 g.) was washed repeatedly (x 25) with aqueous methanol (70:30, methanol:water) until no absorption due to bromoform was visible in the infrared. The pentane solution was dried and concentrated to yield 5.7 g. of material. This concentrate, after chromatography on alumina (Grade II, 180 g., pentane as eluant, 5 ml. fractions) yielded pure mono-adduct (135), 42 g.

and diadduct [(136), 0.8 g.] rrespectively.

The combined yield from this reaction was 8.35 g. (34%) of monoadduct (135), and 1.4 g. (4%) of diadduct (136). Although the reaction was repeated several times, the yield of diadduct never exceeded 10% (corresponding yield of monoadduct 31%).

(ii) Bromoform (7.6 g., 0.03 mole) was added over 1 hr. to a stirred slurry of potassium tert-butoxide (from 1.2 g. potassium) and the monoadduct [(135), 5 g., 0.02 mole, obtained as under (i)] in dry pentane at 0-5°. Stirring was continued for a further 23 hrs., during which time the temperature rose to ambient. Water was added, the mixture extracted with ether, the extracts washed, dried and concentrated to yield an oil. A pentane solution of this oil was washed repeatedly with aqueous methanol to yield 4.6 g. of bromoform free product. This, after chromatography on alumina, gave 1.3 g. (15%) of the diadduct (136), and a recovery of 2.8 g. (55%) of the starting mono-adduct material (135).

Attempted Preparation of Octa-1,2,6,7-tetraene.

(i) From 1,2-Bis(2,2-dibromocyclopropyl) ethane[115] (136)

A solution of methyl-lithium in ether was prepared and estimated by titration, using standard methods.[180] In general, an ethereal solution of methyl-lithium was added dropwise to a solution (25 ml.) of the diadduct (136) in dry ether (in a 2.5:1 molar ratio) over 20 mins. with stirring and cooling, (-30° - -40°). Stirring was continued for

30 mins. at this temperature, then for a further 30 mins. at ambient. Water was added, the ether layer separated off, washed till neutral, dried and concentrated.

Reaction times were varied from 1 to 2 hrs., temperatures from -75° to 15°, and the ratio of base to diadduct from 2.5:1 to 4:1, but in every case, only starting material could be recovered, (as determined by i.r. and t.l.c.). The diadduct (136) was resistant to methyl-lithium under these conditions.

(ii) From Octa-1,7-diyne[116]

Phosphorus pentachloride (61 g.; 0.3 mole) and octa-1,7-diyne (6.75 g., 0.068 mole) were stirred vigorously in benzene (150 ml.) for 60 hrs. at room temperature. The pale yellow suspension was poured onto crushed ice (~ 400 g.), and this mixture was stirred for 1 hr., then extracted with ether. The benzene/ether solution was washed with brine, dried (sodium sulphate), and concentrated. The resulting semi-solid was taken up in light petroleum (40°-60°) and extracted with 10% potassium bicarbonate. The aqueous alkaline extract was acidified with dilute sulphuric acid, and the liberated chlorophosphonic acid (138) isolated by ether extraction as a brown gum (4.25 g.) after concentration. This had ν_{max}^{film} 3400 (s), 2300 (m), 1730 (s), 1680 (s), 1620 (s), 1120 (s), 1030 (s), 950 (s), 850 (m), 760 (m) cm.$^{-1}$

The crude chlorophosphonic acid [(138), 4 g.] was dissolved in 2N sodium hydroxide (40 ml.), and the solution heated under reflux

(5 hrs.) on a steam bath. The reaction mixture was extracted with pentane (after cooling), and the extracts were washed, dried, and concentrated to give an oil (250 mg., 13%) which had $\nu_{\max}^{\text{film}}$ 3300 (m), 1970 (m), 1710 (w), 1620 (m), 860 (s), 840 (s) cm.$^{-1}$ (lit.[116] $\nu_{\max}^{\text{film}}$ 860, 840 cm.$^{-1}$) and $\lambda_{\max}^{\text{pentane}}$ 208, 212 mμ.

Analytical g.l.c.[50 m. poly(ethyleneglycol) capillary, 53°, 17 p.s.i./5.8, total flow = 55 ml./min.] showed two major compounds, which had retention times of 12.52 and 39.36 min. respectively, neither of them octa-1,7-diyne (R_T = 20.28 min.) comprising 71% and 18% of the total product. The first compound was assumed to be octa-1,2-diene-7-yne (139); the later compound was not thought to be the diallene (125). Due to scarcity of material, no further data was obtained, but the second component may be octa-1,3-diene-7-yne (140), obtained by further rearrangement of the allenic moiety.

SECTION IV.

Base catalysed Isomerisation of C_8H_{10} Hydrocarbons and Related Species.

General Procedure:

The hydrocarbon under examination was heated under reflux (~160°) in a dispersion of potassium tert-butoxide in diglyme (molar ratio 1:2) for 3-4 hrs. under nitrogen. The isolation procedure was identical to that used in the isomerisations of octa-1,7-diyne. The products were capillary] examined by i.r. and analytical g.l.c. [50 m. poly(ethyleneglycol) capillary], which gave a quantitative evaluation (using peak heights, Table V).

o-Xylene and Ethylbenzene:

These hydrocarbons were recovered unchanged, m- and p-xylene were absent.

Cycloocta-1,5-diene:

On heating under reflux with the above reagent this hydrocarbon yielded cycloocta-1,3-diene (60%), starting material (38%) and others (2%). Reaction with potassium hydroxide in diglyme for 3 hrs. produced starting material (60%), the conjugated diene (38%) and others (2%) as before. Reaction with potassium tert-butoxide in tert-butanol for 4 hrs. yielded only starting material.

Cyclohepta-1,3,5-triene:

The standard treatment for 3 hrs. yielded unchanged cycloheptatriene. Heating in diglyme without base did not cause isomerisation either.

Methylcyclohepta-1,3,5-trienes:

Each of the methylcycloheptatriene isomers (i.e. 7-, 1-, 2-, and 3-methyl) was heated under reflux with the basic medium to form identical equilibrium mixtures in each case (Table VI). Aromatic products were not detected.

These same methylcycloheptatrienes, when refluxed (without base) under identical conditions again produced equilibrium mixtures, but of varying composition, probably because longer reaction times are necessary for true equilibrium to be attained (Table VII). (These equilibrations, especially of the 7-methyl isomer, constitute a simple preparation of the other isomers in only three stages).

TABLE VI

Base Catalysed Isomerisation of Methylcyclohepta-1,3,5-trienes

Isomers in Product (% composition)

Starting isomer	7-Methyl	1-Methyl	2-Methyl	3-Methyl
7-Methyl	2	61	15	20
1-Methyl	3	55	15	23
2-Methyl	2	58	14	19
3-Methyl	2	62	15	20

TABLE VII

Thermal Isomerisation of Methylcyclohepta-1,3,5-trienes.

Starting isomer	Isomers in product (% composition) 7-Methyl	1-Methyl	2-Methyl	3-Methyl
7-Methyl	32	14	0	55
1-Methyl	4	86	5	5
2-Methyl	4	50	33	4
3-Methyl	6	31	4	56

Cycloocta-1,3,5-triene:

The triene, on treatment with the standard reagents was recovered largely unchanged (52%). However, by analytical g.l.c. on several columns [20% silver nitrate/tri(ethyleneglycol); 5% B 34/5% dinonylphthalate; 50 m. poly(ethyleneglycol) capillary] it was shown that ethylbenzene (10%) was also produced, along with bicyclo[4:2:0]octa-2,4-diene (28%, the valence tautomer of cycloocta-1,3,5-triene,[31] and several other minor compounds, (11% of total).

Octa-1,2-diene-7-yne (139):

The crude allene-yne was heated under reflux (8 hrs.) with a 6:1 molar excess of the base. The products analysed as o-xylene (51%), ethylbenzene (30%), m- and p-xylene (9% and 4%) with 6% other compounds. Neither of the two major constituents of the starting material were present.

Octa-1,7-diyne:

The diyne, when heated under reflux (8 hrs.) in diglyme without base, was recovered unchanged.

Octa-1,2-diene-7-yne (139):

Similarly, heating under reflux (8 hrs.) without base of the crude allene-yne material gave o-xylene (7%), ethylbenzene (4%), m-xylene (23%) and p-xylene (9%), together with some recovery of the constituents (38% and 13% respectively) originally in the starting material, as well as other minor products, (6% total).

SECTION V

Preparation and Dehydrobromination of the Tetrabromocyclooctanes

Preparation of Tetrabromocyclooctanes (205), (206).

(i) A solution of pyridinium bromide perbromide[43,181] (120 g., 0.33 mole) in pyridine/methanol (4:1, 400 ml.) was added slowly with stirring to a solution of cycloocta-1,5-diene (20 g., 0.185 mole) in benzene/methanol (1:1, 400 ml.) at room temperature and the mixture allowed to stand overnight. Most of the methanol was removed under reduced pressure, the mother liquors added to water (500 ml.), and extracted with ethyl acetate. The extracts were washed with 6N hydrochloric acid, dried, concentrated, and the residues (39 g.) crystallised from ethanol to give the tetrabromide as colourless crystals (16.2 g., 21%) m.p. 100-110° (lit.[110] 97-110°). Thin layer chromatography showed two spots (silica; petrol; iodine spray). Chromatography on silica (500 g.), with the mixture (10 g.) dry-packed onto the column, and elution with petrol-carbon tetrachloride (25 ml. fractions) separated the isomeric tetrabromides. The first tetrabromide (5.2 g.) had m.p. 133.5-135° (lit.[110] 135°); $\nu_{max.}^{nujol}$ 1214 (s), 1010 (s), 994 (s), 963 (m), 890 (m), 785 (m), 693 (m), 673 (s) cm.$^{-1}$ (Fig. 17). N.m.r. had absorption at 5.15-5.25 (doublet), 7.05 (trip.), 7.25 (doublet), 7.5 (singlet), 7.8 (singlet), 8.0 (singlet)τ (Fig. 16). Found C, 22.22; H, 2.86. Calculated for $C_8H_{12}Br_4$, C, 22.44; H, 2.80. The mass spectrum (hot box) failed to show a parent ion, but peaks due to P -Br at $^{m}/e$ 345, 347, 349, 351, (quartet, 1:3:3:1 ratio) were present. Peaks at 266, 268, 270 (1:2:1) and 187, 189 (1:1) due to P -2, and P -3 bromine atoms respectively were also present.

The second tetrabromide (2.9 g.) had m.p. 136.5-138° (lit.[110] 139°); $\nu_{\text{max.}}^{\text{nujol}}$ 1250 (s), 1148 (s), 1075 (s), 928 (s), 913 (s), 810 (s), 665 (s), 657 (s) cm.^{-1} (Fig. 17). N.m.r. showed broad singlets at 5.4 and 7.5τ, (Fig. 16). Found C, 22.21; H, 2.94. Calculated for $C_8H_{12}Br_4$, C, 22.44; H, 2.80. The mass spectrum was identical with that of the first isomer.

(ii) Bromine (16 g., 6 ml.) in carbon tetrachloride (50 ml.) was added to cycloocta-1,5-diene (5 g.) in 25 ml. carbon tetrachloride (with stirring) over 3 hrs. at room temperature. Stirring was continued overnight; the solution was washed thoroughly, dried, and then concentrated to give 6.8 g. (34%) of the same tetrabromides (t.l.c.; i.r.) as a solid of m.p. 103-121°, plus a large amount of oil which gave a positive test for halogen and showed absorption due to <u>cis</u> double bonds in the i.r.

Zinc Debromination of the Tetrabromides[110]

Each of the tetrabromides (400 mg.) in ethanol (10 ml.) was stirred and heated under reflux (8 hrs.) with a suspension of activated zinc[182] (500 mg.). After cooling the reaction mixture, water was added, and the solution was extracted with pentane (after filtering off excess zinc). The pentane extracts were washed, dried, and concentrated. Analytical g.l.c. [50 m. poly(ethyleneglycol) capillary, 51°, 20 p.s.i./6.8, total flow = 80 ml./min.] and i.r. showed the product to be cycloocta-1,5-diene, with only traces of other material. The result for each tetrabromide was identical.

Dehydrobromination of the 1,2,5,6-Tetrabromocyclooctanes.[43]

(i) A solution of the mixed tetrabromides (10.1 g., 0.024 mole) in diglyme (50 ml.) was added over 30 mins. with stirring to a suspension of potassium tert-butoxide (from 6.6 g. potassium, 0.169 mole) in diglyme (50 ml.) under nitrogen at 30°. Heating was started after the initial exothermic reaction (causing a black coloration) had moderated and continued at 130° for 8 hrs. The mixture was cooled, water added, and then extracted with pentane. The pentane solution was washed repeatedly, dried, and concentrated. The brown oil (1 g., 40%) was filtered through alumina (Grade I) to give a clear oil after concentration; ν^{film} 1640 (w), 1610 (w), 845 (w), 820 (m), 790 (vs), 750 (m), 725 (vs), 710 (vs) cm.^{-1}; $\lambda_{\text{max.}}^{\text{c.hexane}}$ 254 (sh), 260, 266, 272 mμ (Fig. 18) [benzocyclobutene[51] $\lambda_{\text{max.}}^{\text{EtOH}}$ 260, 266, 272 mμ. Analytical g.l.c. (Fig. 19a) [50 m. poly(ethyleneglycol) capillary, 50°, 20 p.s.i./6.3, total flow = 70 ml./min.] showed the mixture to consist of styrene (7%), benzocyclobutene (32%), cyclooctatetraene (1%), and a major unknown compound (42%). Comparison of available data left by Willis showed this last compound to be the same unknown as obtained by him, and which has now been identified as cyclo-octa-1,3,5-triene (p.126).

(ii) A solution of the mixed tetrabromides in diglyme was dehydrobrominated under identical conditions to those described above. Aliquots of 1 ml. were removed at regular intervals over 24 hrs. and worked up as described previously. The products were then examined by g.l.c. (conditions as before). The percentage compositions were calculated from the peak heights of the components in the mixture and plotted against reaction time. (See Fig. 20).

Dehydrobromination of Tetrabromides I and II (205), (206).

The following method was used for both isomers.

(i) A solution of the tetrabromide (1 g.) in 10 ml. diglyme was added over 5 mins. to a suspension of potassium tert-butoxide (from 0.66 g. potassium, 1:7 molar ratio) in 25 ml. diglyme at 30° and under nitrogen. Heating was commenced after addition and the reaction mixture maintained at 130° for 10 hrs. when, as before, water was added, and the mixture extracted with pentane. The extracts were washed, dried and concentrated. The yields of the isomerisation product from tetrabromides I and II were respectively 91.3 mg. (30%) and 126.3 mg. (50%). Analytical g.l.c. [50 m. poly(ethyleneglycol) capillary, 52°, 17.5 p.s.i./6.3, total flow 65 ml./min.] showed that their products consisted of benzocyclobutene

(57% and 52%), styrene (17% and 12%), cyclooctatetraene (4% and 0%), cycloocta-1,3,5-triene (identified later, 19% and 31%), and bicyclo[4:2:0]octa-2,4-diene (identified later, 2% and 6%). In each case the composition is similar to that obtained from a mixture of both, though the amount of cycloocta-1,3,5-triene present this time was less - possibly due to the longer reaction time and resultant polymerisation.

Dehydrobromination of the Tetrabromides Under Other Conditions.

(ii) 1 g. of the mixed tetrabromide isomers in 25 ml. dimethylsulphoxide (previously dried and distilled from calcium hydride, b.p. 75°/10 mm.) was added to a solution of potassium tert-butoxide (from 472 mg. potassium, 5:1 molar ratio of base to tetrabromide) in 25 ml. of the solvent. This was stirred at room temperature for 24 hrs., then at 70° for a further 6 hrs. The mixture was cooled, water added, then extracted with pentane; the extracts were washed repeatedly, dried and concentrated. Analytical g.l.c. (as above) showed that cyclooctatetraene (66%), benzocyclobutene (4%) and styrene (26%) were present as well as 4% unidentified material.

This reaction was repeated on the same quantity of material, in the same proportions, except that heating was commenced immediately after addition of the tetrabromide to the basic solution, and the temperature was maintained at 80-90° for 24 hrs. The extraction procedure was as before. Analytical g.l.c. showed that cyclooctatetraene

(26%), benzocyclobutene (19%) and styrene (6%) formed 51% of the total reaction products, the remainder having shorter retention times. (These may be further reduction products).

(iii) A suspension of potassium tert-butoxide in diglyme was filtered hot through sintered glass under nitrogen. This solution was titrated to estimate the concentration of base present. A volume of this, sufficient to provide a 6:1 molar ratio was added to a solution of the tetrabromide in diglyme. The mixture was then heated under reflux for 8 hrs. under nitrogen. This was then cooled, water was added, and the mixture was extracted with pentane. The extracts were washed dried and concentrated. Analytical g.l.c. showed that the product contained styrene (35%), benzocyclobutene (37%), cycloocta-1,3,5-triene (24%) and its valence isomer, bicyclo[4:2:0]octa-2,4-diene (6%).

(iv) 5,7-dibromocycloocta-1,3-diene [(133b), see Appendix] was heated under reflux (10 hrs. at 160°) with potassium tert-butoxide (1:8 molar ratio) in diglyme under nitrogen. Benzocyclobutene (44%), styrene (3%), and cyclooctatetraene (9%) as well as cycloocta-1,3,5-triene (32%) were obtained as usual.

SECTION VI

Isomerisation of Cycloocta-1,3,5,7-tetraene. (Table IX)

General Procedure.

(i) Cyclooctatetraene (ex Aldrich, one peak on g.l.c., 3.1 g.) was heated under nitrogen at 130° for 8 hrs. with potassium tert-butoxide (from 5 g. potassium, 1:4 molar ratio) in diglyme (100 ml.). Isolation of the product with pentane in the usual way gave a brown oil (1.23 g., 40%) which yielded a colourless liquid after filtration through alumina (Grade I); ν^{film} 1640 (w), 1610 (w), 845 (w), 820 (m), 790 (vs), 750 (m), 725 (vs), 710 (vs) cm.^{-1}; $\lambda^{\text{c.hexane}}_{\text{max}}$ 212, 259, 266 (sh), 272 (sh) $m\mu$. (Fig.21). Analytical g.l.c. [50 m. poly(ethyleneglycol) capillary], showed the mixture to consist of benzocyclobutene (9%), styrene (2%), cyclooctatetraene (1%), and another major component (37%) which corresponded to the unknown obtained by Willis (later identified as cycloocta-1,3,5-triene). The remainder of the mixture consisted of materials with shorter retention times, presumed to be reduced materials (Fig. 19b).

(ii) A solution of cyclooctatetraene in diglyme was treated with base and heated under conditions identical to those described above. Aliquots of 1 ml. were removed at regular intervals over 24 hrs., and their products examined by g.l.c. (as before). The percentage composition was again calculated from the peak heights of the components, and plotted against reaction time, (Fig. 22).

Separation and Identification of Isomerisation Products.

(i) Samples (200 μl.) of a pentane solution of the reaction mixture from the isomerisation of cyclooctatetraene were injected onto a 25% Cyano 'P' column (15' x $\frac{3}{8}$", 115°, 150 ml./min.). Five cuts were taken (Fig. 23a), and each was checked by analytical g.l.c. (20% Cyano 'P', 50°, 35 ml./min.). Cuts 3 and 5 contained single compounds; Cut 1 failed to show anything due to insufficient material, while Cut 2 was a mixture of at least two compounds. Isomerisation on rechromatography must have occurred with Cut 4, for apart from the main peak, it showed another with a shorter R_T which could not have been present in the original cut itself.

Cut 1. Insufficient material; no data obtained.

Cut 2. Very little material, but this had $\lambda_{max.}^{pentane}$ 218, 248 mμ.

Cut 3. This had ν^{film} 3015 (s), 2965 (s), 2920 (s), 2880 (s), 1645 (w), 1620 (w), 1375 (w), 1015 (m), 995 (w), 715 (vs), 695 (vs) cm.$^{-1}$; $\lambda_{max.}^{pentane}$ 252 mμ; n.m.r. had peaks at 4.35 (singlet), 7.68-7.75 (mult.), 8.15 (singlet), 8.95-9.05 (doublet) τ. This material was not identified, but its spectral properties were similar to those of 2-methylcyclohepta-1,3,5-triene.

Cut 4. This material had $\nu_{max.}^{film}$ 3005 (s), 2930 (s), 2880 (s), 2825 (m), 815 (m), 775 (s), 745 (m), 705 (s), 645 (s) cm.$^{-1}$; $\lambda_{max}^{pentane}$ 261 mμ; the n.m.r. spectrum showed absorption at 4.15, 4.3, 7.58 τ (all singlets). Comparison of these spectral properties with those of cycloocta-1,3,5-triene (see p.109) confirmed this structural assignment.

Cut 5. This compound showed $\nu^{\text{film}}_{\text{max.}}$ 3065 (m), 2960 (s), 2915 (s), 2815 (m), 1205 (m), 1000 (m), 780 (vs), 718 (vs) cm.$^{-1}$; $\lambda^{\text{pentane}}_{\text{max.}}$ 255 (sh.), 260, 266, 272 mμ; the n.m.r. spectrum showed peaks at 2.95 (doublet), 6.8 (singlet) τ in a 1:1 ratio. These spectral properties, identical to those exhibited by benzocyclobutene, as well as comparison with an authentic sample by analytical g.l.c., proved it to be benzocyclobutene.

(ii) Repetition of this isomerisation, but heating for a period of 24 hrs. instead of 8 hrs. resulted in a difference in composition. Preparative g.l.c. of this product again provided five cuts, (Fig. 23b), checked for purity by analytical g.l.c. [50 m. poly(ethyleneglycol) capillary, 53°, 18 p.s.i./6.1, total flow 60 ml./min.]. This showed that Cut 1 was a mixture of three compounds, Cut 2 was a single compound, while Cut 3 must have decomposed or isomerised because two peaks with shorter R_T than the original cut were obtained.

Cut 1. This material had ν^{film} 3010 (s), 2925 (vs), 1380 (w), 735 (s), 685 (m), 675 (m) cm.$^{-1}$; $\lambda^{\text{pentane}}_{\text{max.}}$ 248 mμ; the n.m.r. spectrum had absorption at 4.3 (doublet), 7.76 (broad singlet), 8.22 (doublet), 8.85-9.0 (doublet) τ. None of the three compounds (g.l.c.) in this cut could be identified.

<u>Cut 2</u>. Both the i.r. and u.v. absorptions of this material were identical with that of Cut 3 from the previous separation. The n.m.r. spectrum obtained this time showed absorption at 4.4 (singlet), 7.7-7.8 (doublet), 8.2 (singlet) τ and nothing at 8.9τ. The mass spectrum showed a parent ion at $^m/e$ 108, (C_8H_{12}), equivalent to a doubly reduced cyclooctatetraene molecule. This C_8H_{12} compound could not be identified.

<u>Cut 3</u>. This compound had ν^{film} 3060 (m), 3020 (s), 2960 (s), 2925 (s), 2870 (m), 1605 (w), 1500 (m), 1455 (s), 1030 (w), 995 (s), 965 (w), 745 (s), 700 (vs) cm.$^{-1}$, very similar to that of ethylbenzene. No ultraviolet absorption could be detected at the concentration used (aromatic absorption <u>is</u> weak), nor was an n.m.r. spectrum available.

<u>Cut 4</u>. This was not collected this time.

<u>Cut 5</u>. Spectral comparison (i.r.) with benzocyclobutene confirmed the identity of this compound.

These "out of sequence" cuts can be explained by the following correlation between the two reactions. (Analytical g.l.c. confirmed this).

			<u>Cuts</u>			
1st reaction (8 hrs.)	1	2	3		4	5
2nd reaction (24 hrs.)		1	2	3	4	5
i.e. components	a	b	c	d	e	f

Isomerisation of Cyclooctatetraene with Other Reagents (Table IX)

(i) Cyclooctatetraene was heated under reflux (10 hrs.) with a molar equivalent of potassium tert-butoxide in diglyme under nitrogen. Analytical g.l.c. showed that the products consisted of benzocyclobutene (13%), styrene (2%), cycloocta-1,3,5-triene (39%) and bicyclo[4:2:0]octa-2,4-diene (11%).

(ii) Cyclooctatetraene was heated under reflux (for either 8 hrs. or 24 hrs.) over potassium hydroxide (1:4.5 molar ratio) in diglyme. Conversion of starting material was more extensive with the longer reaction time (only 13% remaining unchanged as compared to 53 %) and yielded 20% instead of 13% of benzocyclobutene (with a proportionate increase in cyclo:octa-1,3,5-triene).

(iii) A suspension of potassium tert-butoxide in diglyme was filtered hot through sintered glass to remove undissolved solid material, and the resulting solution titrated to estimate the amount of base present. A volume of this solution, sufficient to provide a 1:1 or 2:1 molar ratio, was then employed for isomerisation. With the former ratio, 61% of the starting material was present in the end products (after heating at reflux for 8 hrs.), as compared to 13% for the 2:1 ratio. Simultaneously under these conditions benzocyclobutene (29%) and cycloocta-1,3,5-triene (48%) were also produced.

(iv) Addition of phenothiazine (a free radical inhibitor) to a reaction mixture of cyclooctatetraene and potassium tert-butoxide (1:2

molar ratio) and subsequent heating at reflux (8 hrs. at 160°) yielded as usual starting material (29%), benzocyclobutene (11%), styrene (3%) and cycloocta-1,3,5-triene (7%).

(v) No isomerisation occurred when either potassium tert-butoxide in tert-butanol, potassium hydroxide on alumina or solid potassium hydroxide were used.

(vi) Cyclooctatetraene, when heated in contact with solid potassium tert-butoxide for 4 hrs. was completely isomerised to ethylbenzene (50%), and the o-, m-, and p-xylenes (10%, 7% and 5% respectively), without the production of the other products normally obtained. The other products present evidenced shorter retention times during g.l.c. analysis and were presumed to be reduction products. The mixture had ν^{film} 1660 (w), 1600 (m), 1360 (m), 790 (m), 775 (s), 750 (m), 700 (vs) cm.$^{-1}$, typical of aromatic materials.

(vii) Potassium tert-butoxide in DMSO (cf. tetrabromocyclooctane) was not successful as a catalyst. Heating cyclooctatetraene in this medium (either at 20° or ~75° for 24 hrs.) did not produce any isomerisation products; moreover, the starting material could not be recovered (though several techniques were used) and it must be assumed that either reaction with the medium or decomposition prevented simple isomerisation.

(viii) Cyclooctatetraene, benzocyclobutene, or styrene failed to react on heating under reflux without base (8 hrs. at 160°) in diglyme. Similarly heating under reflux of benzocyclobutene or styrene with a suspension of potassium tert-butoxide (1:4 molar ratio) also failed to bring about any isomerisation.

Preparation, Dehydrobromination, and Isomerisation of C_{12} and C_{14} Compounds

Purification of Cyclododeca-1,5,9-trienes.

Commercially available material consisted mainly of the *cis, trans, trans* (116) and *trans, trans, trans*-cyclododeca-1,5,9-trienes (117). Material obtained from Cities Service Research and Development Co., contained mainly the all *trans* isomer. This was isolated by fractional crystallisation, and recrystallised from pentane (x 2) to give a compound m.p. 29-33°, 99% pure. (lit.[183] 31-32°); $\nu_{max.}^{film}$ 1010 (m), 970 (vs), 950 (vs) cm.$^{-1}$; n.m.r.(CDCl$_3$) showed absorption at 4.97, 7.97 τ (broad singlets, ratio 1:2).

A sample of *cis, trans, trans*-cyclododecatriene (100% pure) was obtained from Aldrich Chemicals; material obtained from Koch-Light was ~98% pure and was used for reactions on a larger scale. The pure material had n_D^{25} 1.5044 (lit.[183] n_D^{25} 1.5051); $\nu_{max.}^{film}$ 1020 (m), 970 (vs), 950 (s), 710 (vs) cm.$^{-1}$; n.m.r. (CDCl$_3$) had absorption at 4.65-4.85, 7.85-7.95 τ (both unresolved multiplets, ratio 1:2).

Bromination of c, t, t-Cyclododeca-1,5,9-triene (116)

(i) With pyridinium bromide perbromide.

A solution of the above reagent (128 g., 0.5 mole) in pyridine/

methanol (4:1, 200 ml.) was added slowly (over 5 hrs.) with stirring to a solution of c,t,t-cyclododecatriene (20 g., 0.125 mole) in benzene/methanol (1:1, 250 ml.) at room temperature, and the mixture allowed to stand overnight. A large volume of water was added (2.5 l.), the solid precipitate filtered off, and the aqueous mixture extracted with ethyl acetate. The ethyl acetate extract was washed with 6N sulphuric acid, aqueous sodium bicarbonate, water and then dried. The solvent was removed to give a brown oil which yielded a further crop of the crystalline hexabromide (222) on standing (49.3 g. total, 61%) m.p. 190-192° (lit.[161] 194-195°). The i.r. spectrum had $\nu_{max.}^{nujol}$ 890 (m), 860 (m), 850 (w), 830 (m), 690 (w), 670 (m) $cm.^{-1}$, identical with that obtained by McCrae;[47] the n.m.r. (pyridine) had absorption at 5.1 (singlet), 5.3-5.45 (triplet), 5.8-6.0 (triplet), 7.65 (broad singlet)τ (Fig. 24a and b). Found, C, 22.11; H, 2.85; $C_{12}H_{18}Br_6$ requires C, 22.44; H, 2.80. T.l.c. showed only one spot (silica, 5% ethyl acetate/petrol, iodine spray).

(ii) With bromine/ethanol.[160]

A solution of bromine (64 g., 0.37 mole) in ethanol (100 ml.) was added with vigorous stirring at room temperature to a mixture of c,t,t-cyclododecatriene (20 g., 0.125 mole) and ammonium carbonate (8 g.) in ethanol (60 ml.) over 4 hrs. Water was added (1 l.) and the reaction mixture extracted with ethyl acetate. This extract was then washed with water and dried. Concentration of this solution gave a brown oil, which yielded some crystalline material on standing (19 g., 24%). Comparison (t.l.c., m.p., i.r., n.m.r.) with the product from (i), showed it to be the same compound.

Bromination of t,t,t-Cyclododeca-1,5,9-triene (117)

(i) With pyridinium bromide perbromide.

A method identical to that used for the bromination of the c,t,t, isomer was used. Reagent quantities and extraction procedures were also the same. The crystalline hexabromide (223) so obtained (31 g., 38%) had m.p. 178-179° (lit.[161] 177-178°); $\nu_{max.}^{nujol}$ 900 (m), 860 (m), 790 (m), 780 (m), 740 (m), 660 (s) cm.$^{-1}$; n.m.r. (pyridine) had absorption at 4.72, 5.25, 7.6 τ (all broad singlets; Fig. 24a and b). Found, C, 22.68; H, 2.98; $C_{12}H_{18}Br_6$ requires C, 22.44; H, 2.80. T.l.c. showed one spot only (silica, 5% ethyl acetate/petrol, iodine spray).

(ii) With bromine/ethanol

The method and quantities used were again identical to those used in the bromination of the c,t,t. isomer. The crystalline solid so obtained (5 g., 6%) was found by comparison (t.l.c., m.p., i.r., n.m.r.) to be the same as obtained in (i) above.

Dehydrobromination of Hexabromocyclododecanes.

(i) 1,2,5,6,9,10-Hexabromide from c,t,t-cyclododecatriene (222).

A solution of the hexabromide (1 g.) in diglyme (10 ml.) was added over 5 mins. to a suspension of potassium tert-butoxide (from 0.6 g.

potassium; molar ratio of hexabromide: base = 1:10) in diglyme (50 ml.) under nitrogen at $\sim 30^\circ$. Heating was started as soon as the initial exothermic reaction had moderated, and was continued at 130° for 14 hrs. The mixture was cooled, water was added, and then extracted with ether. The ethereal solution was washed repeatedly, dried, then concentrated. The brown gum (0.46 g.) so obtained was filtered through alumina (Grade I) with pentane as eluant, to give a clear bromine free liquid on concentration (187 mg., 77%); ν^{film} 1640 (w), 1490 (m), 810 (m), 780 (s), 760 (s), 730 (s), 690 (m) cm.^{-1}; $\lambda^{\text{pentane}}_{\text{max.}}$ 240 $\text{m}\mu$. Analytical g.l.c. [50 m. poly(ethyleneglycol) capillary, 132°, 20 p.s.i./5.5, total flow 50 ml./min.] showed three main components (55%, 15%, 24% respectively) in the reaction mixture. (Fig. 25).

(ii) <u>1,2,5,6,9,10-Hexabromide from t,t,t-cyclododecatriene (223)</u>.

The same reaction was carried out on the other isomer, using identical quantities and conditions. Again a brown gum (255 mg.) was obtained after extraction and yielded a clear liquid (148 mg., 61%) after filtration through alumina. This had ν^{film} 1640 (w), 1495 (m), 820 (m), 790 (m), 770 (s), 730 (m), 685 (m) cm.^{-1}; $\lambda^{\text{pentane}}_{\text{max.}}$ 264 $\text{m}\mu$. Analytical g.l.c. (same conditions), showed the same three components to be present, but these formed 10%, 4%, and 74% respectively of the reaction mixture. (Fig. 25). The reaction was repeated to check the composition of the product, and analysis by g.l.c. again showed it to consist of 11%, 3%, and 68% respectively of the same major components.

Separation and Identification of Dehydrobromination Products of 1,2,5,6,9,10-Hexabromide from c,t,t-Cyclododecatriene (222).

The dehydrobromination was repeated on a larger scale (20 g. hexabromide) under identical conditions (ratio of base to hexabromide, 10:1; heated at ~ 140° for 14 hrs.) to yield 5.4 g. of a brown gum after extraction with ether. This gave 4.73 g. (94%) of a clear oil after filtration through alumina. Analytical g.l.c. (conditions as before) showed that the same three major components were present (14%, 2%, 75% respectively). T.l.c. showed (silica, petrol, iodine spray) one main spot and traces of two others, so the bulk of the product was purified by chromatography (150 g. Merck silica, 50 ml. fractions, iso-pentane as eluant). Fractions 8-23 contained the major constituent of the mixture. These fractions were checked for purity by analytical g.l.c. and purified further by preparative g.l.c. [20% poly(ethyleneglycol), 2 m. x $\frac{1}{4}$" o.d., 150°, 35 ml./min.]. The major constituent was distilled after collection b.p. ~140°/14 mm.; n_D^{20} 1.5963; (lit.[47] b.p. 70°/0.8 mm.; n_D^{20} 1.5980); ν^{film} 1645 (w), 1495 (m), 805 (m), 755 (s), 725 (s), 645 (m) cm.^{-1}; $\lambda_{\text{max.}}^{\text{hexane}}$ 264 $\text{m}\mu$. (ε = 6,450); n.m.r. showed absorption at 2.85 (singlet; 4H), 3.2-4.35 (multiple singlet; 4H) τ and unresolved multiplets centred at 6.4, 7.0, 7.45 τ (total 4H) (Fig. 26). A mass spectrum had a parent ion at $^m/_e$ 156, i.e. corresponding to $C_{12}H_{12}$. This spectral data corresponds to that quoted by McCrae[47] for 1,2-benzocycloocta-1,3,5-triene (225a).

Hydrogenation of the dehydrobromination product (10% palladium/charcoal) gave only one product (as shown by g.l.c., conditions as before). This was shown to be identical (by g.l.c. on several columns) with the product obtained from the dehydrobromination of the tetrabromocyclododecane isomers, i.e. (226).

Dehydrobromination of the Hexabromocyclododecane Isomers in DMSO.

The same quantities and conditions were used in the dehydrobromination of both isomers.

A solution of the hexabromide (1 g.) in DMSO (10 ml.) was added to a suspension of potassium tert-butoxide (from 0.6 g. potassium; molar ratio of base to hexabromide, 10:1) in DMSO (50 ml.) under nitrogen at room temperature. The mixture was heated at 80-90° for 20 hrs. It was then cooled, water added (100 ml.) and extracted with pentane. This extract was washed, dried and then concentrated. The resulting dark brown solution was examined by g.l.c. [50 m. poly(ethyleneglycol) capillary, 132°, 20 p.s.i./5.6, total flow 55 ml./min.]. In each case the peak corresponding to 1,2-benzocycloocta-1,3,5-triene (225a) was the major component (31% and 79% from the hexabromides of c,t,t. and t,t,t. respectively). A series of smaller peaks with much longer retention times was also observed; these may be caused by either poly-unsaturated C_{12} carbocycles or aromatic isomers other than those with a single benzene nucleus. The ultraviolet spectra of both extracts showed broad absorption at $\lambda_{\text{max.}}^{\text{hexane}}$ 245 mμ., but as well as this, both showed ill-defined maxima of lower intensity at $\lambda_{\text{max.}}^{\text{hexane}}$ 310, 330, 345 mμ.

Preparation of Cyclododecene.

Cyclododecanol (1 g.) and sulphuric acid (50 ml.; 1:1 ratio of water:conc. sulphuric acid) were heated on a steam bath for 6 hrs. The reaction mixture was cooled, water (50 ml.) was added, and the mixture neutralised (sodium hydroxide). This was then extracted with ether, the extracts washed, dried, and concentrated to give an oil (0.85 g., 94%) $\nu_{\text{max.}}^{\text{film}}$ 995 (s), 740 (m), 720 (m) cm.$^{-1}$. Analytical g.l.c. [50 m. poly(ethyleneglycol) capillary, 102°, 15 p.s.i./5.0, total flow 35 ml./min.] showed three components. The first (14%) was identified by comparison with an authentic sample as cyclododecane. The other two (57% and 29%) were taken to be trans and cis-cyclododecene [(230) and (231)].

Reduction of Cyclododeca-1,5,9-trienes.

(i) trans,trans,trans-Cyclododeca-1,5,9-triene. (117)

Cyclododecatriene (1 g.) in ethanol (50 ml.) was added with stirring to hydrazine hydrate (100%, 3.5 g.) containing copper sulphate (100 mg.). This mixture was stirred vigorously while air was bubbled through it for 26 hrs. Water (250 ml.) was then added, the mixture neutralised (dil. sulphuric acid) and extracted with pentane. This pentane extract was washed thoroughly, dried and concentrated. Aliquots removed in the course of the reaction were extracted in an identical fashion. The pale yellow oil obtained had $\nu_{\text{max.}}^{\text{film}}$ 995 (s), 990 (s), 985 (m), 730 (s) cm.$^{-1}$. Analytical g.l.c. [50 m. poly(ethyleneglycol) capillary, 102°, 15 p.s.i./5.0, total flow 35 ml./min.] showed four compounds to be present in the mixture (61%, 20%, 11% and 8% respectively), of which the first, second, and last were identified as cyclododecane (233), trans-cyclododecene (230), and starting t,t,t. The third compound was taken to be trans,trans-cyclododeca-1,5-diene (232). This compound formed 29% of the mixture after 4 hrs., but thereafter its concentration decreased steadily.

(ii) cis,trans,trans-Cyclododeca-1,5,9-triene (116)

The same quantities and conditions were used as in (i) above, but the reaction was terminated after 6 hrs. The product had $\nu_{\text{max.}}^{\text{film}}$ 980 (s), 710 (m) cm.$^{-1}$. Analytical g.l.c. again showed that three components were present (19%, 54%, 27% respectively) of which the first and third were identified as cis-cyclododecene (231) and starting c,t,t. The second component was taken to be the cis,trans-cyclododeca-1,5-diene (229).

(iii) Reaction (ii) was repeated on a larger scale as it produced more cyclododeca-1,5-diene.

C,t,t. (100 g.) in ethanol (500 ml.) was added with stirring to hydrazine hydrate (175 g.) containing copper sulphate (500 mg.). The mixture was stirred and air bubbled through it for 30 hrs. (during this time aliquots were withdrawn and analysed to check the rate of reduction). The reaction mixture was extracted as before, and yielded a yellow oil (90.4 g.) after removal of solvent. This had $\nu_{max.}^{film}$ 985 (s), 710 (s) $cm.^{-1}$. Analytical g.l.c. showed cis-cyclododecene (29%), cis,trans-cyclododeca-1,5-diene (49%) and c,t,t. (22%) to be present in the product. These compounds were not separated.

Bromination of cis,trans-Cyclododeca-1,5-diene (229)

Bromine (80 g.) in glacial acetic acid (250 ml.) was added over 7 hrs. with stirring to a solution of the crude cyclododeca-1,5-diene mixture (50 g.; contains 50% of the diene) in glacial acetic acid (250 ml.). Stirring was continued for a further 3 hrs. during which a solid precipitated out of the reaction mixture. This solid (9.4 g.) was filtered off, and identified as the hexabromide of c,t,t. (222) (by t.l.c., m.p., i.r.). Water (500 ml.) was added to the acetic acid solution, followed by aq. sodium bicarbonate till neutral. This solution was extracted with ether, and the extracts washed, dried, and concentrated to give a brown gum (111.7 g.). T.l.c. (silica, petrol, iodine spray) showed the absence of starting material (and only a trace of hexabromide), but two slower moving spots were observed. These spots showed that they contained bromine when sprayed with silver nitrate/fluorescein.

Distillation of this gum was abandoned due to gross decomposition and lack of separation. Chromatography was more successful. The gum (73 g.) was chromatographed over silica (500 g.) with petrol-diethyl ether (200 ml. fractions) as eluant. Fractions 4-13 contained the first compound (19.2 g.) while fractions 14-27 contained mainly the second product (51.7 g.).

A pure sample of the first product was obtained by preparative t.l.c. and distillation, b.p. ~120°/0.35 mm. (lit.[185] 129-131°/0.25 mm.). This yellow oil had $\nu_{max.}^{film}$ 1245 (m), 760 (m), 750 (m), 700 (m), 670 (m) cm.$^{-1}$; the n.m.r. ($CDCl_3$) spectrum had absorption at 5.65 (multiplet; 1,2H), 7.93 (unresolved multiplet; 4H), 8.65 (broad singlet; 16H)τ; in pyridine these values changed to 5.55 (multiplet; 2H), 7.95 (unresolved multiplet; 4H), 8.75 (broad singlet; 16H)τ. Found C, 44.38; H, 6.63. $C_{12}H_{22}Br_2$ requires C, 44.18; H, 6.75. A mass spectrum showed parent ions at $^{m}/e$ 326, 328, 330 (ratio 1:2:1) due to the presence of the two bromine atoms in the molecule. These physical and spectral properties are sufficient to identify this compound as 1,2-dibromocyclododecane (234) - produced from the *cis*-cyclododecene in the starting material.

The crude gum (16 g.) containing the second major component was rechromatographed again over silica (200 g. Merck), with petrol-diethyl ether as eluant (50 ml. fractions). Fractions 34-55 contained the required material (7.5 g.) which consisted of two spots very close together on t.l.c. (silica; 5% diethylether/petrol; iodine spray) and gave a positive test for bromine when sprayed with silver nitrate/fluorescein. A sample of this material was further purified by preparative t.l.c. to give a low melting gum. This had ν^{film} 1250 (m), 910 (w), 790 (w), 670 (m) cm.$^{-1}$; n.m.r. (pyridine) showed absorption at 5.2 (broad singlet; 4H), 7.9 (unresolved multiplet; 8H), 8.6 (broad singlet; 8H)τ. Found C, 31.7; H, 4.5; calculated for $C_{12}H_{20}Br_4$, C, 29.8; H, 4.1. A mass spectrum (probe) showed no parent ion at $^m/e$ 480, but ions at $^m/e$ 401, 403, 405, 407, (1:3:3:1 ratio) due to P-Br were clearly visible. Further fragmentation ions due to loss of more bromine ions were also present. T.l.c. showed this gum to consist of two spots very close together, which had an R_f value intermediate between that of the dibromo- and the hexabromocyclododecanes. These properties and spectral characteristics would indicate this to be a mixture of the 1,2,5,6-tetrabromocyclododecane isomers (235).

Dehydrobromination of Tetrabromocyclododecane (235)

The dehydrobromination of the tetrabromide isomers (1 g.) in diglyme (50 ml.) with potassium tert-butoxide (from 650 mg. potassium; 1:8 molar ratio of tetrabromide to base) was carried out under identical conditions to those given on p.134 for the dehydrobromination of the hexabromocyclododecanes. Heating at 130° was continued for 16 hrs. under nitrogen. Extraction of the reaction mixture with diethyl ether gave 0.54 g. of a brown oil after concentration, and 0.3 g. (91%) of a clear liquid after filtration through alumina (Grade I) with pentane as eluant. Analytical g.l.c. [50 m. poly(ethyleneglycol) capillary, 132°, 20 p.s.i./5.6, total flow 55 ml./min.] showed only one compound, with a retention time identical to that of the hydrogenated 1,2-benzocycloocta-1,3,5-triene [i.e. 1,2-benzocyclooct-1-ene, (226)]. This material was distilled, b.p. ~120°/14 mm.; n_D^{20} 1.5383; (lit.[184] b.p. 64°/0.8 mm.; n_D^{20} 1.5398), and had ν^{film} 1605 (w), 1495 (s), 755 (vs), 710 (s) cm.^{-1}, identical with that obtained by McCrae[47]; $\lambda_{\text{max.}}^{\text{hexane}}$ 252, 257 (ε = 910), 265, 272 mμ. (ε = 820), (lit.[47] $\lambda_{\text{max.}}^{\text{hexane}}$ 265 mμ. (ε = 408); the n.m.r. had absorption at 2.95 (singlet; 4H), 7.25 (triplet; 4H), 8.2-8.7 (broad multiplet; 8H)τ. A mass spectrum had a parent ion at $^{m}/e$ 160, i.e. equivalent to $C_{12}H_{16}$. This evidence proves the compound to be 1,2-benzocyclooct-1-ene (226).

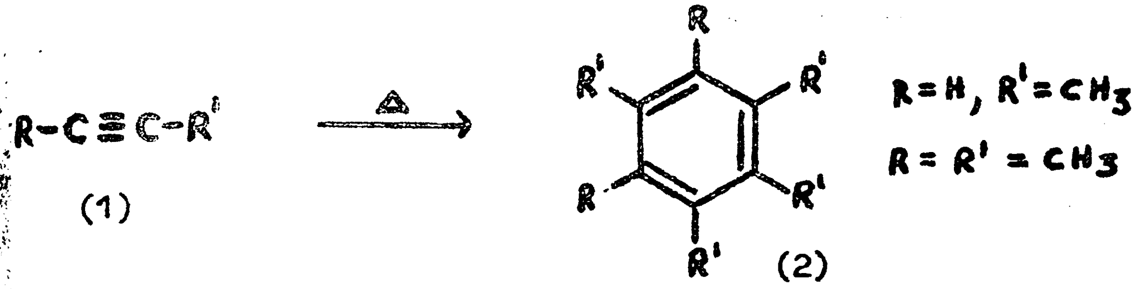
Preparation of Cyclotetradeca-1,8-diyne[43, 46] (53, m = n = 5)

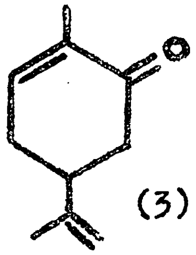
Nona-1,8-diyne (119, n = 5), 1.2 g.; prepared by the general method outlined on p. 89 in dry ether (35 ml.) was added with stirring over 15 mins. to a solution of sodamide in liquid ammonia (from 0.48 g. of sodium and 1 l. ammonia). After 2 hrs. pentamethylenedibromide (2.3 g.) in dry ether (100 ml.) was added over a further 2 hr. period. The reaction mixture was stirred for a further 40 hrs. (more liquid ammonia was added as necessary). Solid ammonium chloride (~10 g.) was then added, followed by ether (100 ml.) and the remaining acetylides were decomposed by the addition of an iced solution of ammonium chloride. The mixture was extracted with ether, the extracts washed, dried and concentrated, to yield the solid cyclotetradeca-1,8-diyne (0.74 g.; 40%) m.p. 98°, (lit.[46] 97–98°); n.m.r. showed absorption at 7.8 (broad singlet; 8H), 8.55 (unresolved multiplet; 12H)τ.

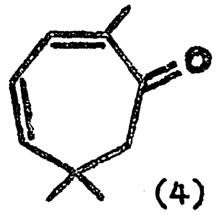
Base Isomerisation of Cyclotetradeca-1,8-diyne (53, m = n = 5)

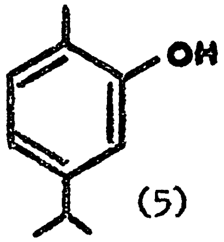
Cyclotetradeca-1,8-diyne (200 mg.) in diglyme (10 ml.) was added to a suspension of potassium tert-butoxide (from 235 mg. of potassium; ratio of base to diyne, 6:1) in diglyme (40 ml.) under nitrogen, and heated under reflux for 14 hrs. The reaction mixture was cooled, water was added, and it was extracted with pentane. The pentane extracts were washed, dried and concentrated to yield a yellow oil (176 mg.; 88%) after concentration. This was distilled, b.p. ~130°/14 mm., and had ν^{film} 1660 (w), 1495 (w), 785 (w), 770 (w), 750 (m), 735 (m), 700 (w) cm.$^{-1}$; $\lambda_{\text{max.}}^{\text{hexane}}$ 250, 274 $m\mu$. (ε = 2,150 and 1,750); n.m.r. had absorption at 2.9 (singlet), 3.2–4.7 (multiple singlets), 7.15 (triplet), 7.75 (multiplet), 8.5 (multiplet)τ. Analytical g.l.c. (50 m. Ap'L' capillary, 160°, 20 p.s.i./5.3, total flow 45 ml./min.) showed two major components (25% and 53%) as well as some starting diyne (14%).

Hydrogenation of the isomerisation product (10% palladium/charcoal) in ethyl acetate gave a colourless oil which was distilled, b.p. ~110°/ 14 mm., and had ν^{film} 1495 (m), 785 (m), 770 (m), 745 (s), 735 (m), 700 (m) cm.$^{-1}$; $\lambda_{\text{max.}}^{\text{hexane}}$ 266, 274 mμ. (ε = 280 and 290); n.m.r. showed absorption at 2.9 (singlet), 7.15 (triplet), 8.45 (singlet), 8.65 (singlet) τ, and no ethylenic protons. Analytical g.l.c. (same conditions) showed three main constituents (25%, 25%, 43%), the first of which was cyclotetradecane. The latter two had retention times identical to two of the components in the unhydrogenated product. At least one of these must be due to an aromatic compound, while the other may be a bicyclic hydrocarbon with a similar retention time to one of the other isomerisation products.


R-C≡C-R'
(1)
Δ
R
R'
(2)
R=H, R'=CH3
R = R' = CH3


(3)


(4)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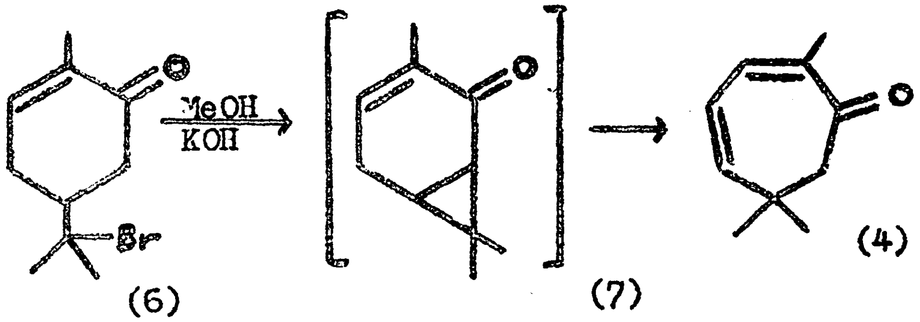
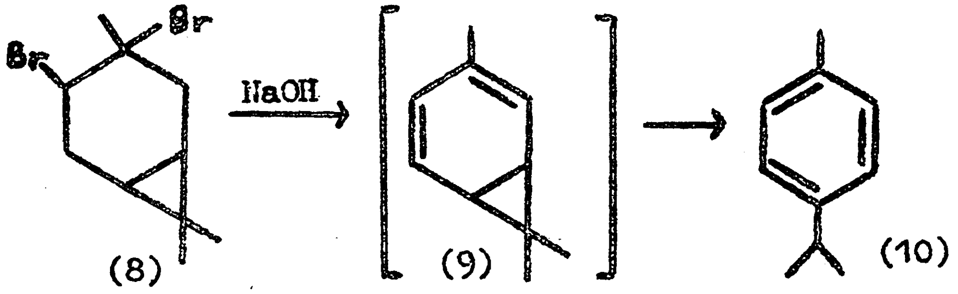
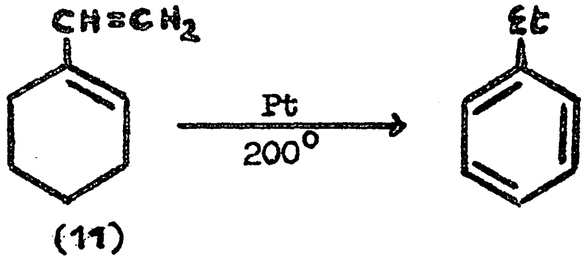
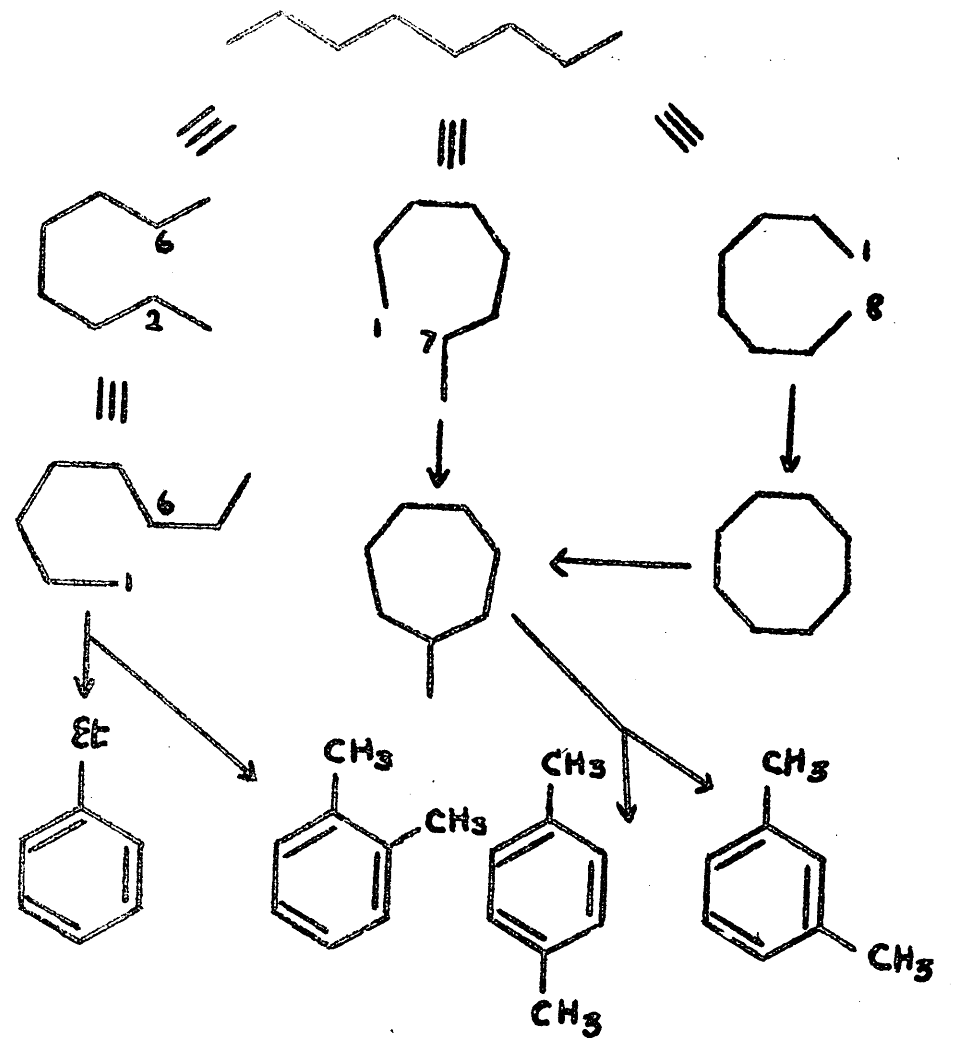
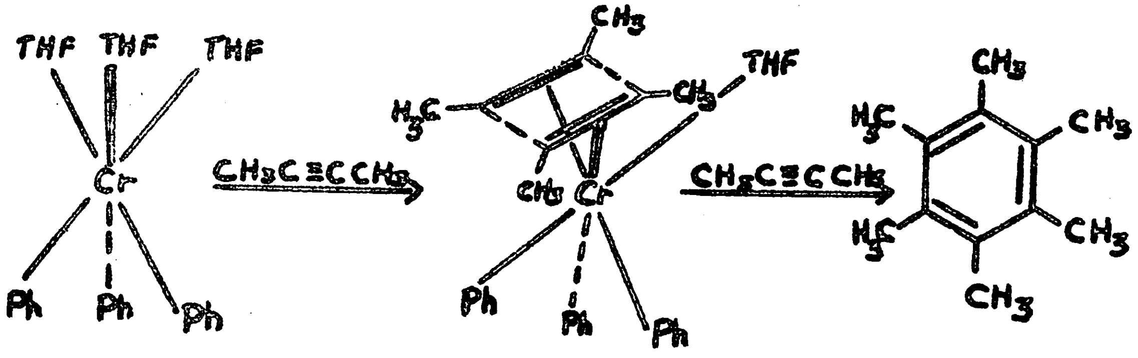

MeOH
KOH
Br
O
(6)
(7)
(4)


Br
Br
NaOH
(8)
(9)
(10)

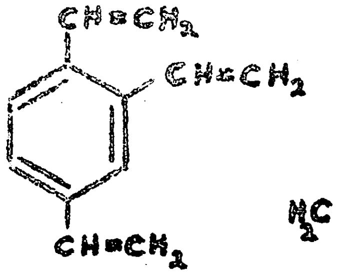

CH=CH2
Pt
200°
Et
(11)



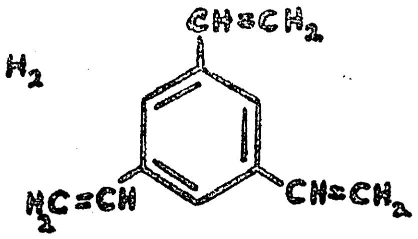
Scheme I



(12) Scheme II (13)



(14)



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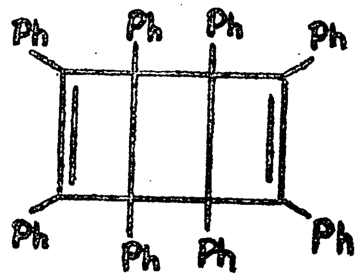

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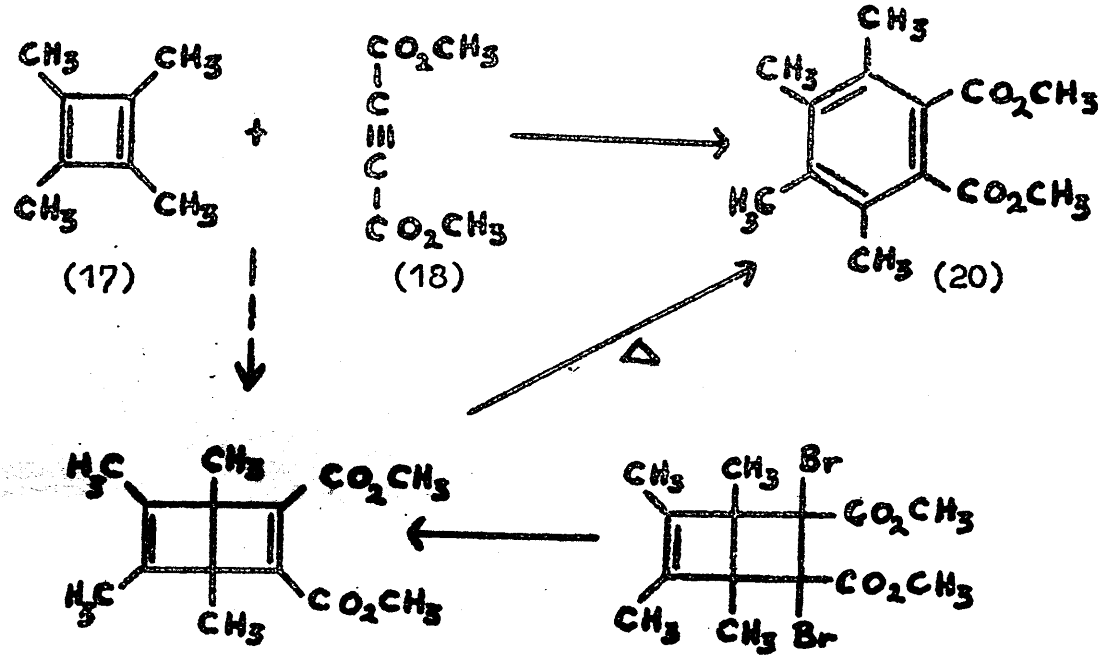
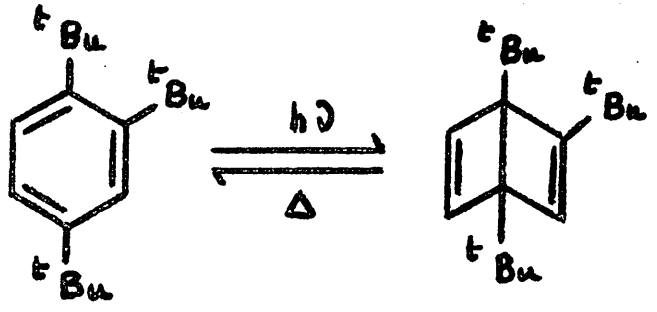


(17) (18) (20)

(19) (21)



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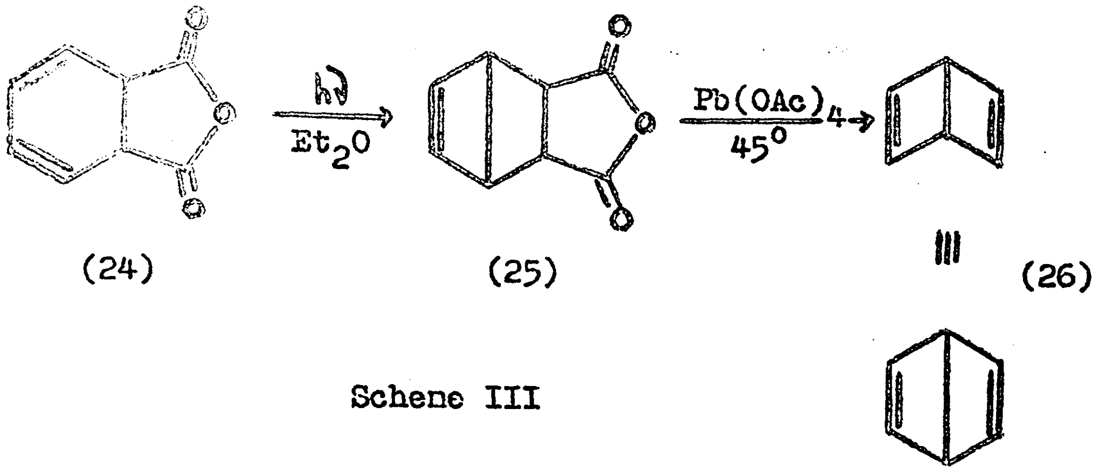
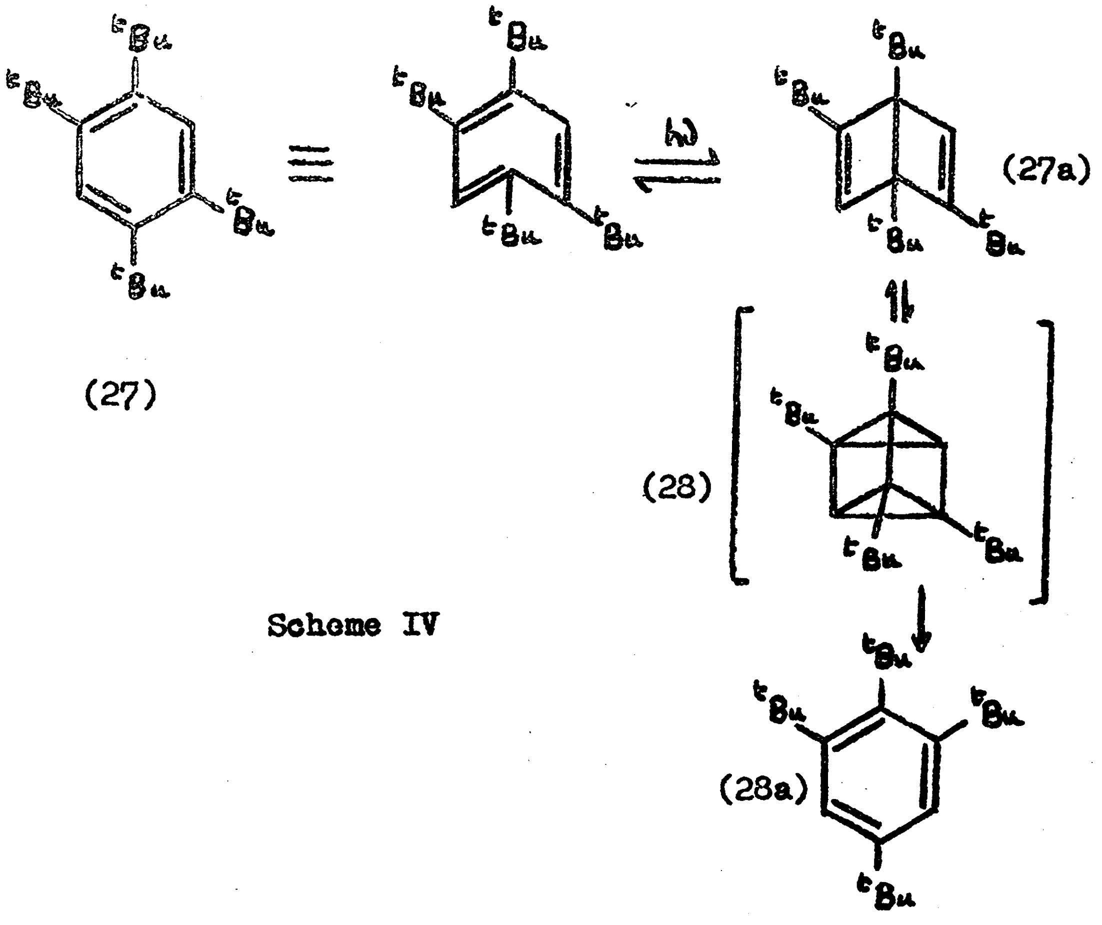
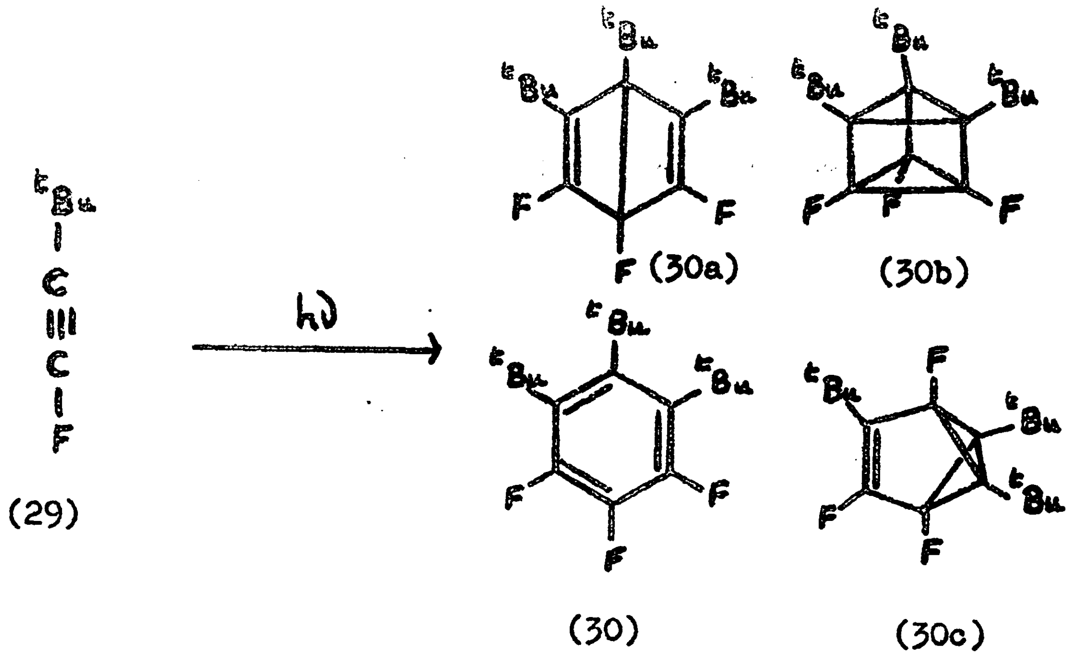


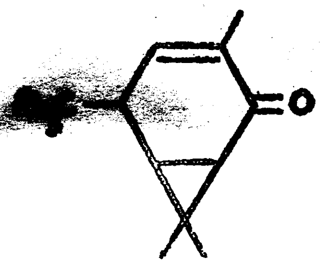
Scheme III



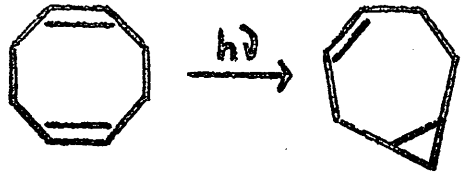
Scheme IV



Scheme V

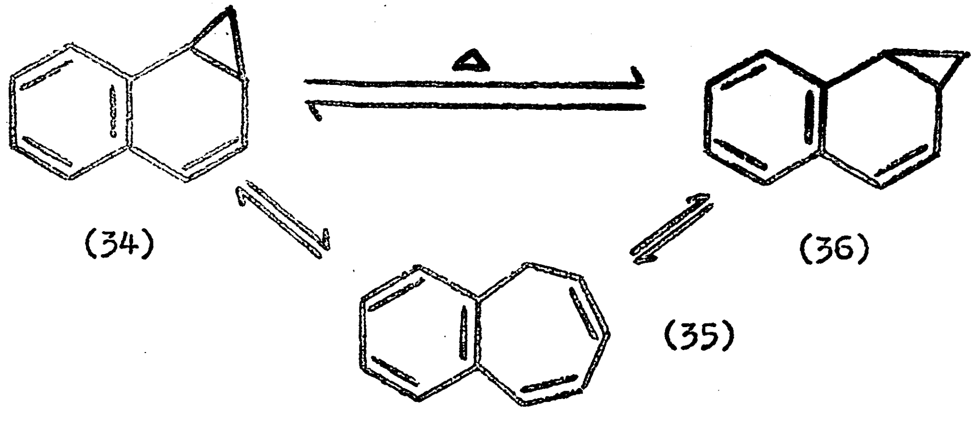


(31)



(32)

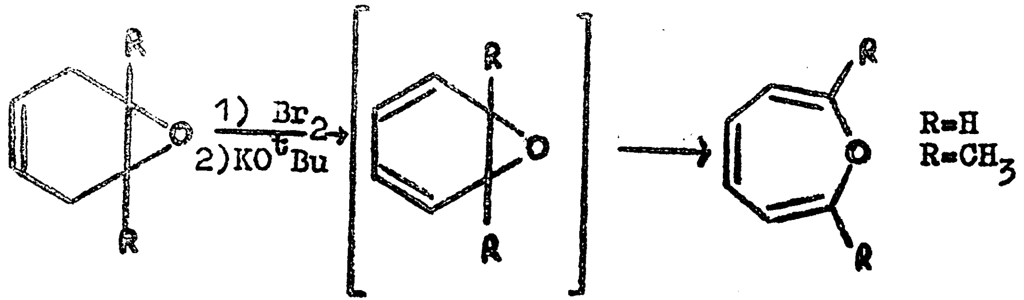
(33)



(34)

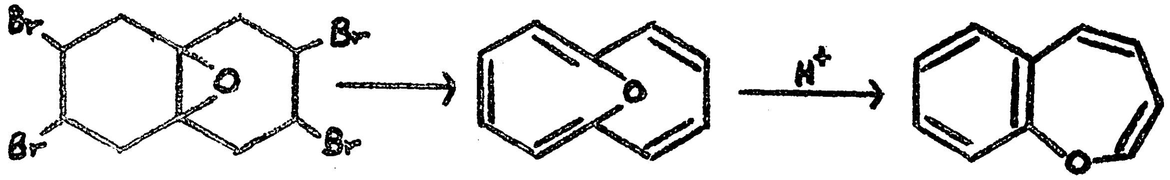
(36)

(35)

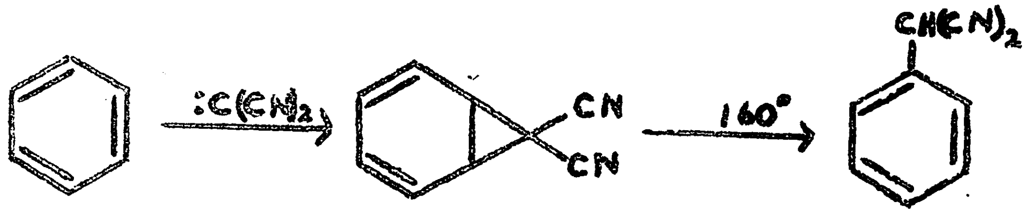


R=H
R=CH$_3$

(37) (38) (39)



(40) (41) (42)



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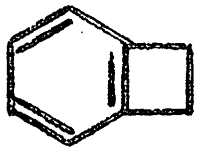

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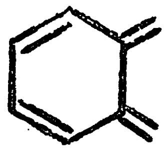

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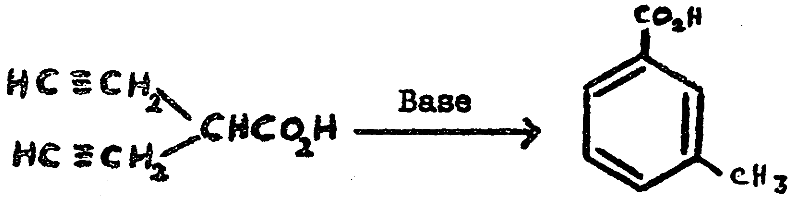

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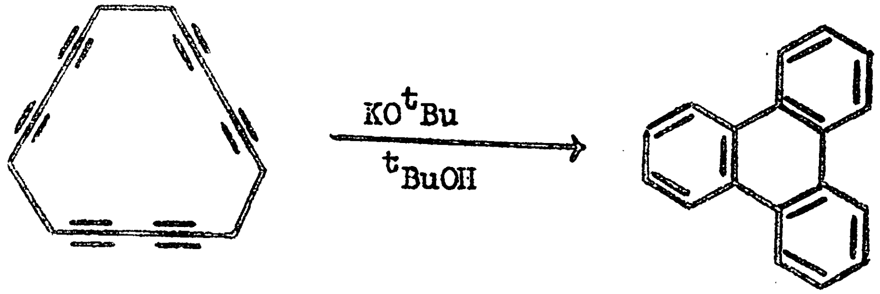
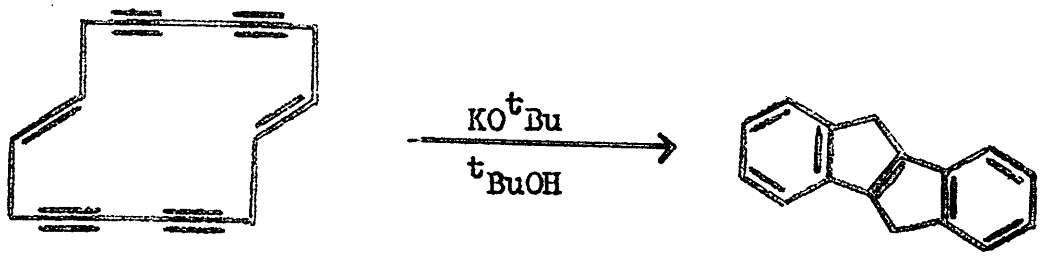


(49) (50)



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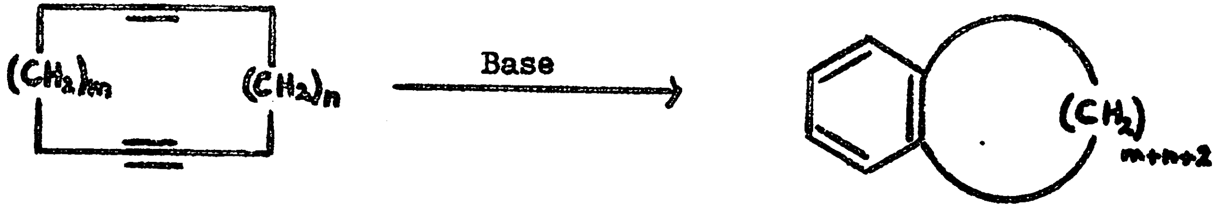

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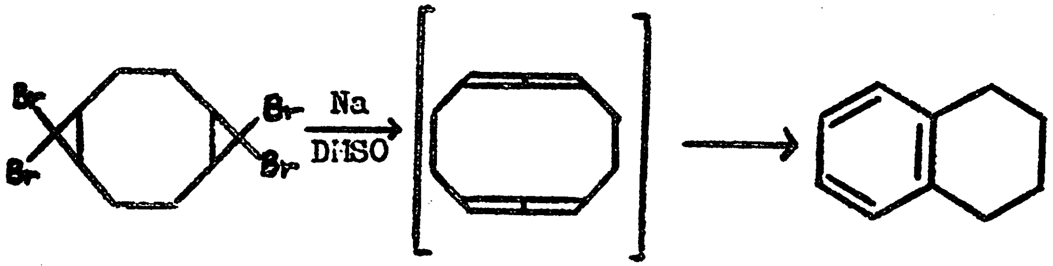
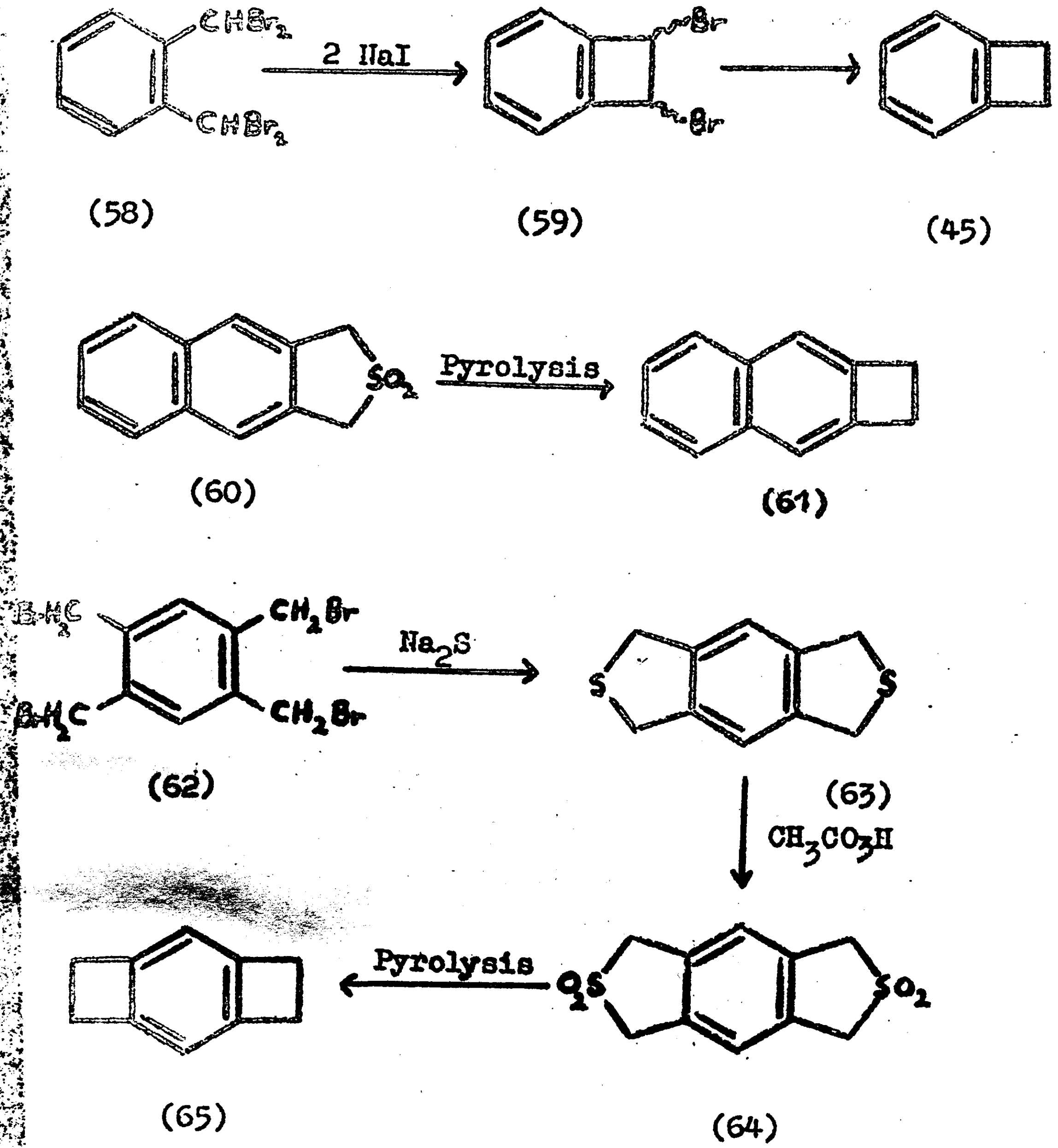
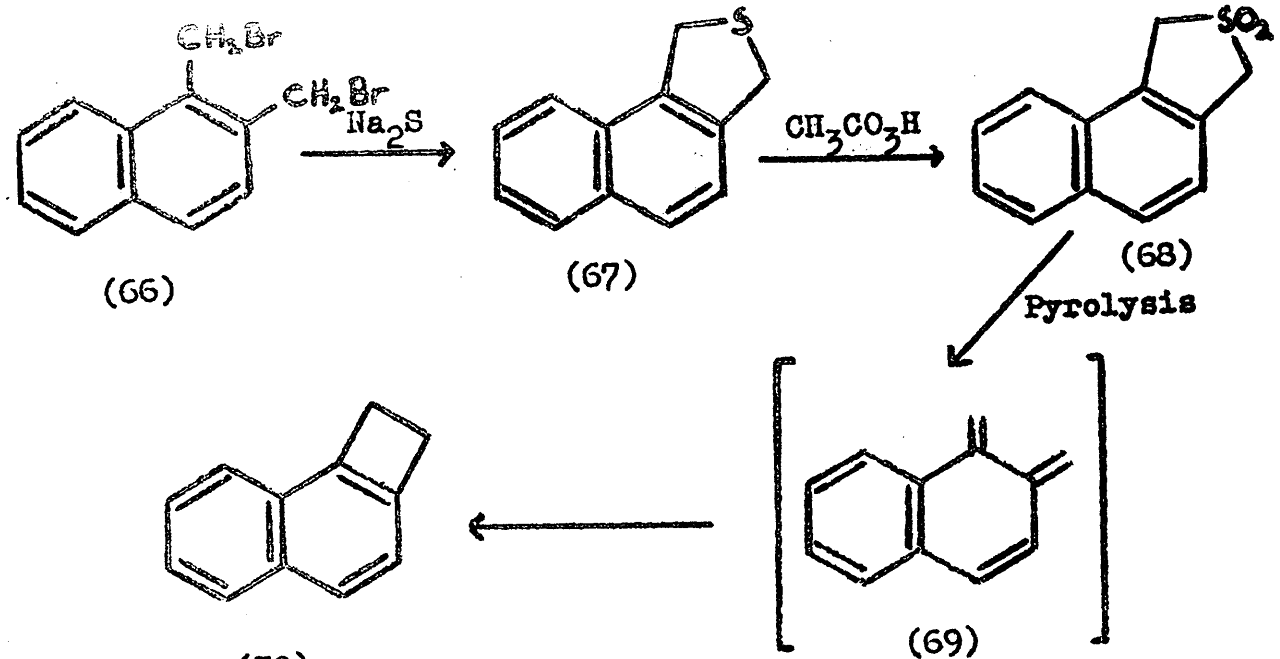
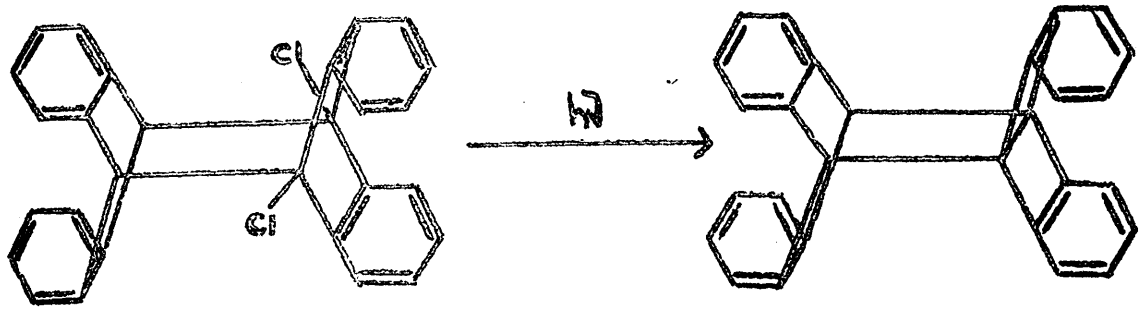


(55) (56) (57)

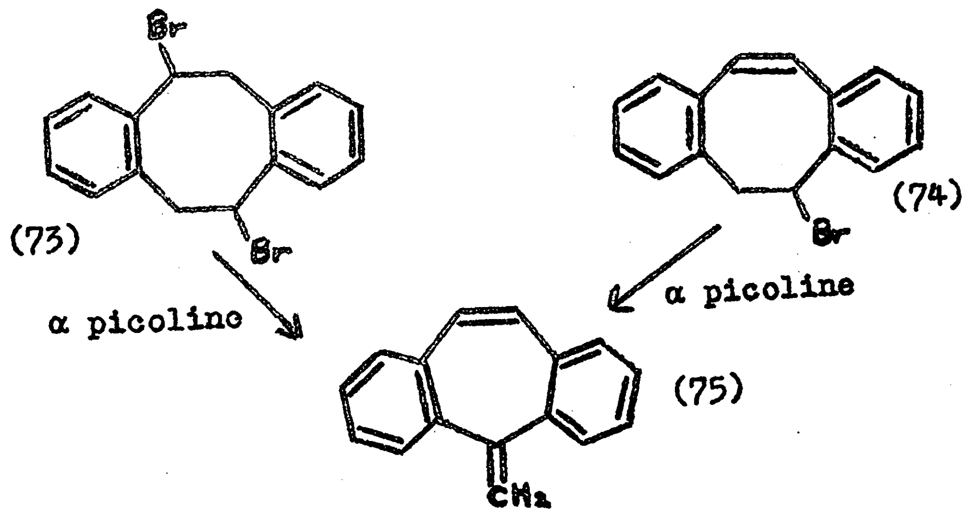

CHBr$_2$
CHBr$_2$
2 NaI
Br
Br
(58)
(59)
(45)
SO$_2$
Pyrolysis
(60)
(61)
BrH$_2$C
BrH$_2$C
CH$_2$Br
CH$_2$Br
Na$_2$S
S
S
(62)
(63)
CH$_3$CO$_3$H
O$_2$S
SO$_2$
Pyrolysis
(65)
(64)



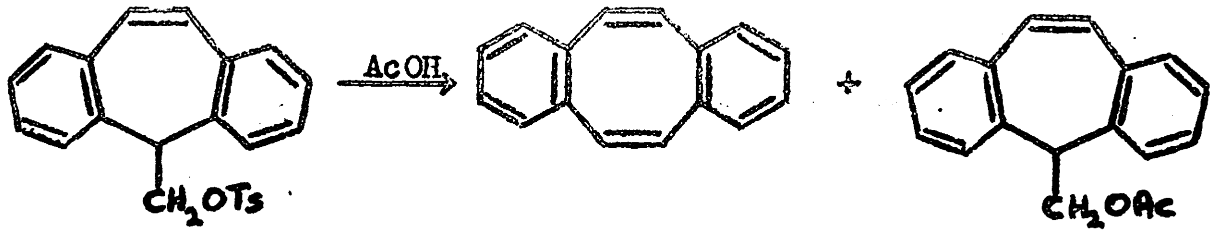
(66) (67) (68) (69) (70)



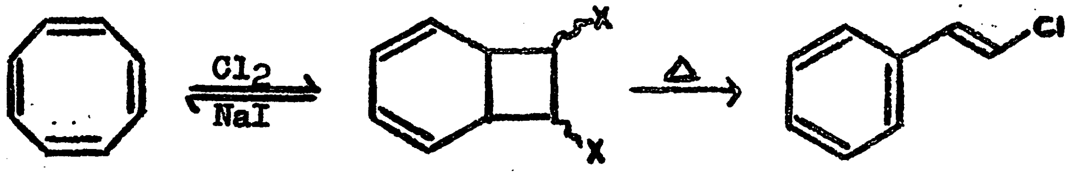
(71) (72)



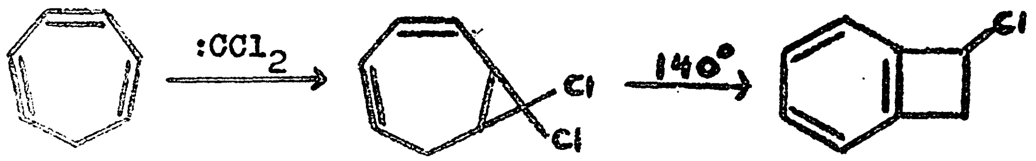
(73) (74) (75)



(76) (77) (78)

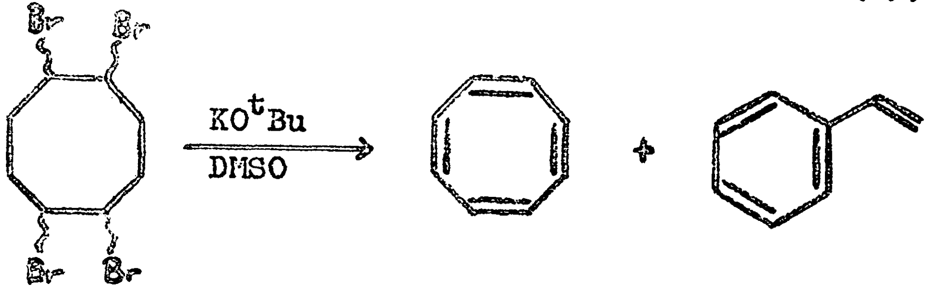


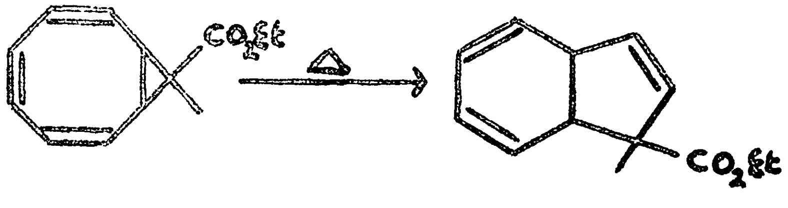
(79) (80; X=Cl) (81)



(82) (83)

(84)





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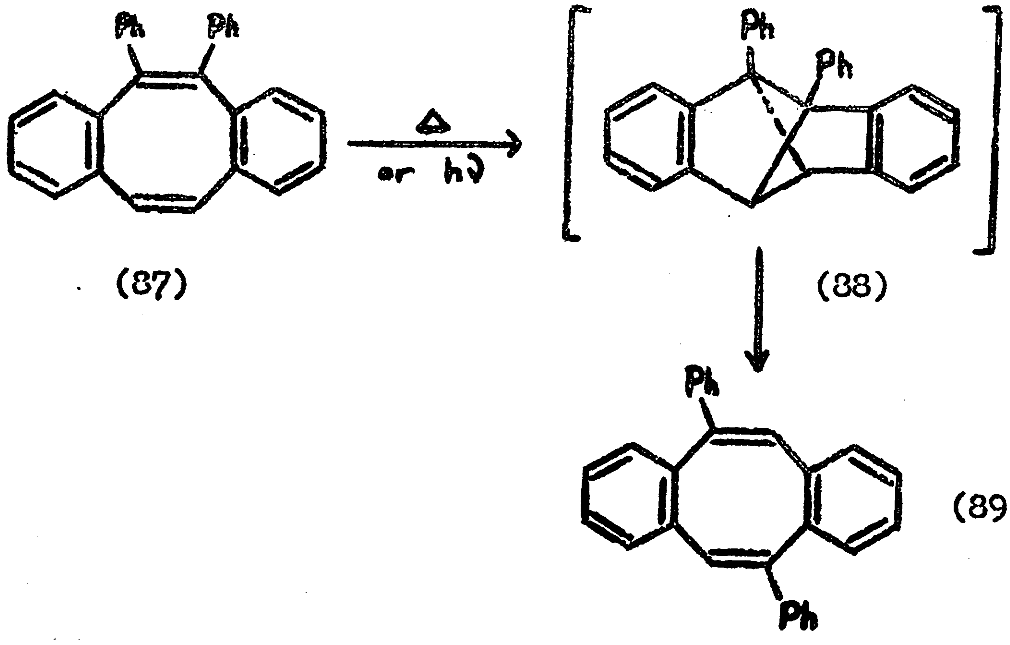

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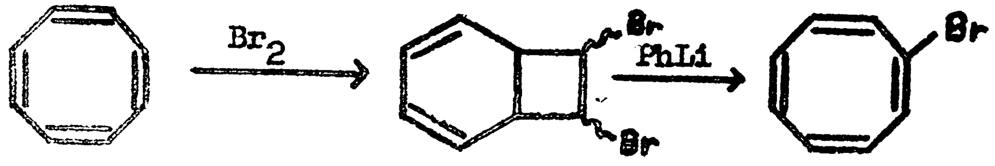

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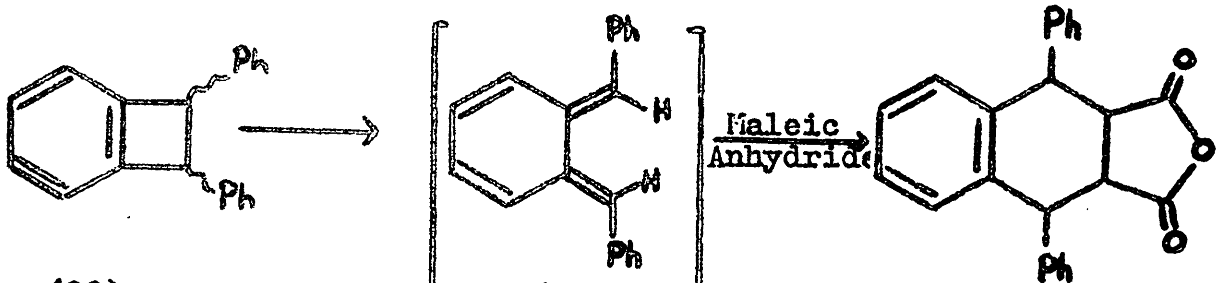
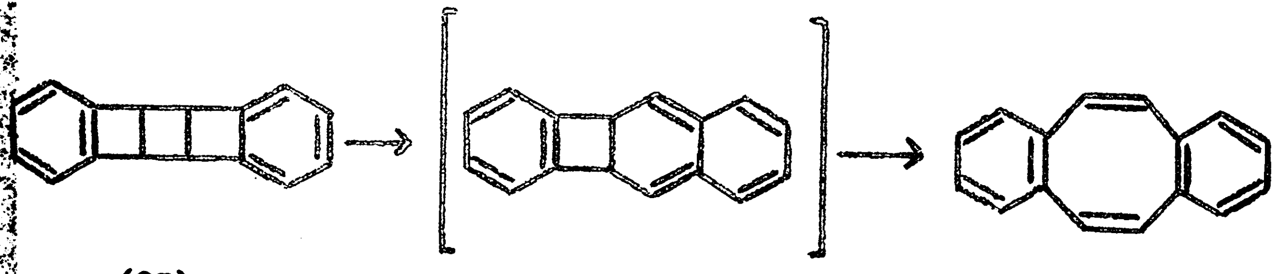


(92) (93) (94)



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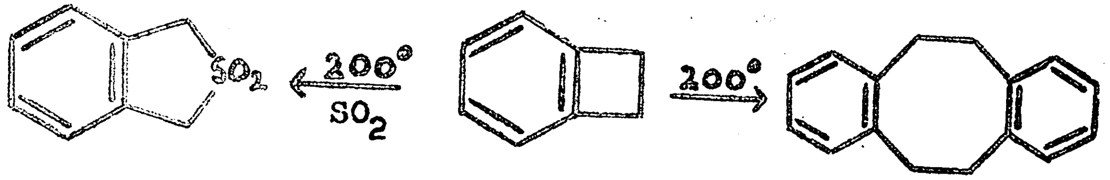
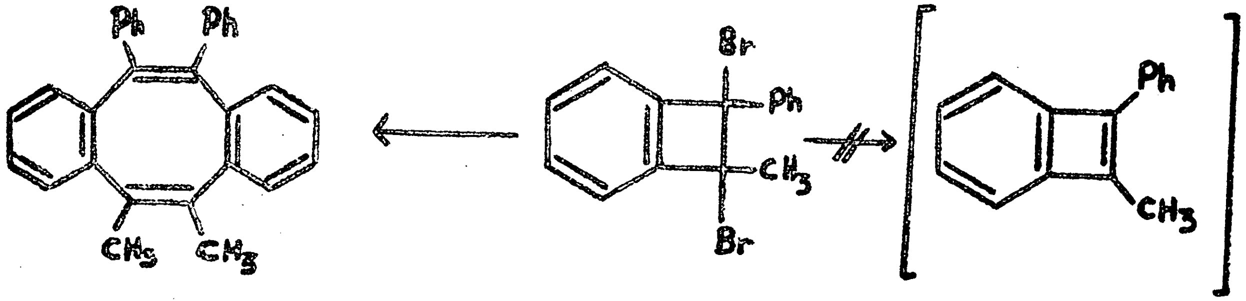


(97)

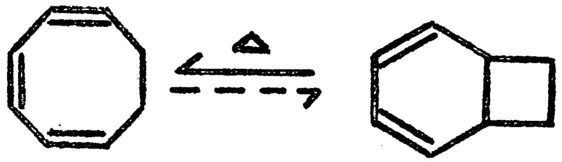
(93)



(100)

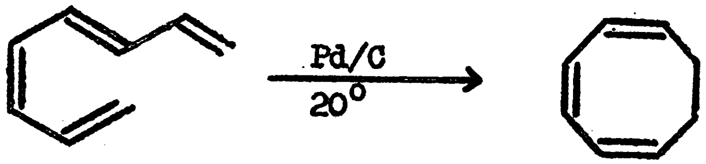
(99)

(100a)



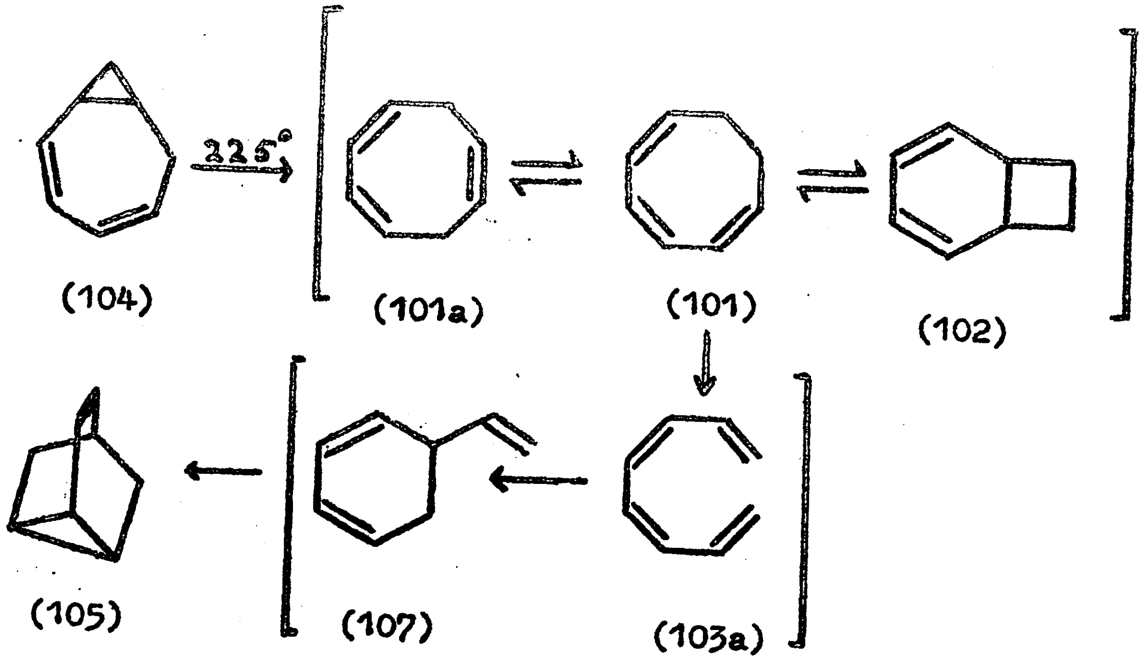
(101)

(102)

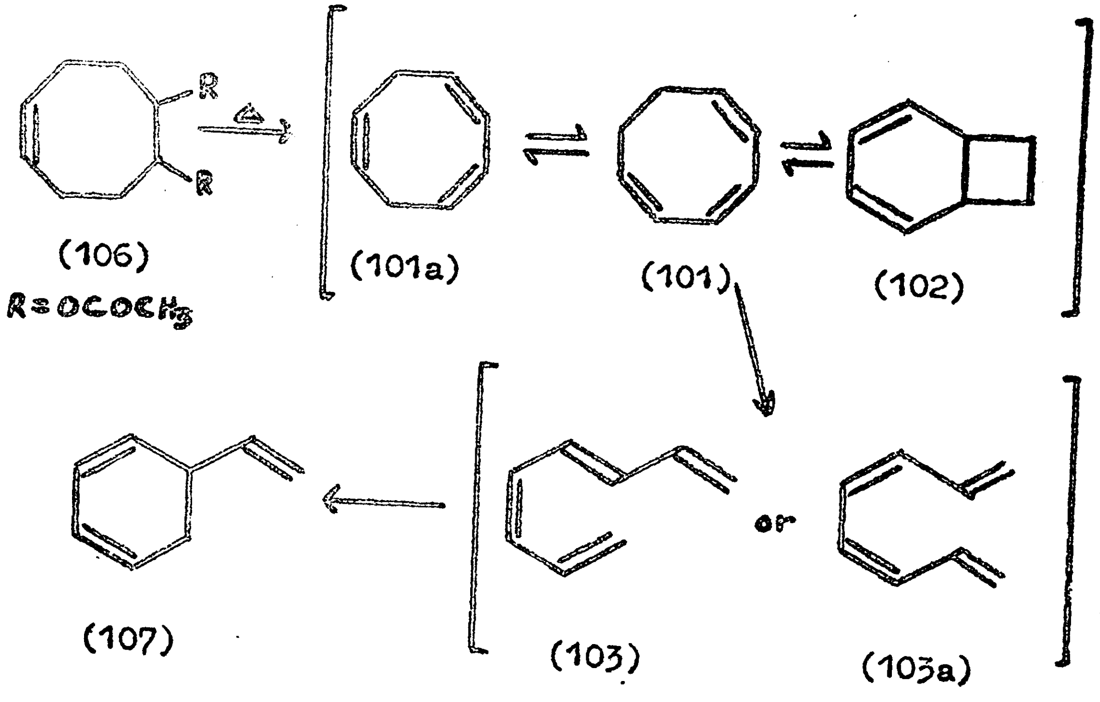


(103)

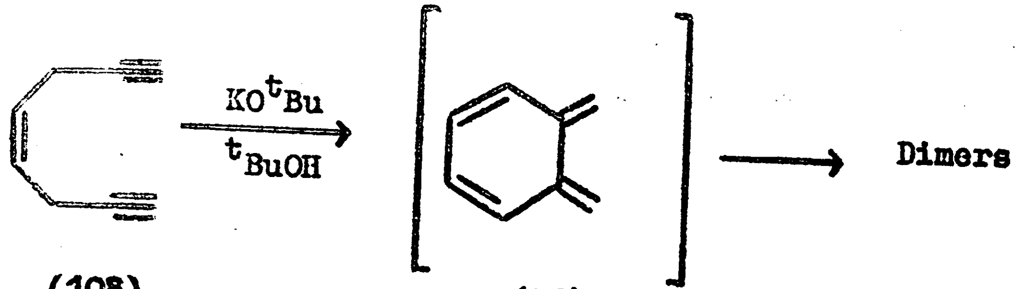
(101)



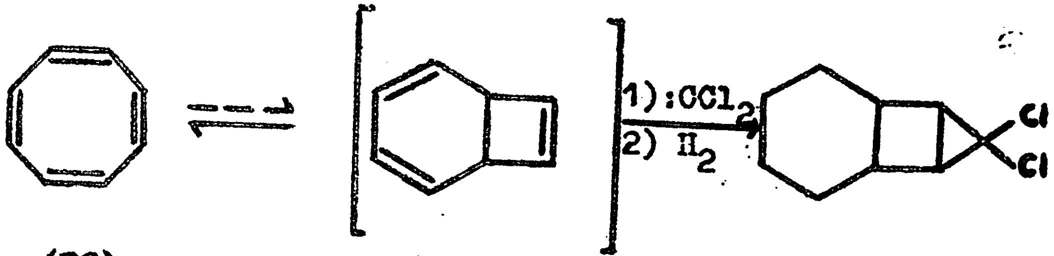
Scheme VI



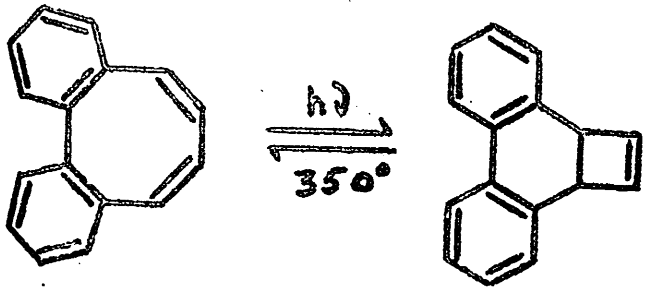
Scheme VII



(108) (46)



(79) (109) (110)



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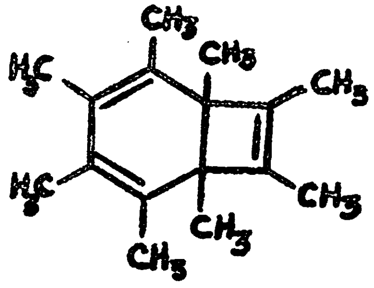

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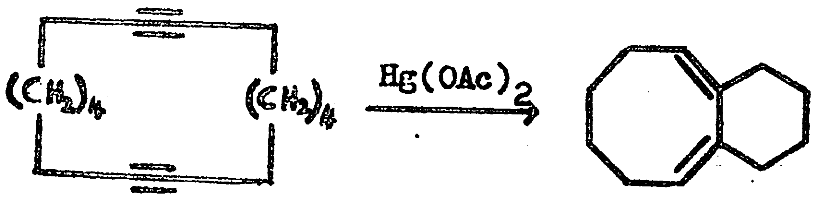
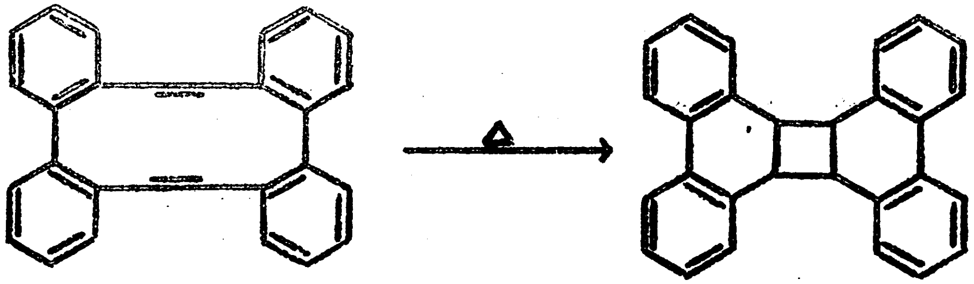
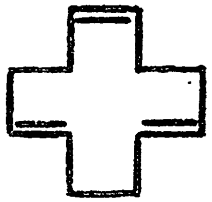


(53; m=n=4) (113)



(114) (115)



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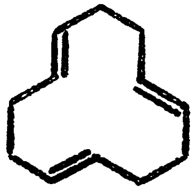

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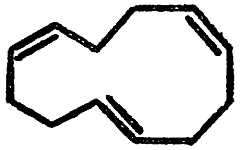
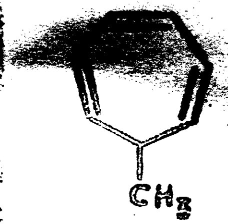
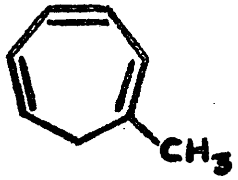


(118)

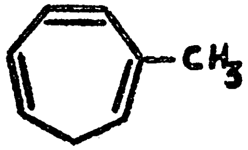
$HC\equiv C(CH_2)_nC\equiv CH$ (119)



(120)



(121)



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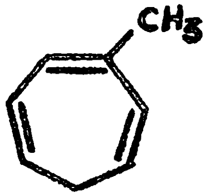


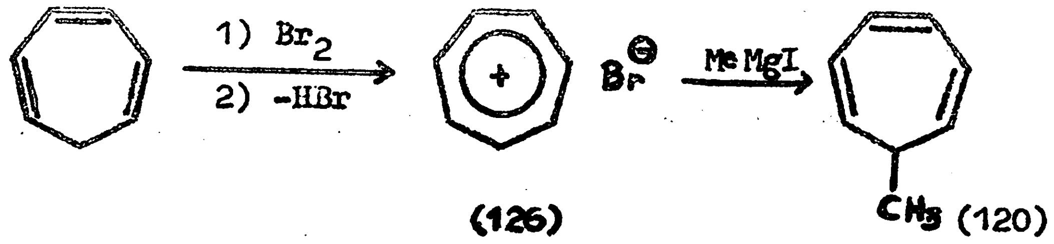
(123)

$CH_3C\equiv C(CH_2)_6C\equiv CCH_3$

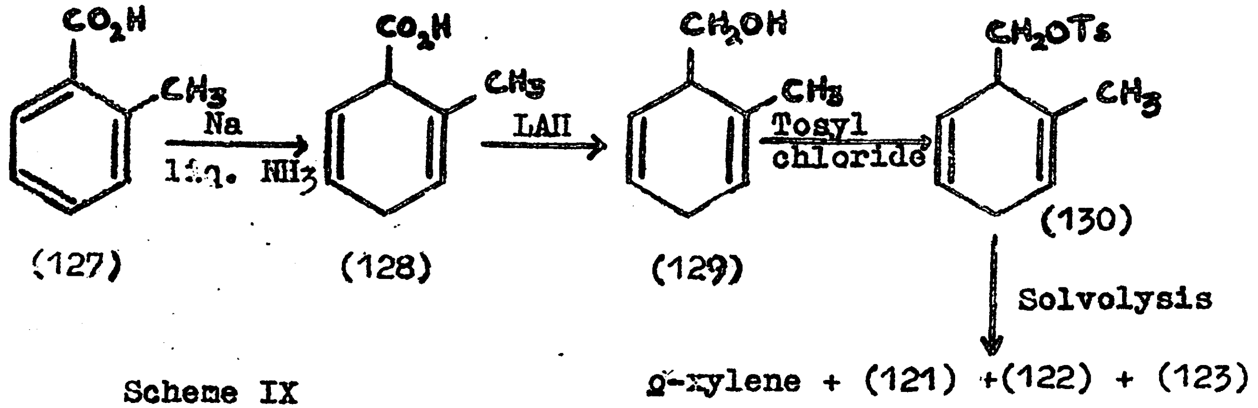
(124)

$CH_2{=}C{=}CHCH_2CH_2CH{=}C{=}CH_2$

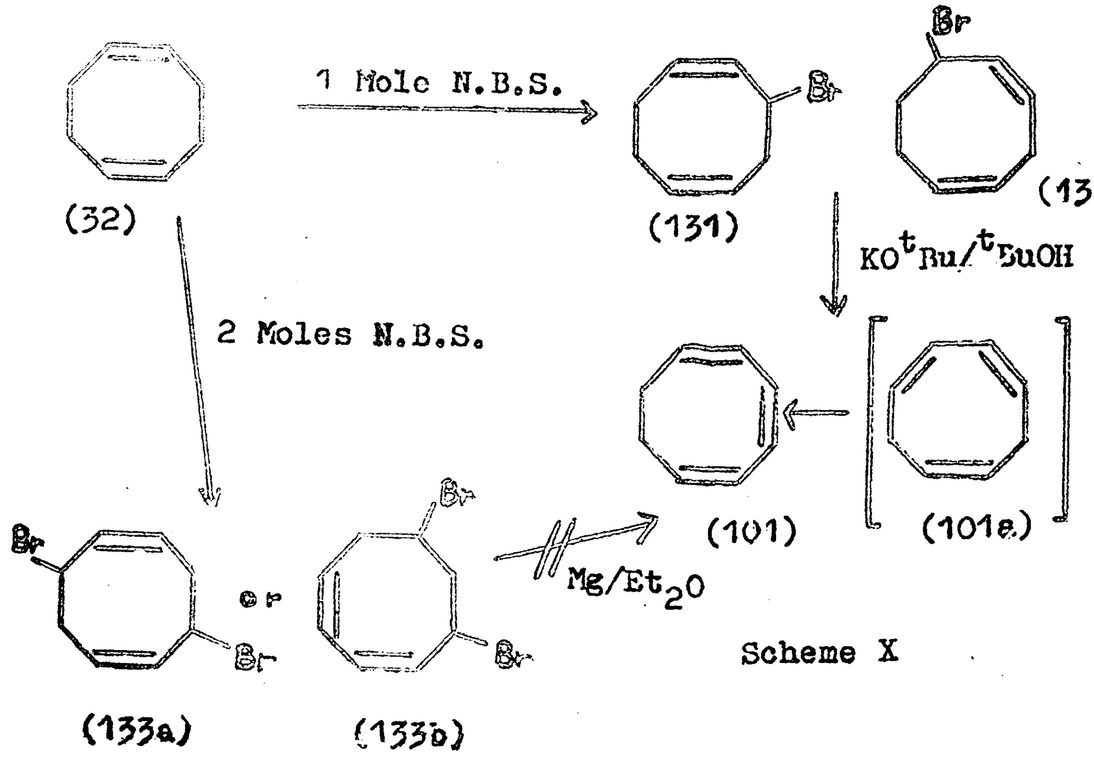
(125)



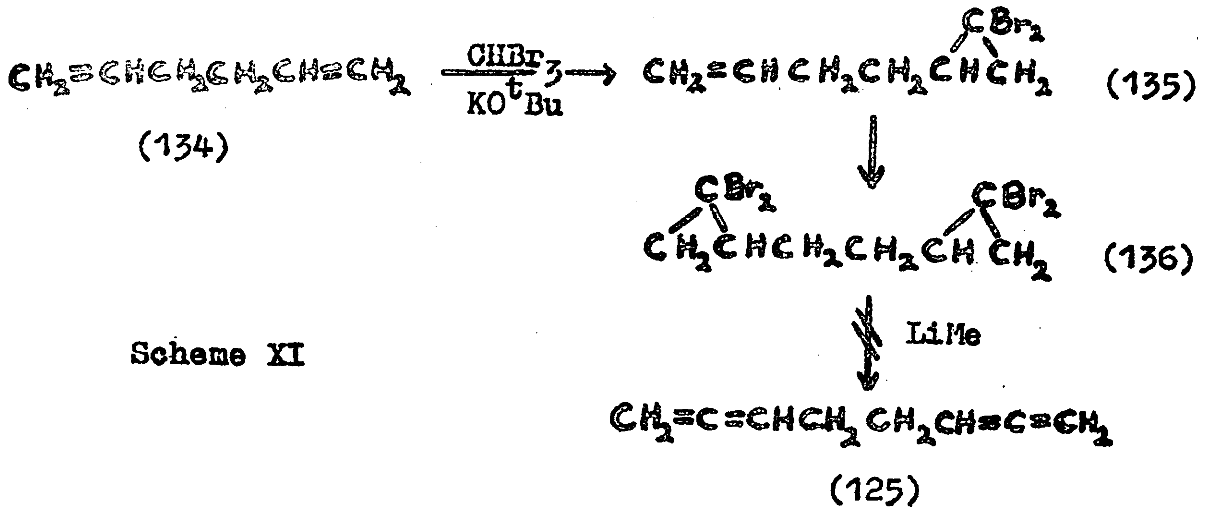
Scheme VIII



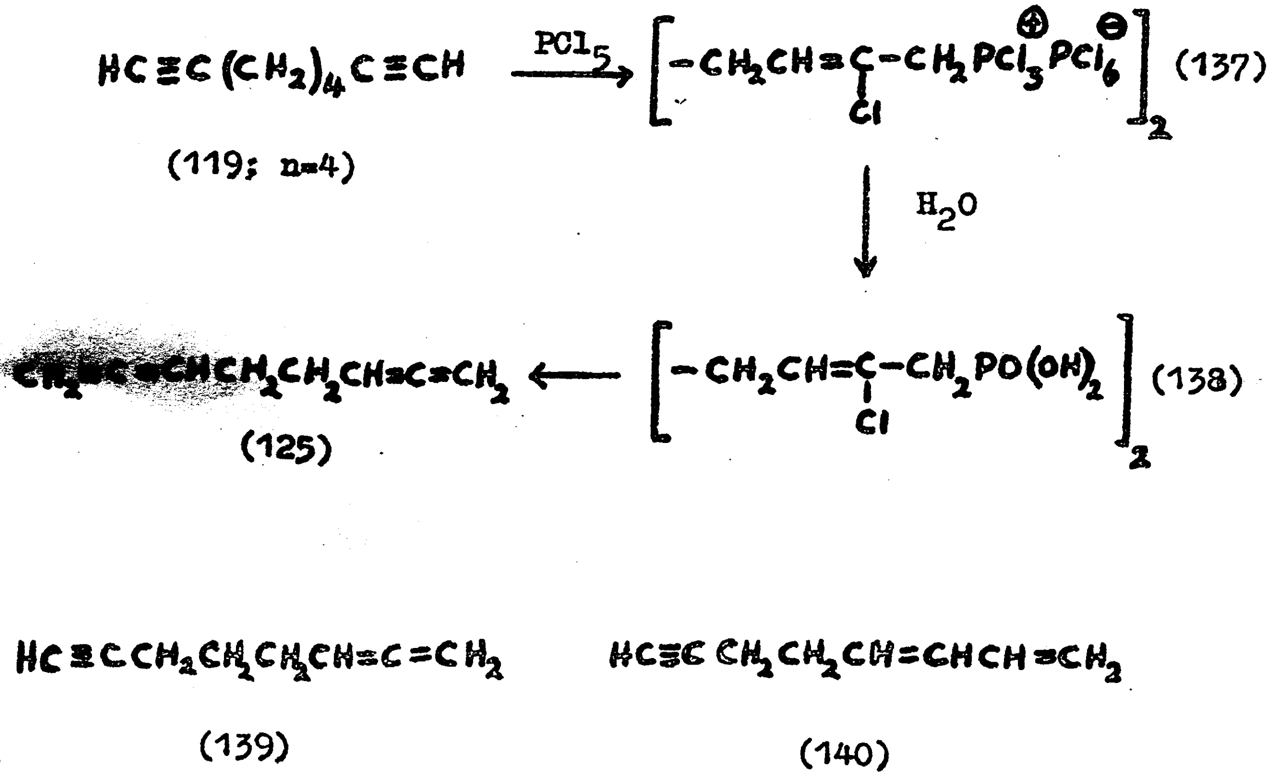
Scheme IX



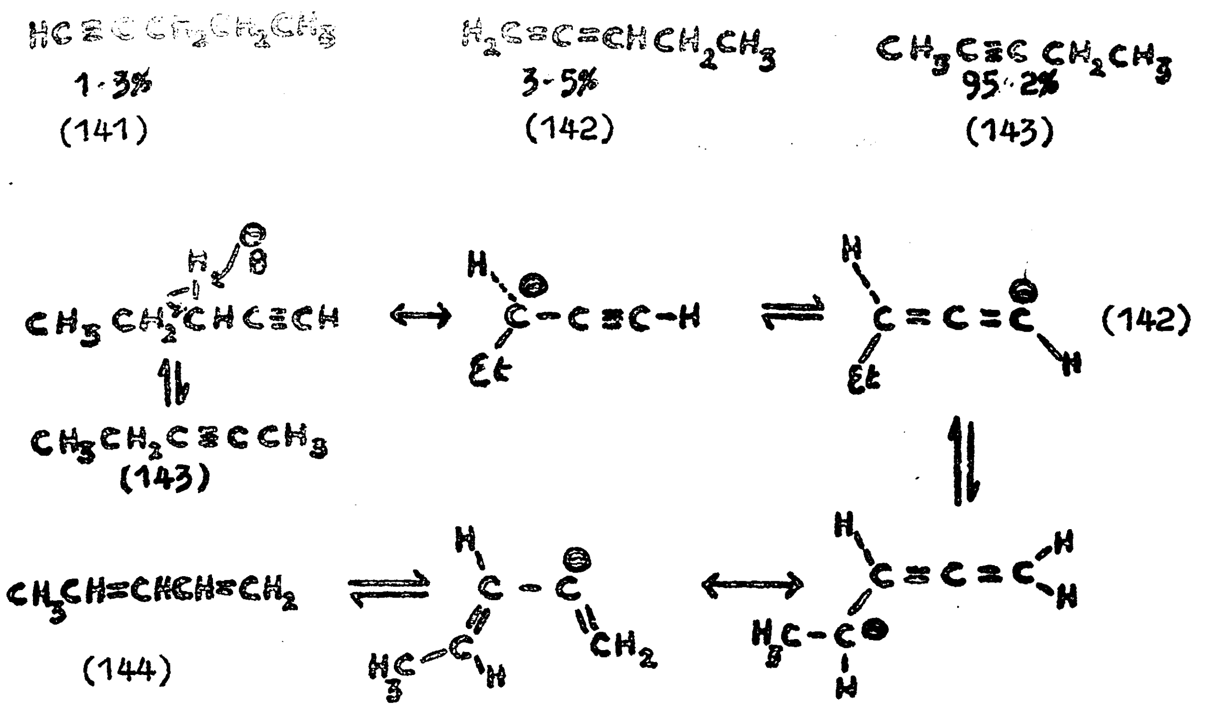
Scheme X



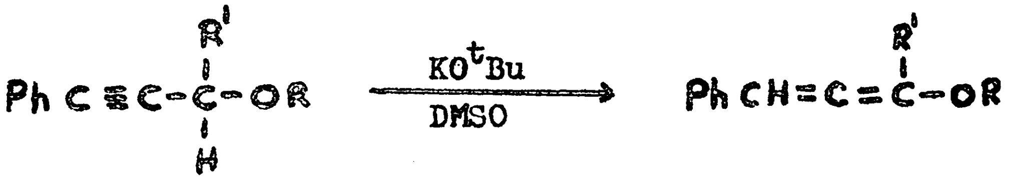
Scheme XI



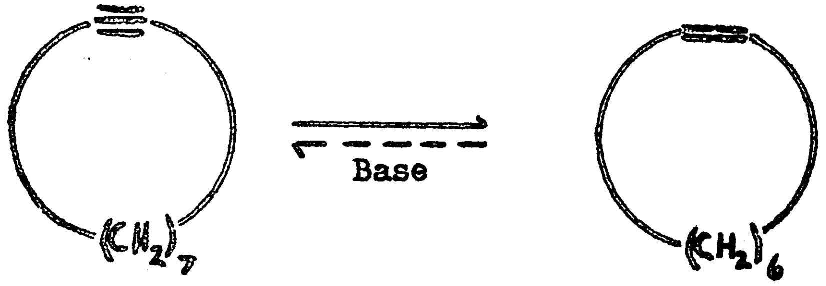
Scheme XII



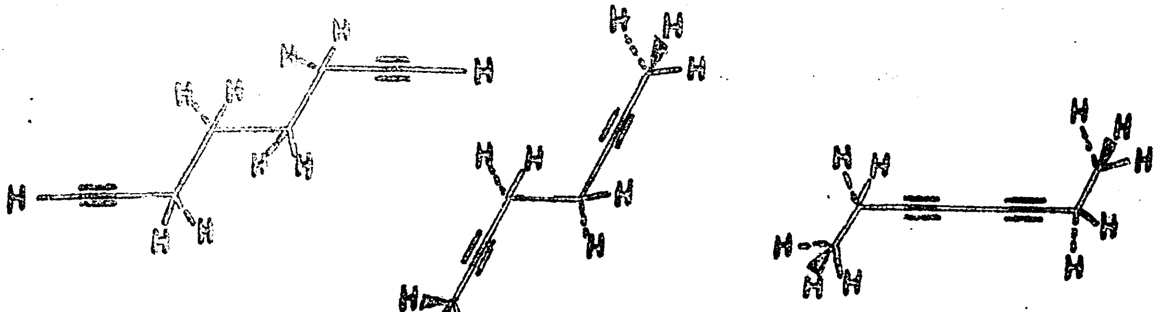
Scheme XII



(145) (146)



(147) (148)



(147) (148) (149)

$$HO_2CCH_2C\equiv C-C\equiv CCH_2CO_2H \xrightarrow[KOH]{aq.} HO_2CCH=CHCH=CHC\equiv CCO_2H$$

(150) (151)

(152) $CH_3(CH_2)_4CH=CHCH_2CH=CH(CH_2)_7CO_2H$

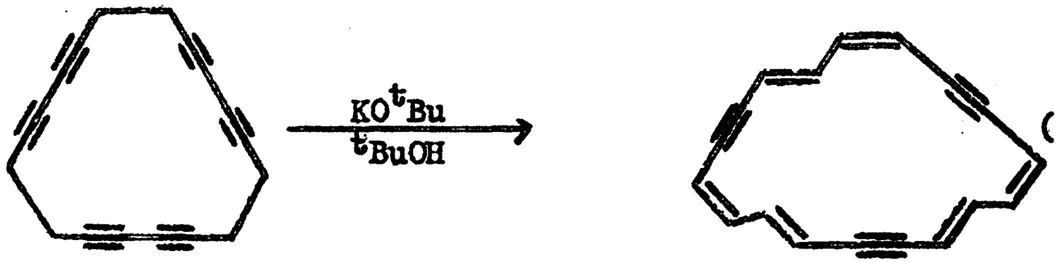
$$\big\downarrow \text{KOH}$$

(153) $CH_3(CH_2)_nCH=CHCH=CH(CH_2)_{12-n}CO_2H \quad n=4,5$

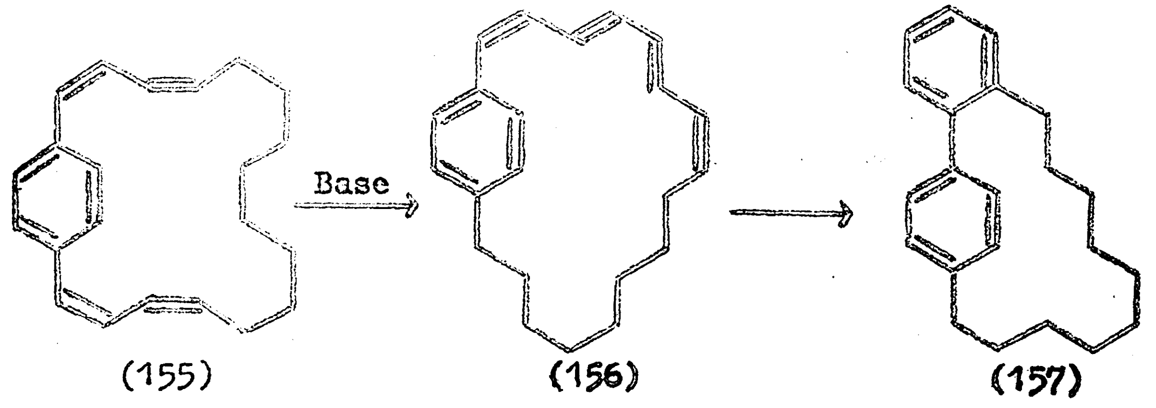
$$\big\downarrow$$

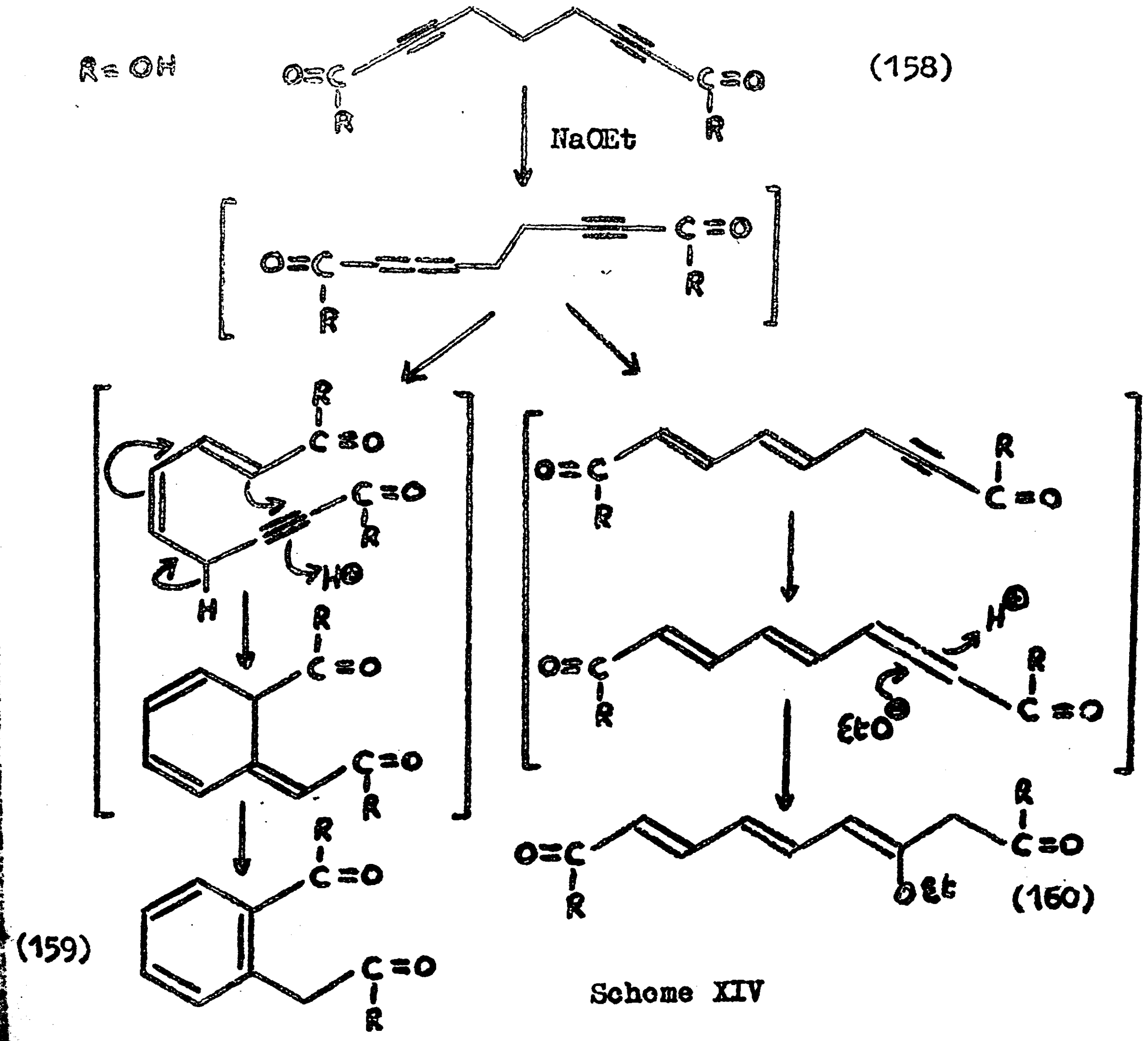
$$CH_3(CH_2)_{12}CO_2H + CH_3(CH_2)_{14}CO_2H + CH_3CO_2H$$

(49)



(154)

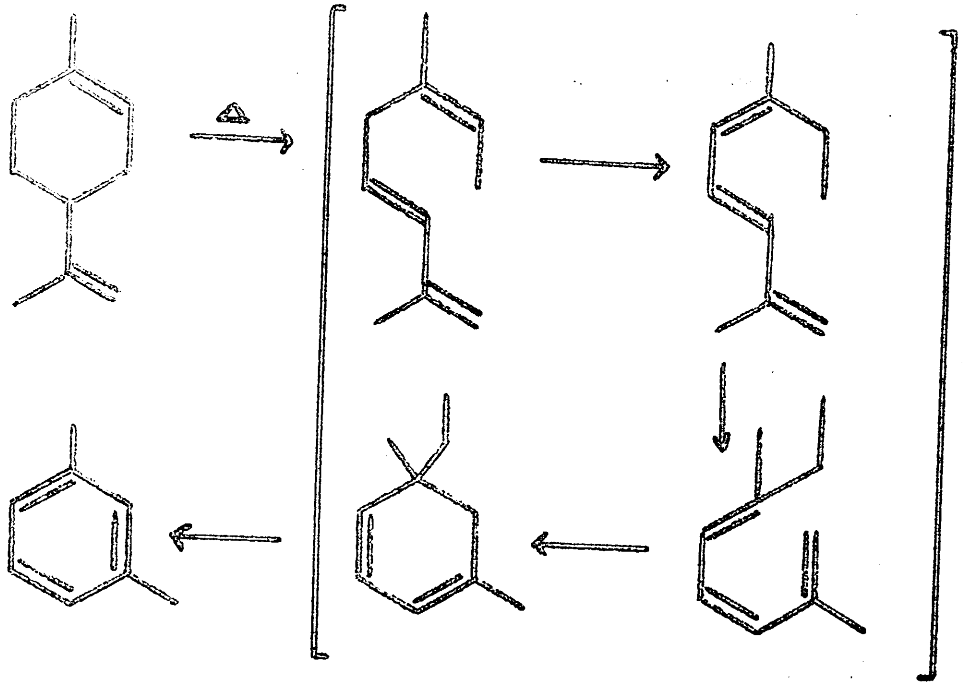




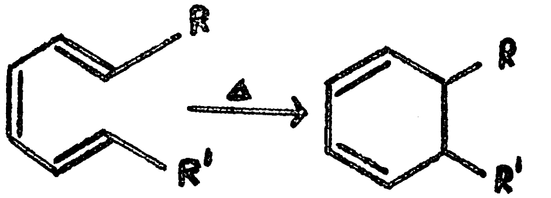
Scheme XIV

(161)

(162)

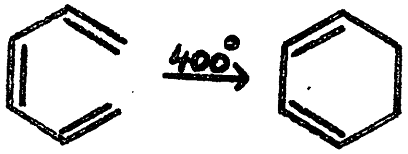


Scheme XV

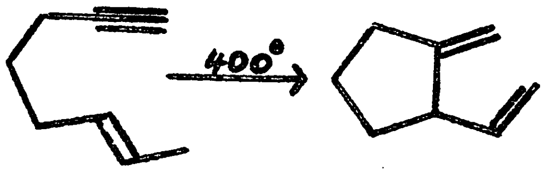


$R = C_4H_9$, $R' = (CH_2)_7CO_2H$

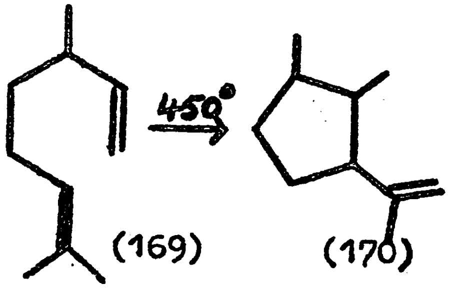
(163) (164)



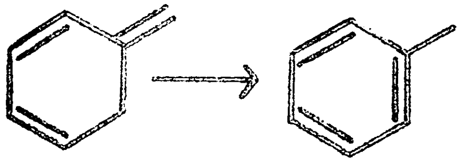
(165) (166)



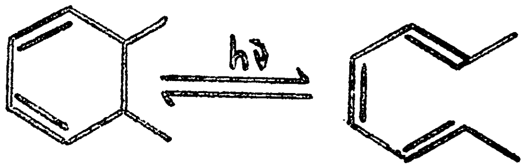
(167) (168)



(169) (170)

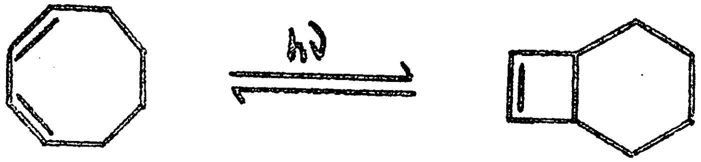


(171) (172)



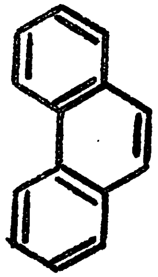
(173) (174)

(175)

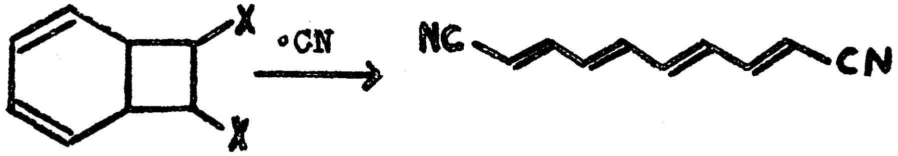


(176)

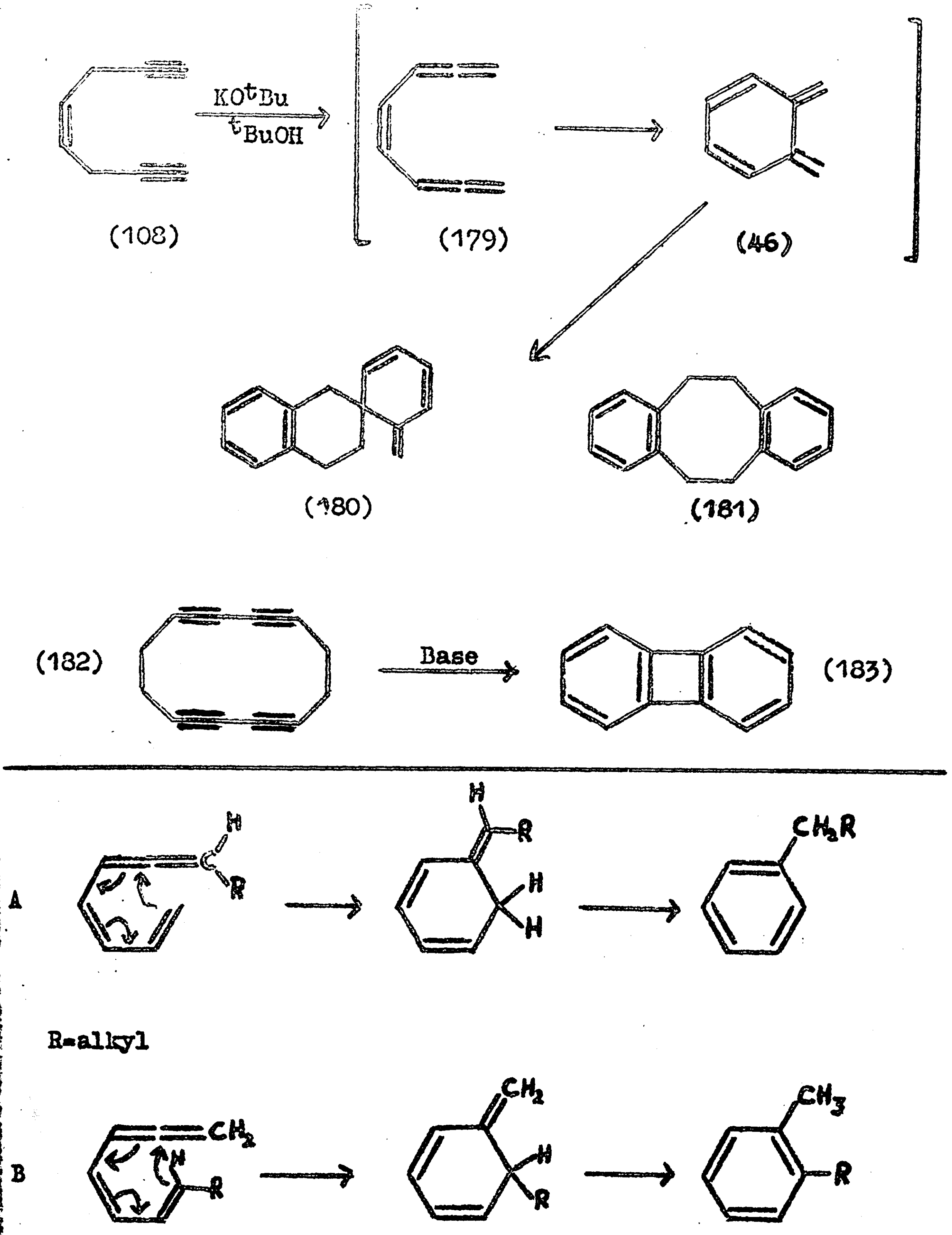
(114) $\longrightarrow$ (115) $\longrightarrow$



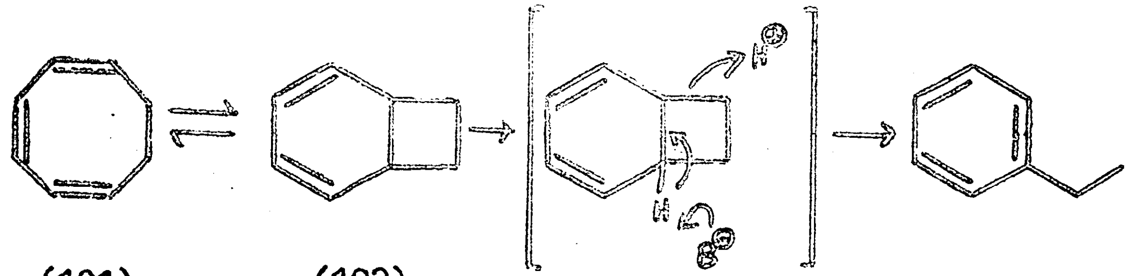
(177)



(80; X=Br) (178)

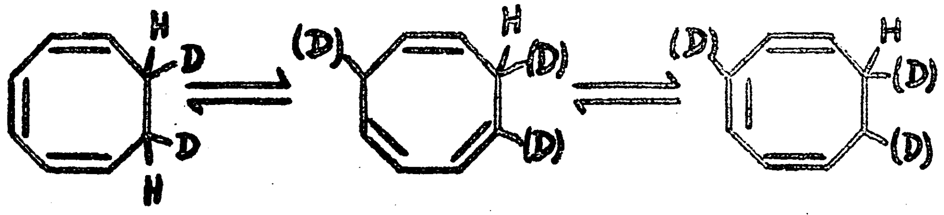

KO^tBu
^tBuOH
(108)
(179)
(46)
(180)
(181)
(182)
Base
(183)
A
H
R
H
R
H
H
CH₂R
R=alkyl
B
CH₂
H
R
CH₂
H
R
CH₃
R

Scheme XVI



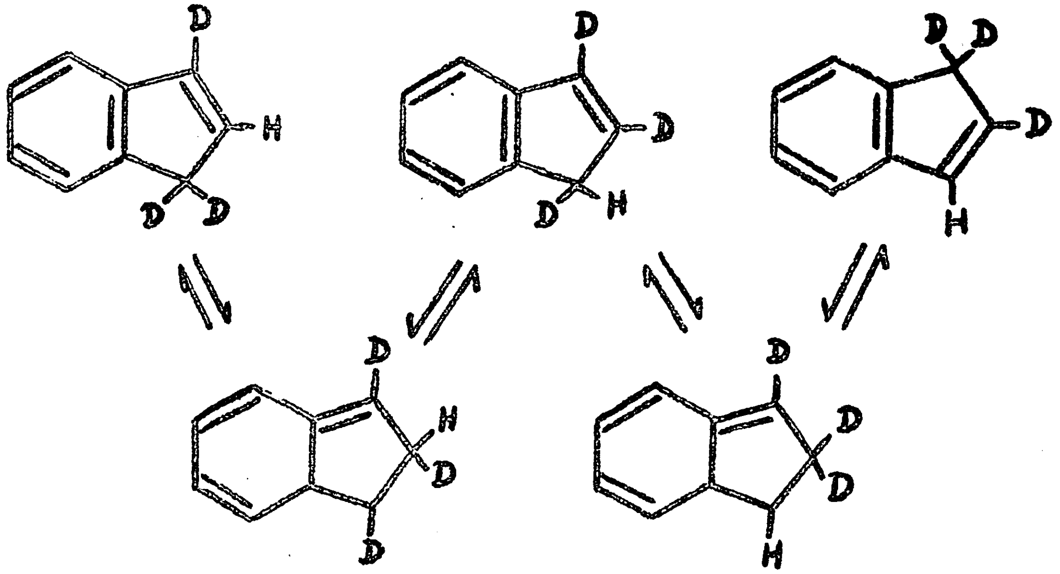
(101) (102)

Scheme XVII

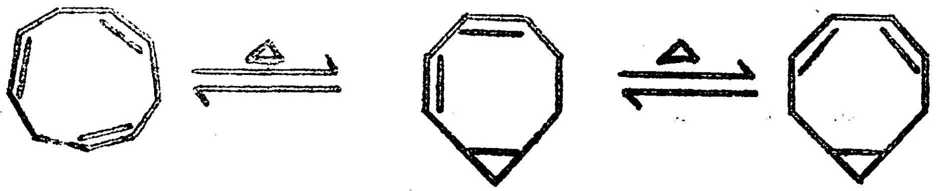


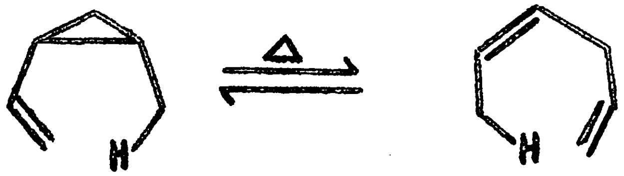
(D) = alternative positions

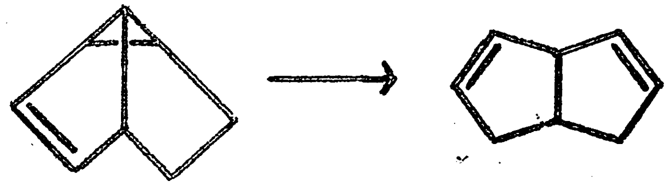
Scheme XVIII

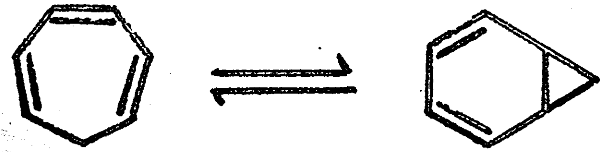


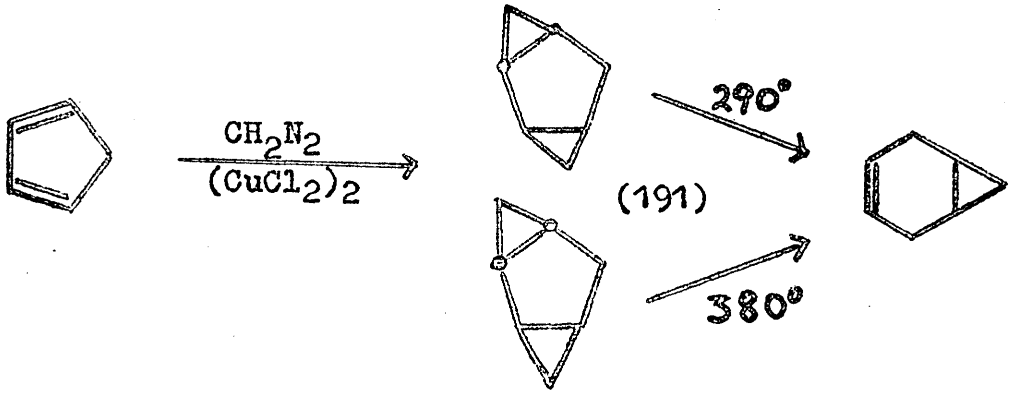
Scheme XIX


(184) (104) (185)

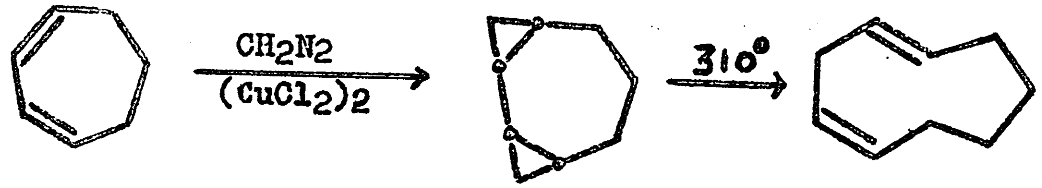
(186)

(187)

(188)

(189)

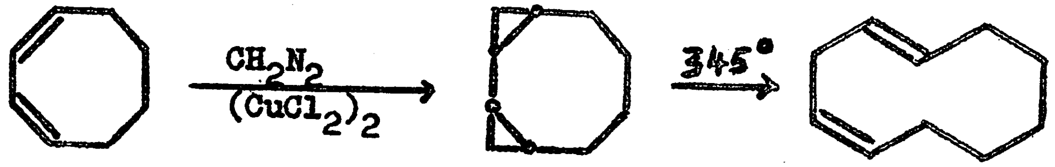

(190)



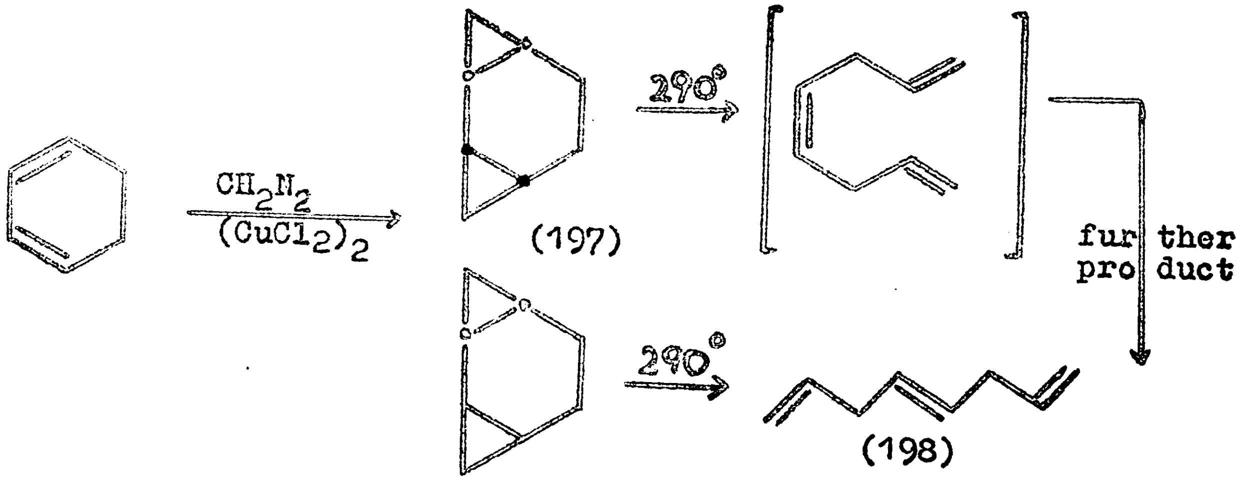
(191) (192)

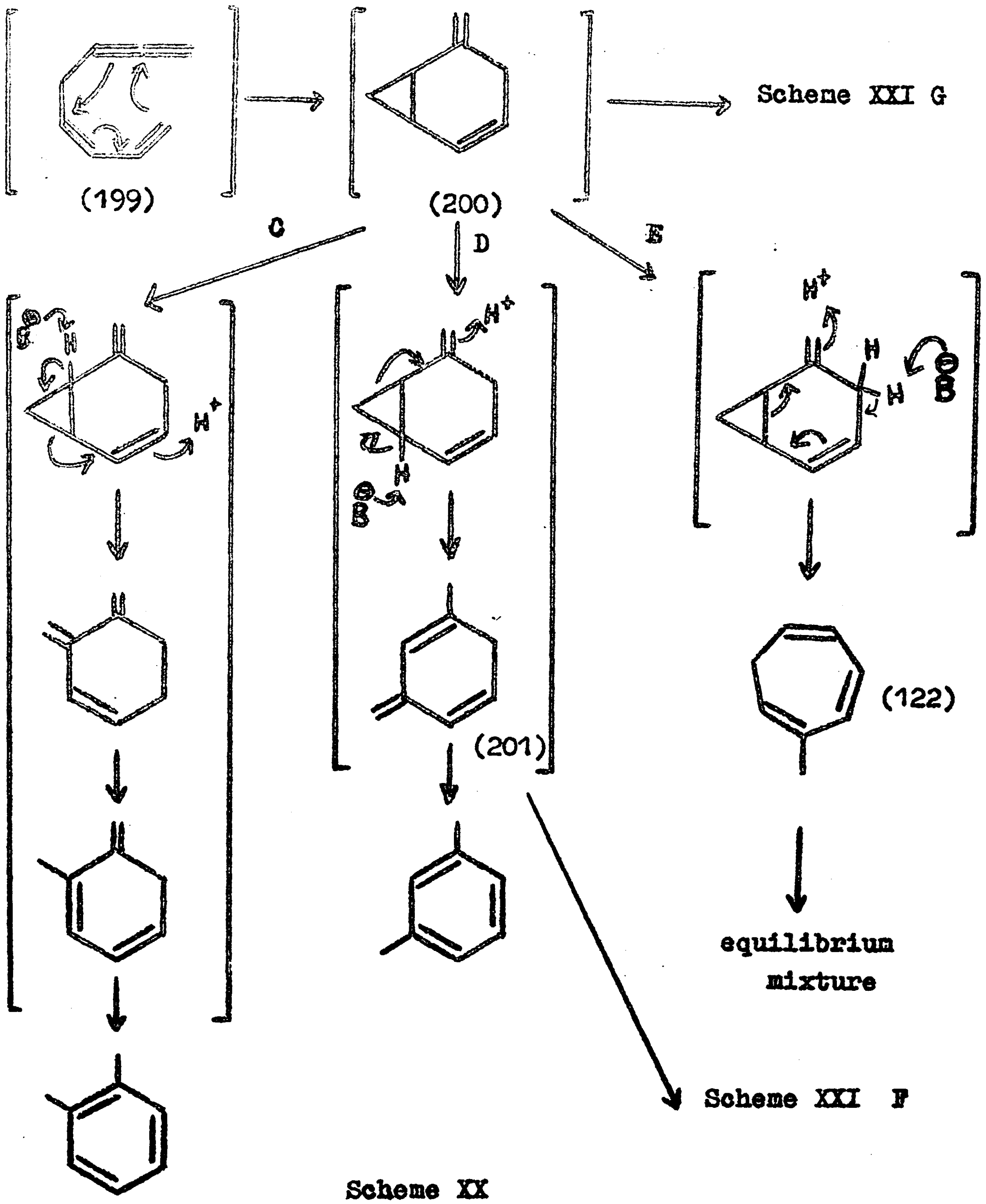


(193) (194)

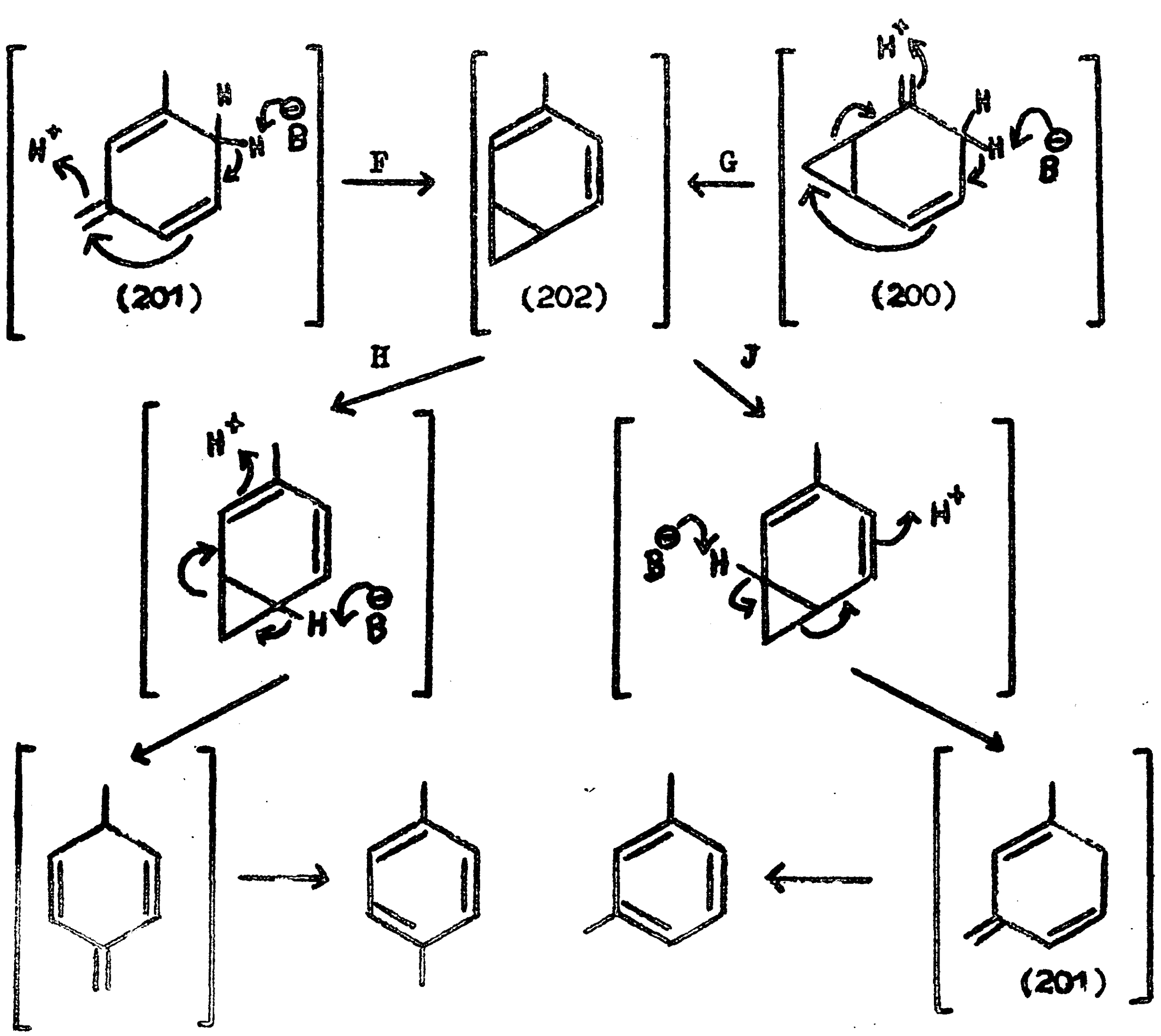


(195) (196)

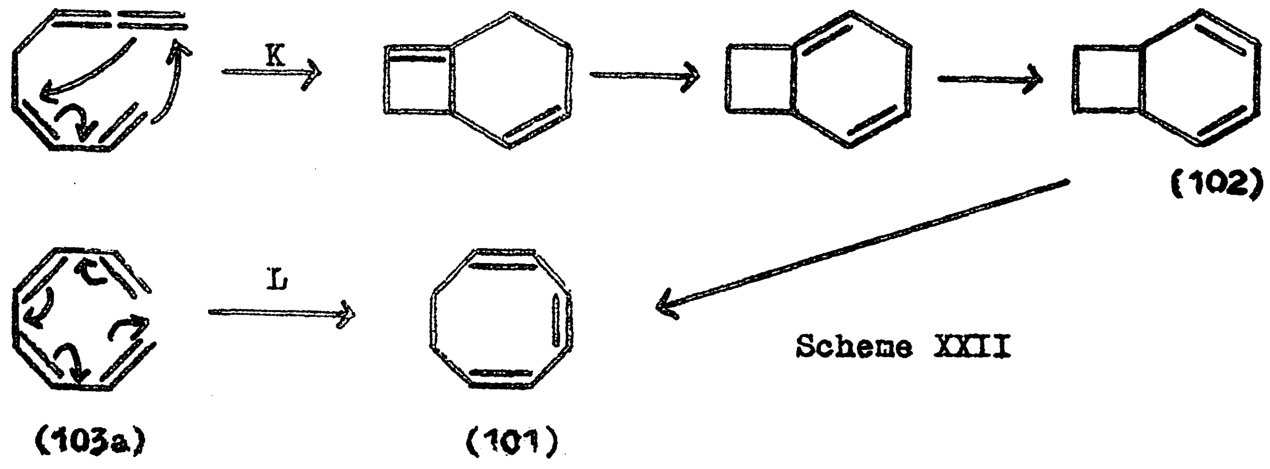



(199)
(200)
Scheme XXI G
C
D
E
H
H⁺
B
(201)
(122)
equilibrium mixture
Scheme XXI F

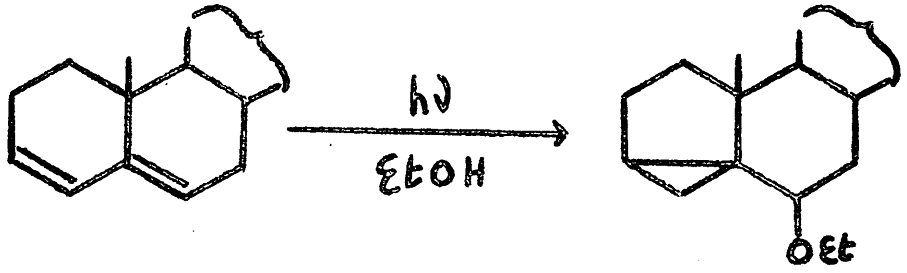
Scheme XX



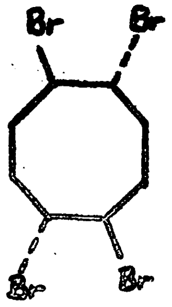
Scheme XXI



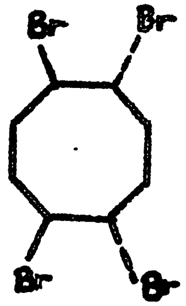
Scheme XXII



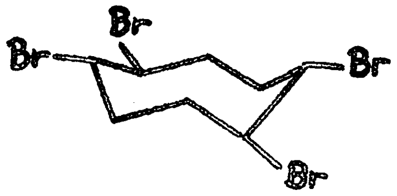
(203) (204)



(205)

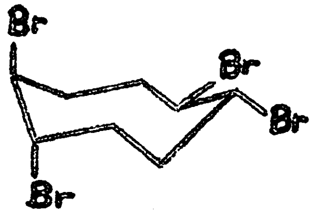


(206)



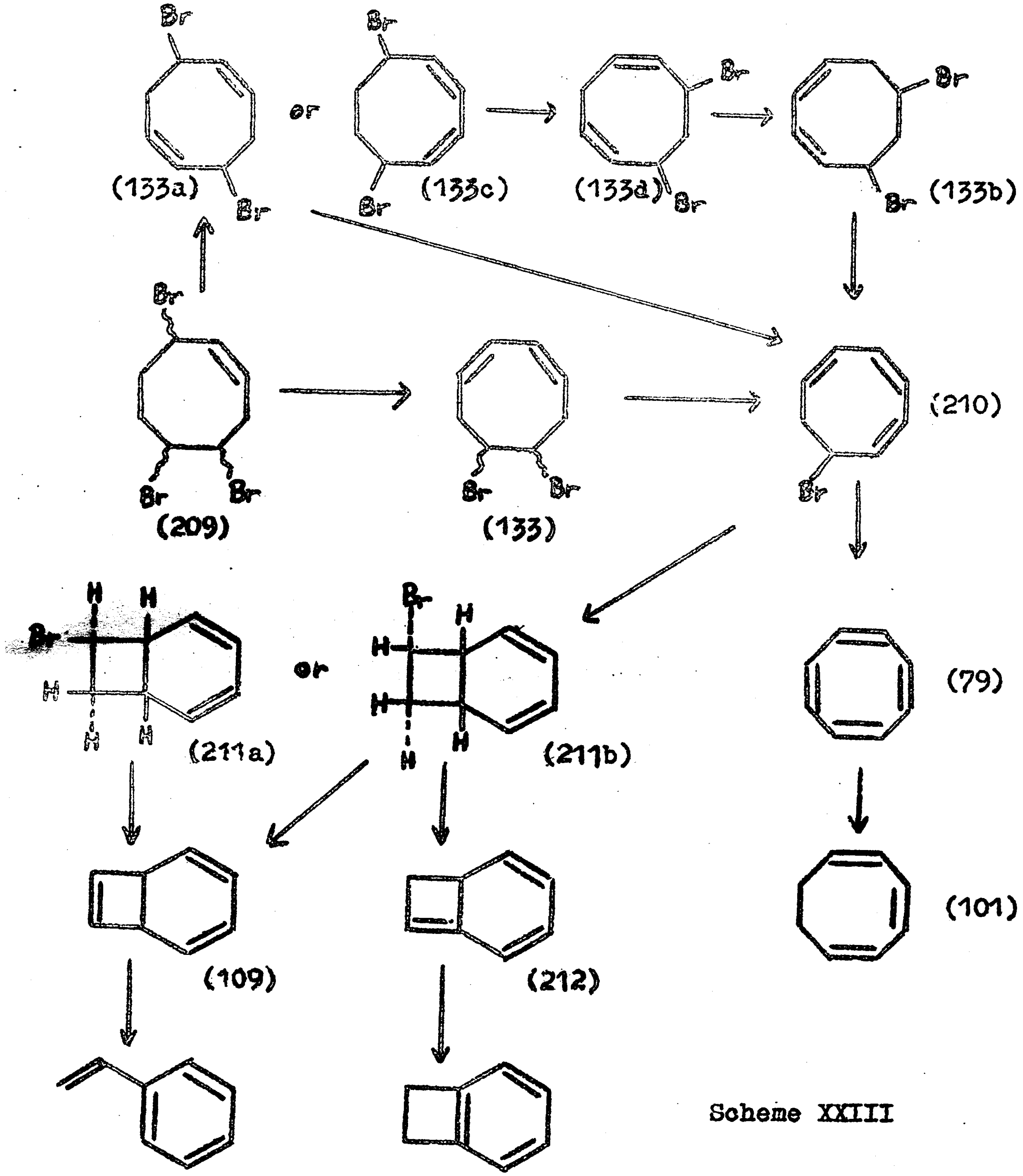
(207)

eeee

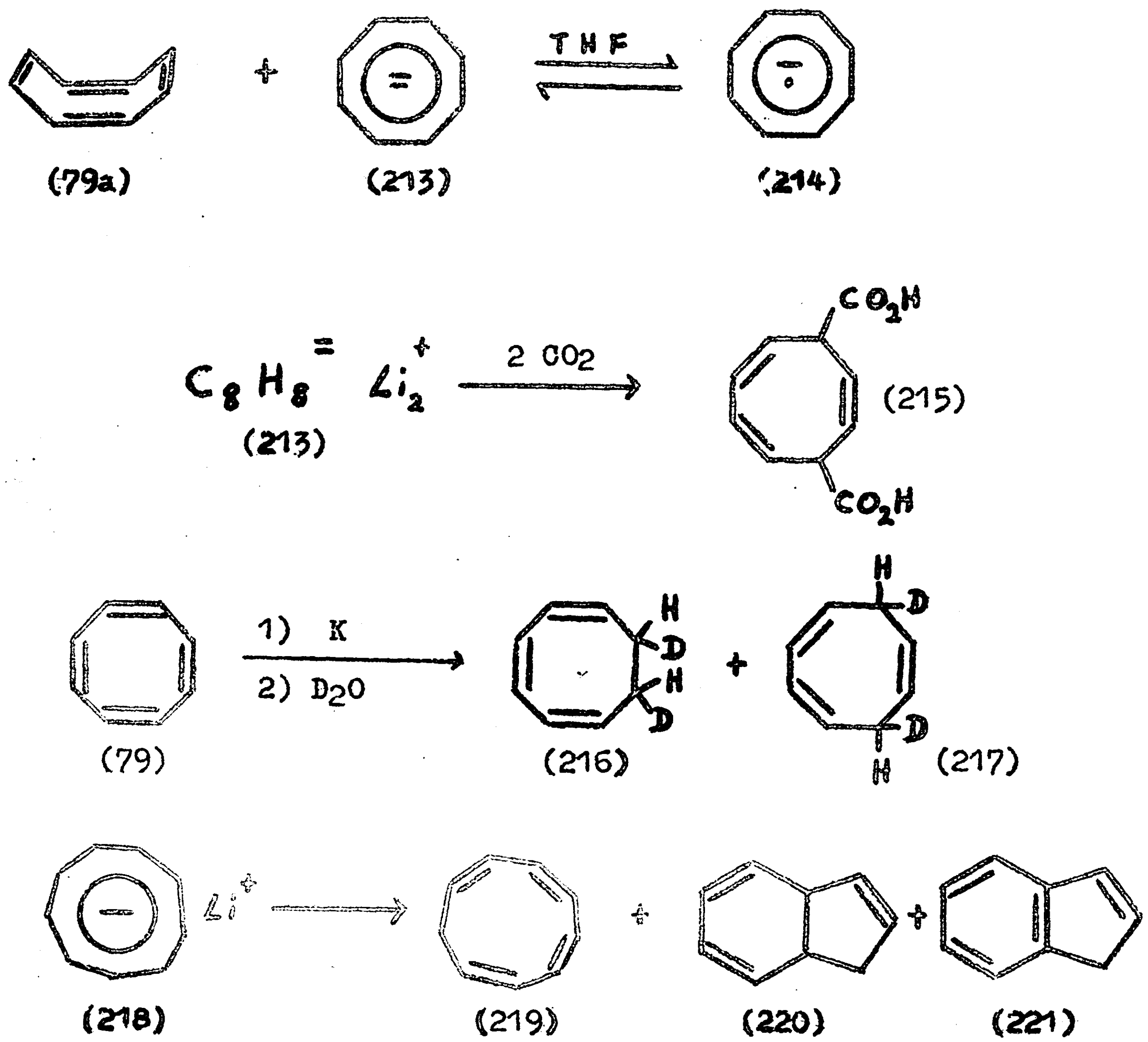


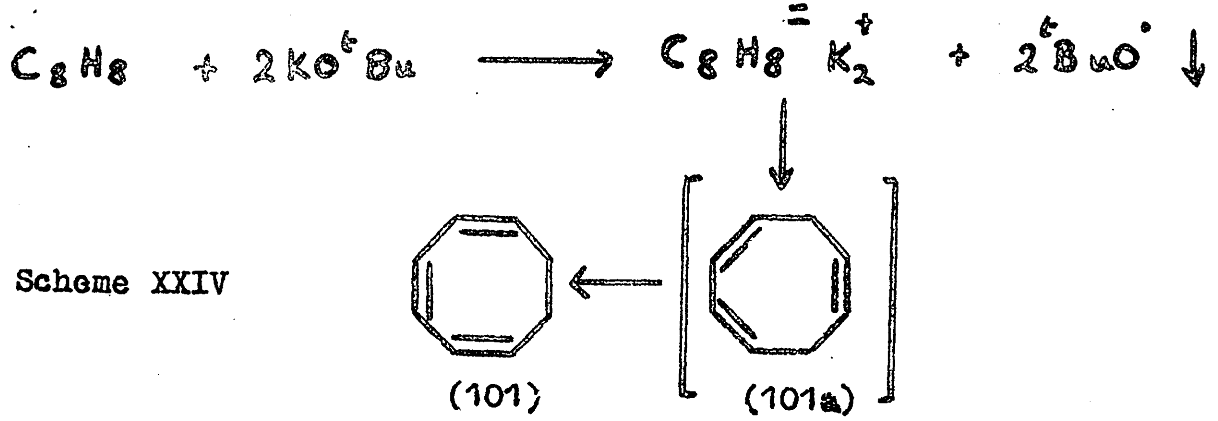
(208)

aaee

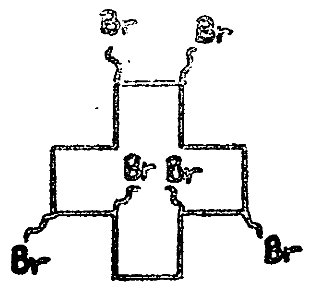


Scheme XXIII

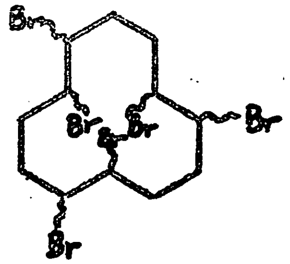

THF
(79a)
(213)
(214)
$C_8H_8^{=}\ Li_2^{+}$
(213)
2 CO2
CO_2H
(215)
CO_2H
(79)
1) K
2) D2O
H
D
H
D
(216)
H
D
D
H
(217)
Li+
(218)
(219)
(220)
(221)


$C_8H_8 + 2KO^tBu \longrightarrow C_8H_8^{=}K_2^{+} + 2\,^tBuO^{\bullet}\downarrow$
(101)
(101a)

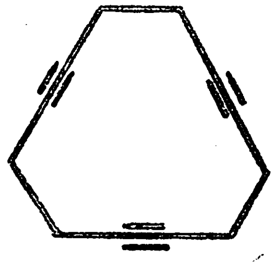
Scheme XXIV



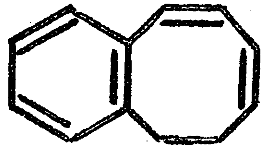
(222)



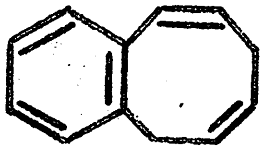
(223)



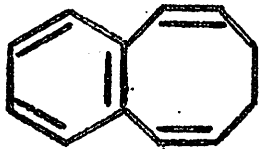
(224)



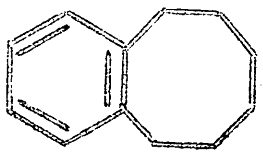
(225a)



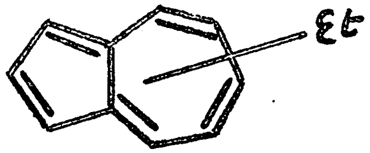
(225b)



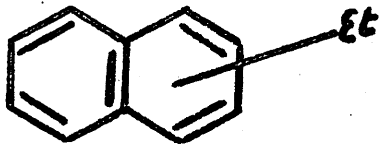
(225c)



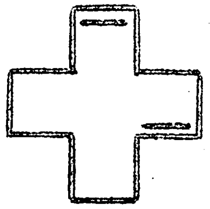
(226)



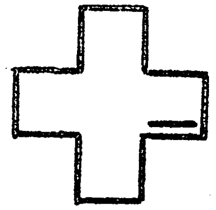
(227)



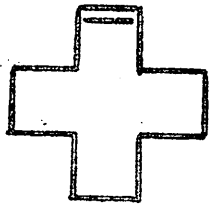
(228)



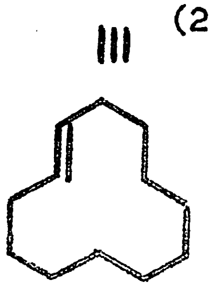
(229)

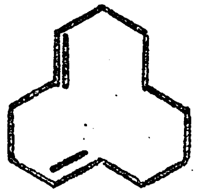


(230)

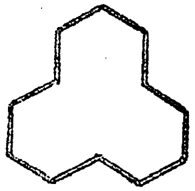


(231)

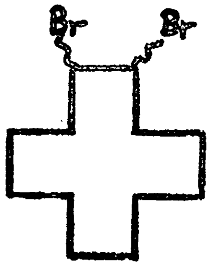




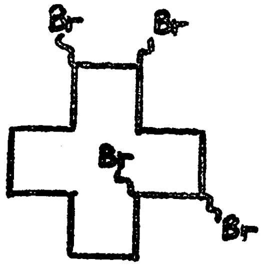
(232)



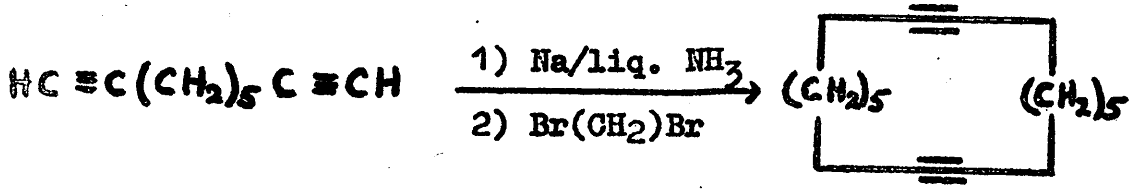
(233)



(234)

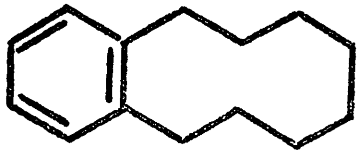


(235)

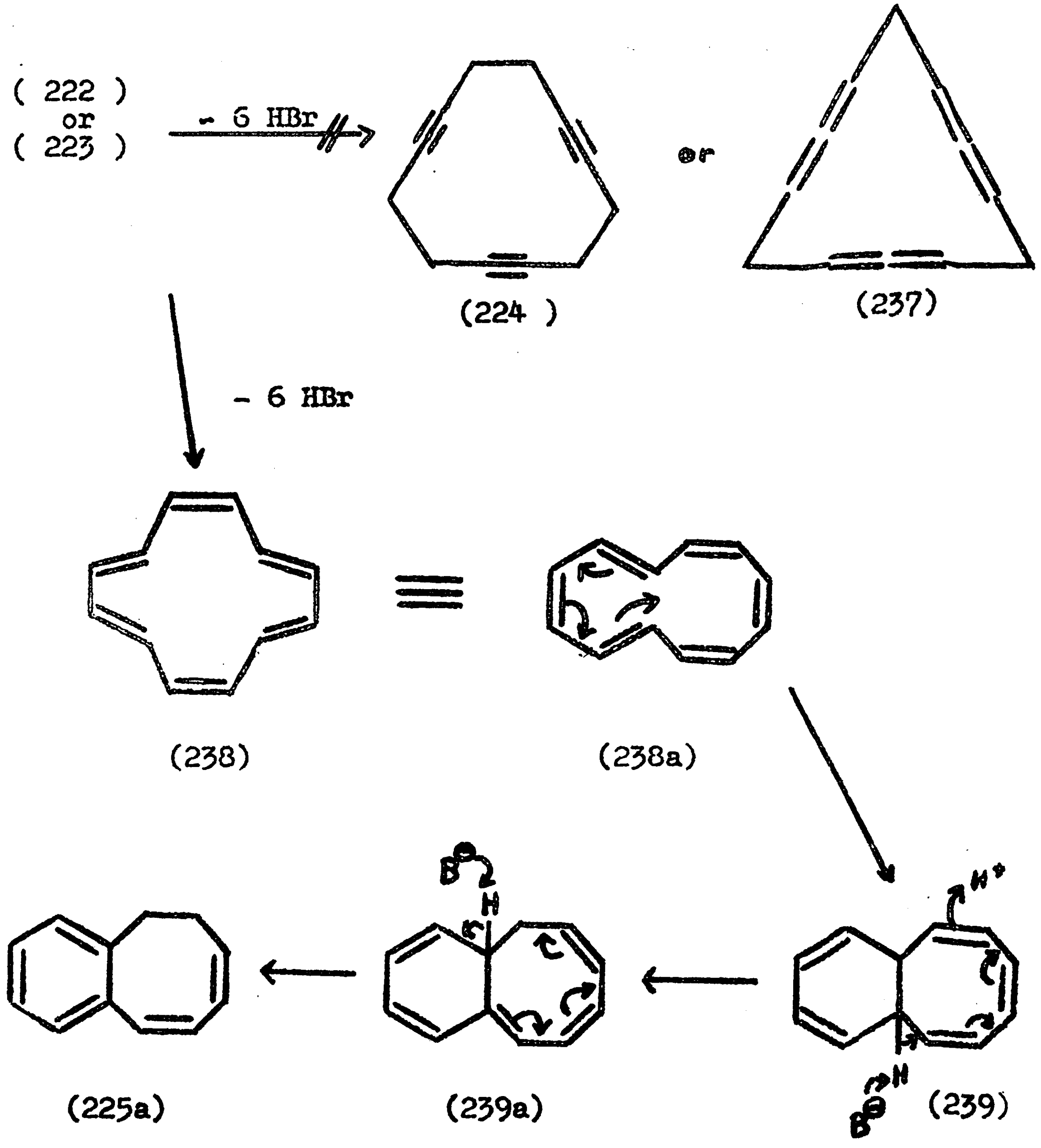


(119; n=5)

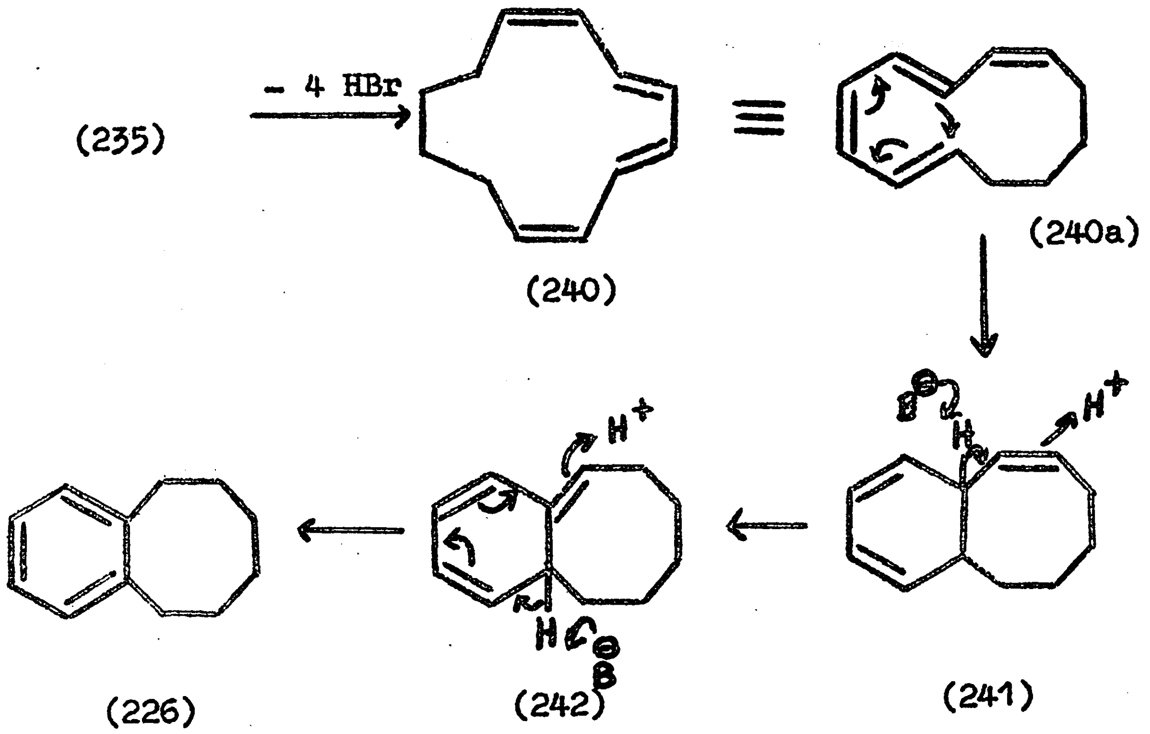
(53; m=n=5)



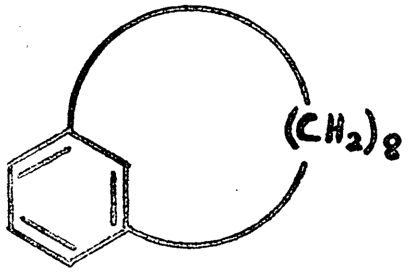
(236)



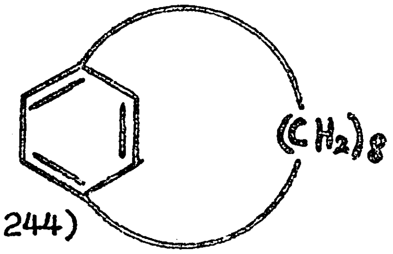
Scheme XXV



Scheme XXVI



(243)



(244)

APPENDIX

Discussion

The spectral properties of the pure $C_8H_{10}Br_2$ compound (m.p. 123°), isolated from the allylic bromination of cycloocta-1,5-diene, are somewhat at variance with the chemical evidence for its structure.

The structure (133c) proposed by Cope and his co-workers[113] for the oil they obtained from an identical reaction was based upon infrared and ultraviolet characteristics and the formation of a derivative. This, a bis-dimethylaminocyclooctadiene, was stated to be the 1,6-cycloocta-1,3-diene derivative [(246), obtained in 31% yield], identified by comparison with a sample obtained previously by another route. Cope also stated that the product from direct bromination of cycloocta-1,3,5-triene had a similar ultraviolet spectrum to this dibromocyclooctadiene. [Of great interest is his observation that a small quantity of solid (m.p. 124-125°) did crystallise from the oil on standing at -80°, and that this analysed as $C_8H_{10}Br_2$.] Reductive debromination of the liquid dibromocyclooctadiene (133c) with lithium aluminium hydride gave a mixture of cyclooctadienes, whereas debromination with magnesium gave a 53% yield of cycloocta-1,3,5-triene (101).

In the present work, a direct spectral comparison (i.r., u.v., n.m.r.) has been made between cycloocta-1,3-diene (175), 5-bromocycloocta-1,3-diene [(132a), synthesised by mono-allylic bromination of cycloocta-1,3-diene], and the solid dibromocyclooctadiene. (Tables X, XI, and XII).

In the infrared spectra, there are distinct similarities in the region below 800 cm.$^{-1}$ for all three compounds (Table X), but in particular between 5-bromocycloocta-1,3-diene (132a) and the solid dibromide. The band at 578 cm.$^{-1}$ in the spectrum of the dibromide can be attributed to the C - Br stretching frequency of the non-allylic bromine atom, for this band is totally absent in the other spectra.

The ultraviolet spectra (Table XI) are again similar (variations in $\lambda_{max.}$ do occur, depending on ring size and substituents[186]), though the intensity of the absorption ($\varepsilon = 6,140$) from 5-bromocycloocta-1,3-diene does seem to be rather high.[92] Quite definitely, the absorption due to the dibromo compound, cannot be ascribed to two isolated double bonds under any circumstances.

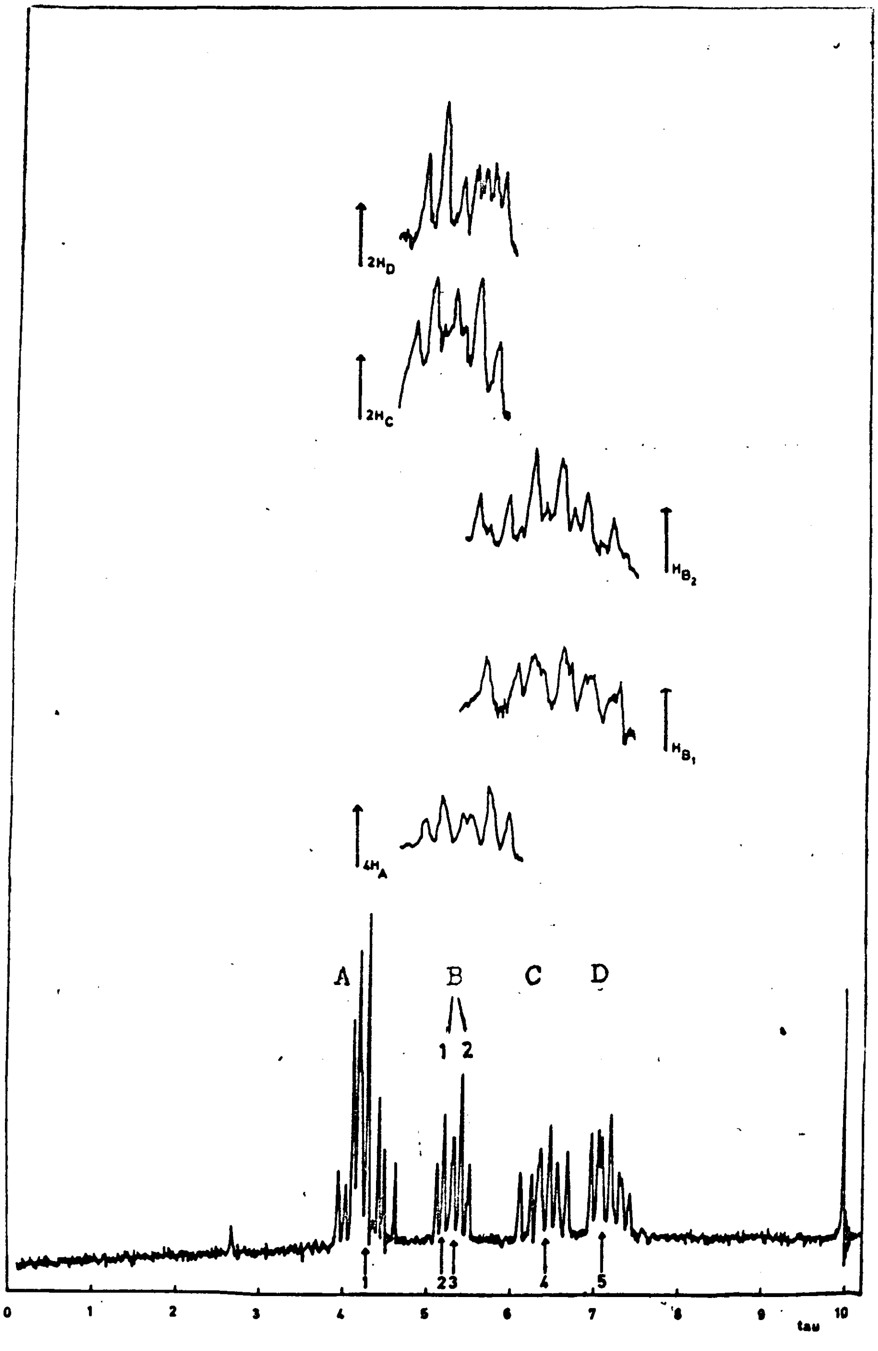
The n.m.r. spectrum (Fig. 30) of this compound is rather interesting. It can be divided naturally into four groups (protons in the ratio 2:1:1:1), each of which consists of sharp multiplets, possibly indicative of a rigid structure. By comparison with other reference compounds (Table XII), several of these groups can be allocated to the protons responsible without any difficulty. The integration also shows four olefinic protons, two protons on the same carbon atoms as the bromines, and two other separate pairs, probably due to the adjacent methylene protons. This evidence will be discussed more fully later.

Several reactions, similar to those carried out by Cope, were also attempted. Reaction of the dibromide with lithium aluminium hydride/lithium hydride in tetrahydrofuran gave one major product (comprising 79% of the total, by g.l.c.), which was identified (i.r.; g.l.c.) as cycloocta-1,5-diene (32). Treatment of cycloocta-1,3-diene (175) with this reagent caused no rearrangement. When 5-bromocycloocta-1,3-diene (132a) was treated in a likewise manner, only cycloocta-1,3-diene (175) was obtained.

When the solid dibromide was dehalogenated with either zinc or magnesium, it did not give any product which could be identified as cycloocta-1,3,5-triene (u.v.; g.l.c.).

Titration of the dibromide in methanol/water with silver nitrate solution indicated the presence of one allylic bromine atom per molecule, though as the titration was carried out on a very small scale, this result may have been subject to a disproportionately large error.

From the above data, the chemical evidence favours the presence of an unconjugated diene, though only one allylic bromine seems to be present. However, it is impossible for a cycloocta-1,5-diene structure to have only one allylic bromine, so the only alternatives are the 1,3- and 1,4- isomers. Cope himself[187] has shown that allylic shifts are feasible during reaction, and the possibility of this occurring during the hydride reduction reaction cannot be excluded. The marked failure



N.m.r., single and double resonance spectra at 60 Mc.p.s. of
5,7-dibromocycloocta-1,3-diene.

Figure 30.

of the dibromide to yield cycloocta-1,3,5-triene on treatment with zinc or magnesium, would also seem to eliminate a possible 1,2-dibromo structure.

Thus it seems certain that the structure (133c) proposed by Cope, cannot be applied to this compound. It is likely, from the evidence quoted by him, that he was in fact working with a mixture of at least two isomers, especially as attempts to prepare (133c) by allylic bromination of cycloocta-1,3-diene (175) in the course of this work - and by Cope himself on another occasion[147] - failed completely. It is probable that for steric reasons, structure (133c) is too unstable to be isolated, or even to exist. Also the spectral evidence does not seem to fit this structure either.

From the conflicting evidence so far, the only structure that could possibly fit appears to be (133b), and the results from the spin decoupling experiments, though not clear cut (Fig. 30), seem to fit this structure. Two important deductions can be made from these. Irradiation of either Group B_1 or B_2 protons affects the Group C protons, and hence these protons are probably in a 1,3 position, on either side of the Group C protons. Furthermore, irradiation of Group C has no effect on the protons of either Group A or D, and this must mean that the Group C protons are not adjacent to those of Groups A or D. These facts can only be accommodated - if the interpretation is correct - by structure (133B), in which the protons are assigned according to this interpretation.

A flow sheet embodying the formation of possible dibromocyclooctadiene isomers is shown in Scheme XXVII. Routes A, B or C arise through the formation of the three possible dibromo isomers . Of these, route C is the most probable for steric reasons. This is, of course, neglecting any possible allylic migration of the double bonds prior to bromination. Further allylic rearrangement of bromine atoms would lead to (133c) by route A as proposed by Cope. Similarly route B could lead to (245b) and (246c), both of them 1,2-dibromides, and accordingly ruled out by the spectroscopic and chemical evidence available. Route C is the one that requires to be postulated for the formation of (133b). This also involves an initial allylic bromine migration to give (133d) , which then has to rearrange further by migration of a double bond into conjugation with the other (either bond may migrate) to give (133d), with only one allylic bromine, and the other bromine in a position. At the moment, these routes are all hypothetical, (lacking experimental evidence) and would require further detailed study to decide which is most feasible and actually does take place.

APPENDIX

Experimental

Preparation and Purification of Dibromocyclooctadiene

The method for preparing these compounds from cycloocta-1,5-diene is given in the Experimental Section (p. 108). The solid, (m.p. 122.5-123.5°) under investigation was purified as described, and analysis (C and H; mass spectroscopic) showed it to have the molecular formula $C_8H_{10}Br_2$: ν^{KBr} 1645, 1150, 840, 783, 753, 719, 708, 578 cm.$^{-1}$ (Table X); $\lambda^{c.hexane}_{max.}$ 224 $m\mu$ ($\epsilon = 3,400$); n.m.r., multiplets centred at 4.3 (4H), 5.4 (2H), 6.4 (2H), 7.2 (2H) τ. (Fig. 30).

Reaction of Dibromocyclooctadiene with Lithium Aluminium Hydride/Lithium Hydride[188]

A solution of the solid dibromocyclooctadiene (500 mg.) in dry tetrahydrofuran (40 ml.) was added to a slurry of lithium aluminium hydride (190 mg.) and lithium hydride (570 mg.) in dry tetrahydrofuran (25 ml.) at a rate sufficient to maintain reflux. The mixture was heated under reflux for a further 3 hrs., cooled, and water added slowly (50 ml., 1:1 water and tetrahydrofuran) to decompose excess reagent, followed by aqueous sulphuric acid (75 ml.). The mixture was extracted with ether, washed, dried, and the ether extracts concentrated. The oil obtained had $\nu^{film}_{max.}$ 1640 (m), 800 (s), 700 (vs) cm.$^{-1}$, identical with cycloocta-

1,5-diene (32). Analytical g.l.c. [50 m. poly(ethyleneglycol) capillary, 52°, 18 p.s.i./6.2, total flow 58 ml./min.] showed that it comprised 79% of the total reaction product. Treatment of cycloocta-1,3-diene under the same conditions caused no isomerisation to cycloocta-1,5-diene.

Attempted Dehalogenation of Dibromocyclooctadiene

(i) Using Zinc

A solution of the solid dibromocyclooctadiene (250 mg.) in ethanol (10 ml.) was added to a suspension of activated zinc[182] (4:1 excess) in ethanol (10 ml.) over 5 mins. The mixture was heated under reflux (with stirring) for 2 hrs. It was then cooled, water was added, and the aqueous solution extracted with pentane. This extract was washed, dried and concentrated to yield an oil which had ν^{film} 1660 (m), 1150 (m), 1100 (m), 1070 (m), 1040 (m), 1010 (m), 980 (m), 940 (m), 890 (m), 850 (m), 800 (m), 700 (vs) cm.$^{-1}$; $\lambda^{\text{pentane}}_{\text{max.}}$ 221, 226 mμ. Analytical g.l.c. (as above) showed one peak with R_T less than cyclooctatetraene, but greater than cycloocta-1,3-diene or cycloocta-1,5-diene.

(ii) Using magnesium.

A solution of the dibromocyclooctadiene (100 mg.) in ether (10 ml.) was added to a suspension of magnesium turnings (100 mg.) in ether (10 ml.). This mixture was heated under reflux on a steam bath for 2½ hrs. The remaining magnesium turnings were filtered off and the ether solution concentrated. The resulting oil had $\lambda^{\text{Et}_2\text{O}}_{\text{max.}}$ 215, 255 mμ.

Analytical g.l.c. (as before) showed two peaks, the major one (57%) with a very short R_T, the other (43%) with a longer R_T, though both had R_T
a very short
values less than that of cycloocta-1,3,5-triene.

Titration of the Dibromocyclooctadiene.[189]

A solution (100 μl.) of the dibromocyclooctadiene in methanol/water (4:1 ratio) was titrated with a standard silver nitrate solution (eosin as indicator), till the colour changed from orange to pale yellow. Required 50.5 μl. (mean value). One bromine equivalent requires 54.7 μl., so this was 92.3% of theoretical. Hence only one allylic bromine appears to be present in the dibromocyclooctadiene molecule.

Preparation of 5-Bromocycloocta-1,3-diene (132a)

A mixture consisting of cycloocta-1,3-diene (8.15 g.; 0.075 mole), N-bromosuccinimide (30 g.; 0.17 moles), and benzoyl peroxide (0.5 g.) was heated under reflux (3 hrs.) in carbon tetrachloride (150 ml.). After this period, the precipitate was filtered off and the solution concentrated to give a yellow oil (12 g., 85%). Thin layer chromatography (silica; petrol; iodine) showed that none of the constituents from the allylic bromination of cycloocta-1,5-diene corresponded to the main component of this reaction. Distillation of this oil did not purify it completely, and excessive decomposition during attempted column chromatography prevented further purification. This material had b.p. 52-68°/0.2 mm.; n_D^{23} 1.5506 (lit.[92] b.p. 56°/0.8 mm.; n_D 1.5488);

$\nu^{film}_{max.}$ 1195 (m), 1135 (m), 900 (s), 785 (s), 755 (s), 695 (vs) cm.$^{-1}$; $\lambda^{c.hexane}_{max.}$ 235 mμ. (ε = 6,140); n.m.r., multiplets centred at 4.25 (4H), 5.15 (1H), 7.9 (6H) τ. Found C, 51.4; H, 5.98; $C_8H_{11}Br$ requires C, 51.35; H, 5.88. The mass spectrum (hot box) had a parent ion at $^m/_e$ 214 (corresponding to $C_{16}H_{22}$), and no ions of any significance which could be ascribed to bromine atoms were present. These spectral and physical properties agree with those quoted for 5-bromocycloocta-1,3-diene. None of the reaction conditions tried yielded the desired 5,8-dibromocycloocta-1,3-diene (133c).

Reaction of 5-Bromocycloocta-1,3-diene (132a) with Lithium Aluminium Hydride/Lithium Hydride

A solution of 5-bromocycloocta-1,3-diene (200 mg.) in dry tetrahydrofuran (10 mls) was reacted with lithium aluminium hydride/lithium hydride (60 mg. and 160 mg.) in tetrahydrofuran (10 ml.) as described before (p.151). After extraction the resultant oil had $\nu^{film}_{max.}$ 930 (m), 830 (m), 800 (m), 690 (s) cm.$^{-1}$ Analytical g.l.c. (20% Cyano 'P', 50°, 40 ml./min.) showed only cycloocta-1,3-diene to be present.

TABLE X

Infrared Spectral Data.

Cycloocta-1,3-diene (film cm.$^{-1}$)	5-bromocycloocta-1,3-diene (film cm.$^{-1}$)	Dibromocyclooctadiene (KBr cm.$^{-1}$)	Dibromocyclooctadiene (CCl4 cm.$^{-1}$)
		3026	3035
3008	3004	3009	2998
		2976	
		2960	2960
		2948	
		2934	2937
2926	2924		
			2902
		2879	2882
2852	2850		
2824			
	1663		1654
		1645	1648
1639	1636		
1628	1624		
	1618		
		1487	1488
1445	1442		
1424	1424		
		1289	
	1195		
1166		1164	1164
1155	1151	1150	1147
	1137		
		1110	1114
911	907		914
		840	
810			
	793		
789			
780		783	
757	759	753	
733			
	720	719	
	700	708	
670	673		
660			
	631		
	594		
		578	576
	540		
	496		

TABLE XI

Ultraviolet Spectral Data.

Cycloocta-1,3-diene ($\lambda^{c.hexane}_{max.}$)	5-bromocycloocta-1,3-diene ($\lambda^{c.hexane}_{max.}$)	Dibromocyclo-octadiene ($\lambda^{c.hexane}_{max.}$)
230 mμ. ε = 4240	235 mμ. ε= 6140	224 mμ. ε = 3380

TABLE XII

N.M.R. Spectral Data for Various C_8 Cyclics.

	Compound	τ values (centres of multiplets quoted)						
1.	Cycloocta-1,5-diene	4.45					7.62	
2.	Cycloocta-1,3-diene	4.3					7.85	8.5
3.	Cycloocta-1,3,5-triene	4.23					7.58	
4.	Cycloocta-1,3,5,7-tetraene	4.3						
5.	Tetrabromocyclooctane I		5.2		7.1	7.25	7.8	8.0
6.	Tetrabromocyclooctane II		5.4				7.5	
7.	5-Bromocycloocta-1,3-diene	4.25	5.15				7.9	
8.	Dibromocyclooctadiene	4.4	5.45	6.45	7.25			

All spectra run in CCl_4 except 5 and 6 ($CDCl_3$).

Spin Decoupling Experiments on the Dibromocyclooctadiene

Double irradiation experiments were conducted with the dibromocyclooctadiene (in CCl_4, using the Perkin Elmer RS 10 60 Mc.p.s. instrument). The points of irradiation (1) to (5) are shown diagrammatically in Fig. 30. Due to the complexity of the spectrum, irradiation also caused unwanted interaction with other energetic sub-levels, and this decreased the effectiveness of these irradiations. The results may be summarised as follows.

Irradiation (1)

Group B was resolved into two distinct triplets (ratio 1:2:1), as if two separate protons were interacting with an adjacent methylene group.

The absorption due to Group C was basically unaltered, though one of the peaks appeared to collapse. Group D was completely unaffected.

Hence Group B is adjacent to Group A, i.e. at least one of the two protons in that group must be allylic, for if both were allylic and equivalent, the absorption should be much less complex in the primary irradiation trace.

Irradiation (2)

Group C is resolved into apparently six peaks, which could be ascribed to a double AB system, consisting of a doublet and a quadruplet. This could be due to each proton of the two in that group interacting independently with a single proton which is respectively cis or trans.

Group D is unaffected, and hence not adjacent to Group B_1. Group A could not be checked due to side band disruption in that region.

Irradiation (3)

Group C again appears to be a double AB system with eight separate peaks apparent. The reason should be the same as stated above, except that this time the interaction would be with the protons of Group B_1. The better resolution between these peaks may be due to either more precise irradiation, or to stronger interaction.

Group D does not appear to be affected, but as irradiation is not precisely on Group B_2, so optimum conditions may not have been attained for this to occur.

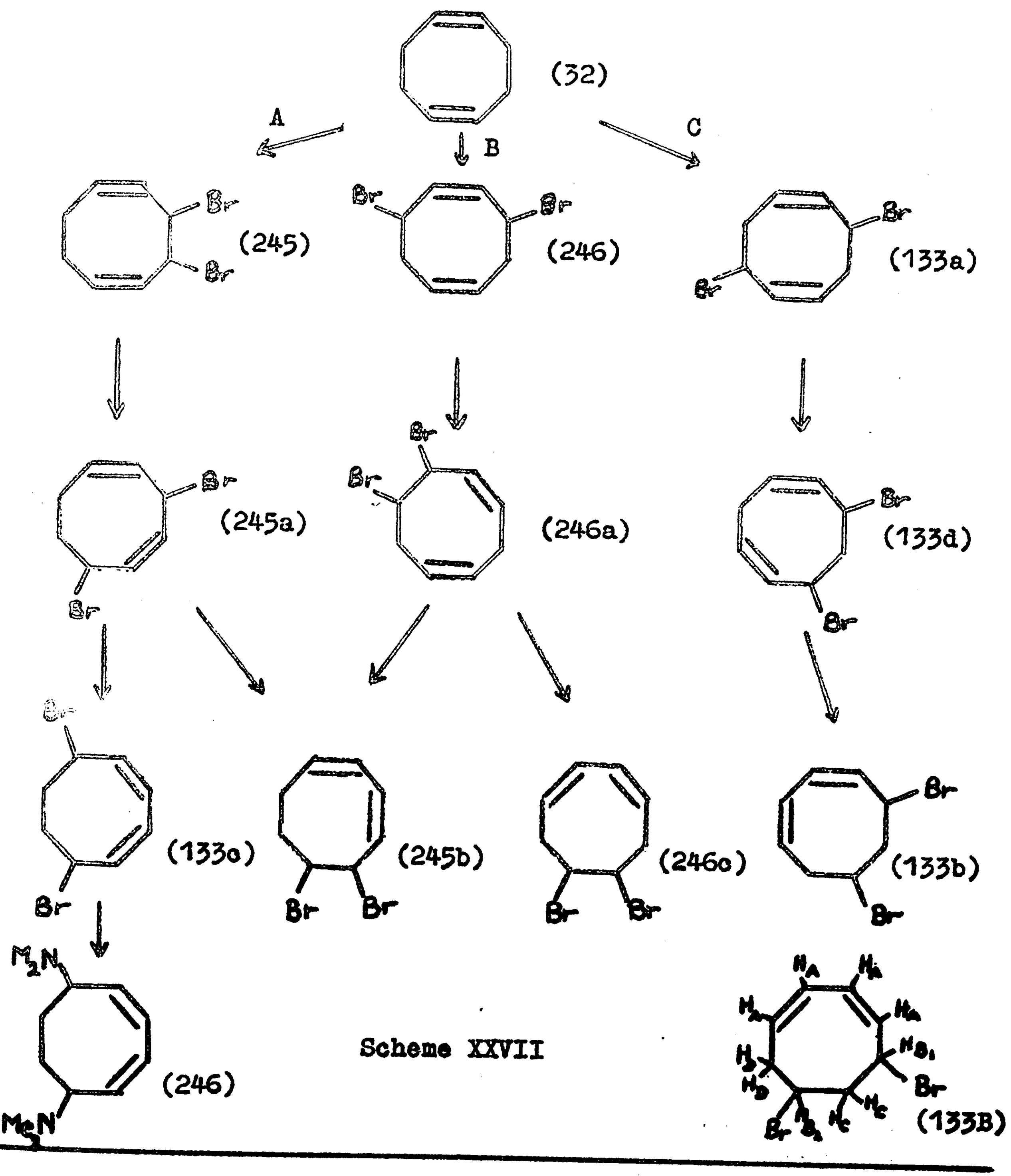
Irradiation (4)

Both Group A and D are unaffected, showing that they are not adjacent to Group C. This can leave only Group B_1 and B_2 next to Group C. The absorption for this group is indeed different, and consists of a triplet (1:2:1 ratio) intermingled with a quadruplet possibly from an AB system. The triplet should arise from the interaction of the proton in Group B_2 with those of Group D, while the quadruplet may be due to the interaction of the B_1 proton with one of the Group A protons, though it is difficult to understand why the coupling should be relatively so great. Another possible reason is that if irradiation of the Group C protons is incomplete, only one of them being fully irradiated, then the other may be interacting with the Group B_1 proton to give the quadruplet (with these protons <u>trans</u> to one another to account for the large separation).

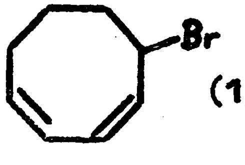
Irradiation (5)

Irradiation of Group D does affect Group A, but the complex pattern cannot be interpreted.

Group B is again transformed into a triplet (1:2:1 ratio) and a quartet (fine splitting). The triplet is probably due to the unaffected proton of Group B_1 interacting as usual with Group A. The quadruplet must be due to interaction between the protons of Group B_2 and those of Group C, though it is not understood why a quadruplet should result.



Scheme XXVII



(132a)

REFERENCES

1. M. Berthelot, Bull. Soc. Chim. France, 1866, 6, 268.

2. G. M. Badger, G. E. Lewis, I. M. Napier, J., 1960, 2825.

3. R. Fittig, A. Sohrohe, Chem. Ber., 1875, 8, 367.

4. Aldedingen, J. Soc. Phys. Chem. Russ., 1881, 13, 392.

5. A. Baeyer, Chem Ber., 1894, 27, 810.

6. T. M. M. Dormaar, Rec. Trav. Chim., 1904, 23, 394.

7. A. Baeyer, Chem. Ber., 1894, 27, 1915.

8. H. Kuczynski, M. Walkowicz, C. Walkowicz, K. Nowak, I. Z. Siemion,
Rocz. Chim., 1964, 38, 1625.

9. R. Ya. Levina, S. Ya. Levina, J. Gen. Chem. U.S.S.R.,
1938, 8, 1776.

10. H. Pines, R. C. Olberg, V. N. Ipatief,
J. Amer. Chem. Soc., 1948, 70, 533.

11. H. Pines, C. T. Chen, J. Amer. Chem. Soc., 1959, 81, 928.

12. V. Prelog, V. Boarland, S. Polyak,
Helv. Chim. Acta., 1955, 38, 434

13. V. Prelog, S. Polyak, Helv. Chim. Acta., 1957, 40, 816.

14. G. H. Badger, J. Novotny, Austral. J. Chem., 1963, 16, 613; 623.

15. H. Pines, C. T. Goetschel, G. H. Csicsery,
J. Org. Chem., 1963, 28, 2713.

16. W. Reppe, O. Schlichting, K. Klager, T. Toepel,
Annalen, 1948, 560, 1.

17. "Organometallic Chemistry", Ed. H. Zeiss, Reinhold Publishing Corp.,
New York, 1960, p. 411.

18. E. F. Lutz, J. Amer. Chem. Soc., 1961, 83, 2551.

19. J. J. Rooney, G. Webb, J. Catalysis, 1964, 3, 488.

20. F. W. Hoover, O. W. Webster, C. T. Handy,
J. Org. Chem., 1961, 26, 2234.

21. E. C. Colthup, L. S. Meriwether, J. Org. Chem., 1961, 26, 5169.

22. G. Drefahl, H. H. Hoerhold, H. Bretschneider,
J. Prakt. Chem., 1964, 25, 113.

23. C. E. Berkoff, R. C. Cookson, J. Hudec, R. O. Williams,
Proc. Chem. Soc., 1961, 312.

24. R. Criegee, F. Zanker, Angew. Chem., 1964, 76, 716.

25. E. E. van Tamelen, S. P. Pappas,
J. Amer. Chem. Soc., 1962, 84, 3789.

26. idem, ibid, 1963, 85, 3297.

27. E. M. Arnett, J. M. Bollinger, Tetrahedron Letters, 1964, 3803.

28. H. G. Viehe, R. Merenyi, J. F. M. Oth, P. Valange,
Angew. Chem. (Int.), 1964, 755.

29. H. G. Viehe, R. Merenyi, J. F. M. Oth, J. R. Senders, P. Valange,
Angew. Chem. 1964, 76, 922.

30. W. von E. Doering, M. R. Willcott, Tetrahedron Letters, 1962, 663.

31. R. Srinivasan, J. Amer. Chem. Soc., 1964, 86, 3318.

32. E. Vogel, D. Wendisch, W. R. Roth, Angew. Chem., 1964, 76, 432.

33. E. Muller, H. Fricke, Annalen, 1963, 661, 38.

34. E. Vogel, R. Schubert, W. A. Boll, Angew. Chem., 1964, 76, 535.

35. E. Vogel, M. Biskup, W. Pretzer, W. A. Boll,
Angew. Chem., 1964, 76, 785.

36. E. Ciganek, J. Amer. Chem. Soc., 1965, 87, 652.

37. E. Clar, "Polycyclic Hydrocarbons", Academic Press, 1964, Vol. I.

38. D. A. Ben-Efraim, F. Sondheimer, Tetrahedron Letters, 1963, 313.

39. S. Meyerson, H. Drews, E. K. Fields,
J. Amer. Chem. Soc., 1964, 86, 4964.

40. W. H. Perkin, J. L. Simonsen, J., 1907, 840.

41. J. M. Harkin, B.Sc. Thesis, Glasgow, 1955.

42. M. Rosenfeld, ibid, 1959.

43. R. G. Willis, Ph.D. Thesis, Glasgow, 1962.

44. Y. Amiel, F. Sondheimer, Chem. and Ind., 1960, 1162.

45. F. Sondheimer, Y. Gaoni, J. Amer. Chem. Soc., 1961, 83, 4863.

46. J. Dale, A. J. Hubert, G. S. D. King, J., 1963, 73.

47. W. McCrae, Ph.D. Thesis, Glasgow, 1960.

48. C. L. Osborn, T. C. Schields, B. A. Shoulders, C. G. Cardenas,
P. D. Gardner, Chem. and Ind., 1965, 766.

49. H. Finkelstein, W. Baker, J. F. W. McOmie,
Chem. Ber., 1959, 92, XXXVII.

50. M. P Cava, D. R. Napier, J. Amer. Chem. Soc., 1957, 79, 1701.

51. idem, ibid, 1958, 80, 2255.

52. idem, ibid, 1957, 79, 3606.

53. "Progress in Organic Chemistry Vol. III" Ed. J. W. Cook, Butterworths, London, 1955, p. 44.

54. W. Baker, J. F. W. McOmie, "Non-Benzenoid Aromatic Compounds" Ed. D. Ginsburg, Interscience Publishers, New York, 1959, p. 43.

55. W. Baker, "Chemistry in Britain", 1965, 191.

56. M. P. Cava, R. L. Shirley, J. Amer. Chem. Soc., 1960, 82, 654.

57. M. P. Cava, A. A. Deana, K. Muth, J. Amer. Chem. Soc., 1960, 82, 2524.

58. M. P. Cava, R. L. Shirley, B. W. Erickson, J. Org. Chem., 1962, 27, 755.

59. D. E. Applequist, R. Searle, J. Amer. Chem. Soc., 1964, 86, 1389.

60. A. C. Cope, S. W. Fenton, J. Amer. Chem. Soc., 1951, 73, 1673.

61. A. C. Cope, R. D. Smith, J. Amer. Chem. Soc., 1955, 77, 4596.

62. E. Cioranescu, A. Bucur, M. Elian, M. Banciu, M. Voicu, C. D. Nenitzescu, Tetrahedron Letters, 1964, 3835.

63. R. E. Benson, T. L. Cairns, J. Amer. Chem. Soc., 1950, 72, 5355.

64. A. C. Cope, M. Burg, J. Amer. Chem. Soc., 1952, 74, 168.

65. A. P. Ter Borg, A. F. Bickel, Rec. Trav. Chim., 1961, 80, 1217.

66. C. G. Cardenas, A. N. Khafaji, C. L. Osborn, P. D. Gardner,
Chem. and Ind., 1965, 345.

67. G. Wittig, A. Krebs, Chem. Ber., 1961, 94, 3260.

68. G. Wittig, R. Pohlke, ibid, 3276.

69. G. Eglinton, R. A. Raphael, R. G. Willis,
Proc. Chem. Soc., 1962, 334.

70. R. Willstatter, E. Waser, Chem. Ber., 1911, 44, 3423.

71. L. E. Craig, Chem. Revs., 1951, 49, 103.

72. R. A. Raphael, "Non-Benzenoid Aromatic Compounds", Ed. D. Ginsburg,
Interscience Publishers Inc., New York, 1959, p. 465.

73. H. Yamazaki, Bull. Chem. Soc. Jap., 1958, 31, 677.

74. E. Migirdicyan, S. Leach, Bull. Soc. Chim. Belges, 1962, 71, 845.

75. G. J. Fonken, Chem. and Ind., 1963, 1625.

76. A. C. Cope, N. A. Nelson, D. S. Smith,
J. Amer. Chem. Soc., 1954, 76, 1100.

77. C. R. Ganellin, R. Pettit, J. Amer. Chem. Soc., 1957, 79, 1767.

78. K. F. Bangert, V. Boekelheide, Chem. and Ind., 1963, 1121.

79. M. Stiles, H. Burckhardt, J. Amer. Chem. Soc., 1964, 86, 3396.

80. S. L. Friess, V. Boekelheide, J. Amer. Chem. Soc., 1949, 71, 4145.

81. S. Bank, A. Schriesheim, C. A. Rowe,
J. Amer. Chem. Soc., 1965, 87, 3244.

82. N. L. Allinger, E. A. Miller, L. A. Tushaus,
J. Org. Chem., 1963, 28, 2555.

83. R. Huisgen, H. Seidl, Tetrahedron Letters, 1964, 3381.

84. A. T. Blomquist, C. G. Bottomley,

J. Amer. Chem. Soc., 1965, 87, 86.

85. M. P. Cava, R. Pohlke, J. Org. Chem., 1963, 28, 1012.

86. F. R. Jensen, W. E. Coleman, A. J. Berlin,

Tetrahedron Letters, 1962, 15.

87. A. C. Cope, A. C. Haven, F. L. Ramp, E. R. Trumbull,

J. Amer. Chem. Soc., 1952, 74, 4867.

88. E. Vogel, O. Roos, K. H. Disch, Annalen, 1962, 653, 55.

89. W. Ziegenbein, Chem. Ber., 1965, 98, 1427.

90. W. von E. Doering, W. R. Roth, Angew. Chem. (Int.), 1963, 115.

91. W. Ziegenbein, Angew. Chem., (Int.), 1965, 70.

92. W. Sanne, O. Schlichting, Angew. Chem., 1963, 75, 156.

93. R. Huisgen, F. Mietzsch, Angew. Chem. (Int.), 1964, 83.

94. F. A. L. Anet, A. J. R. Bourn, Y. S. Lin,

J. Amer. Chem. Soc., 1964, 86, 3576.

95. E. Vogel, W. Frass, J. Wolpers, Angew. Chem., 1963, 75, 979.

96. R. Criegee, W. D. Wirth, W. Engel, H. A. Brune,

Chem. Ber., 1963, 96, 2230.

97. E. Vogel, H. Kiefer, W. R. Roth, Angew. Chem., 1964, 76, 432.

98. F. Sondheimer, Pure and Applied Chem., 1963, 7, 363.

99. A. J. Hubert, J. Dale, J., 1965, 3118.

100. J. Dale, J., 1965, 72.

101. A. J. Hubert, J. Dale, J., 1963, 86.

102. J. Dale, J., 1963, 93.

103. D. J. Cram, N. L. Allinger, J. Amer. Chem. Soc., 1956, 78, 2518.

104. G. Wittig, G. Koenig, K. Clauss, Annalen, 1955, 593, 127.

105. Y. Gaoni, F. Sondheimer, Proc. Chem. Soc., 1964, 293.

106. H. Weber, W. Ring, U. Hochmuth, W. Franke, Annalen, 1965, 681, 10.

107. G. Eglinton, R. A. Raphael, R. G. Willis, J. A. Zabkiewicz,
J., 1964, 2597.

108. W. H. Perkin, J. L. Simonsen, J., 1907, 816, 840, 843.

109. G. Eglinton, R. A. Raphael, R. G. Willis,
Proc. Chem. Soc., 1960, 247.

110. W. O. Jones, J., 1954, 1808.

111. E. W. Abel, M. A. Bennett, R. Burton, G. Wilkinson,
J., 1958, 4559.

112. N. A. Nelson, J. H. Fassnacht, J. U. Piper,
J. Amer. Chem. Soc., 1961, 83, 206.

113. A. C. Cope, C. L. Stevens, F. A. Hochstein,
J. Amer. Chem. Soc., 1950, 72, 2510.

114. L. E. Craig, R. M. Elofson, I. J. Rossa,
J. Amer. Chem. Soc., 1953, 75, 480.

115. L. Skattebol, Acta Chem. Scand., 1963, 17, 1683.

116. A. Meisters, J. M. Swann, Aust. J. Chem., 1965, 18, 155.

117. Favorskii, J. Prakt. Chem., 1898, 37, 382.

118. T. L. Jacobs, R. Arawie, R. G. Cooper,
J. Amer. Chem. Soc., 1951, 73, 1273.

119. E. R. H. Jones, G. H. Whitham, M. C. Whiting, J., 1954, 5201.

120. H. Normant, R. Mantione, Compt. Rend., 1964, 259, 1635.

121. W. R. Moore, R. C. Bertelson, J. Org. Chem., 1962, 27, 4182.

122. W. R. Moore, H. R. Ward, J. Amer. Chem. Soc., 1963, 85, 86.

123. R. G. Ackman, P. Linstead, B. J. Wakefield, B. C. L. Weedon,
Tetrahedron, 1960, 8, 221.

124. R. G. Ackman, R. A. Dytham, B. J. Wakefield, B. C. L. Weedon,
Tetrahedron, 1960, 8, 239.

125. R. A. Dytham, B. C. L. Weedon, Tetrahedron, 1960, 8, 246.

126. F. Sondheimer, R. Wolovsky, J. Amer. Chem. Soc., 1959, 81, 1771.

127. J. Dale, A. J. Hubert, J., 1963, 5475.

128. D. S. Magrill, Ph.D. Thesis, Glasgow, 1964.

129. H. Pines, J. Ryer, J. Amer. Chem. Soc., 1955, 77, 4370.

130. R. F. Paschke, D. H. Wheeler,
J. Amer. Oil Chem. Soc., 1955, 32, 473.

131. K. Alder, H. Brachel, Annalen, 1957, 608, 195.

132. W. D. Huntsman, R. P. Hall, J. Org. Chem., 1962, 27, 1988.

133. W. R. Roth, personal communication.

134. W. J. Bailey, R. A. Baylouny, J. Org. Chem., 1962, 27, 3476.

135. G. J. Fonken, Tetrahedron Letters, 1962, 549.

136. W. G. Dauben, R. L. Cargill, J. Org. Chem., 1962, 27, 1910.

137. C. A. Grob, P. Schiess, Angew. Chem., 1958, 70, 502.

138. E. Vogel, Angew. Chem. (Int.), 1963, 1.

139. R. Anet, Tetrahedron Letters, 1961, 720.

140. H. Hoever, ibid, 1962, 255.

141. R. Wolovsky, F. Sondheimer, J. Amer. Chem. Soc., 1962, 84, 2844.

142. F. Sondheimer, D. A. Ben-Efraim, Y. Gaoni, J. Amer. Chem. Soc., 1961, 83, 1682.

143. R. M. Roberts, E. C. Baylis, G. H. Fonken, J. Amer. Chem. Soc., 1963, 85, 3454.

144. E. J. Corey, H. J. Burke, W. A. Remers, J. Amer. Chem. Soc., 1955, 77, 4941.

145. W. G. Dauben, F. G. Willey, Tetrahedron Letters, 1962, 893.

146. W. O. Jones, J., 1954, 312.

147. A. C. Cope, L. L. Estes, J. Amer. Chem. Soc., 1950, 72, 1128.

148. H. P. Fritz, H. Keller, Chem. Ber., 1962, 95, 158.

149. T. J. Katz, J. Amer. Chem. Soc., 1960, 82, 3784.

150. T. J. Katz, H. L. Strauss, J. Chem. Phys., 1960, 32, 1873.

151. T. J. Katz, W. H. Reinmuth, D. E. Smith, J. Amer. Chem. Soc., 1962, 84, 802.

152. N. L. Allinger, J. Org. Chem., 1962, 22, 443.

153. H. L. Strauss, T. J. Katz, G. K. Fraenkel, J. Amer. Chem. Soc., 1963, 85, 2360.

154. F. A. L. Anet, A. J. R. Bourn, Y. S. Lin,

J. Amer. Chem. Soc., 1964, 86, 3576.

155. W. Reppe, H. Schlenk, Chem. Abs., 1956, 50, P 4207 i.

156. W. R. Roth, Annalen, 1964, 671, 25.

157. E. A. LaLancette, R. E. Benson, J. Amer. Chem. Soc., 1965, 87, 1941.

158. M. Ohno, M. Okamoto, Tetrahedron Letters, 1964, 2423.

159. G. Wilke, Angew. Chem., 1957, 69, 397.

160. R. Aurnhammer, R. Koenig, M. Minsinger, Chem. Abs., 1963, 59, P9839f.

161. L. I. Zakharkin, V. V. Korneva,

Doklady Akad. Nauk. S.S.S.R., 1960, 132, 1078.

Chem. Abs., 1960, 54, 20918e.

162. R. Alexander, B.Sc. Thesis, Glasgow, 1960.

163. F. Sondheimer, Pure and Applied Chem., 1963, 7, 363.

164. H. Brockmann, H. Schodder, Chem. Ber., 1941, 74, 73.

165. E. Haati, T. Nikkari, K. Juva, Acta. Chem. Scand., 1963, 17, 538.

166. E. Stahl, Chemiker-Ztg., 1958, 82, 323.

167. J. L. Everett, G. A. R. Kon, J., 1950, 3131.

168. T. H. Vaughn, R. R. Vogt, J. A. Nieuwland,

J. Amer. Chem. Soc., 1934, 56, 2120.

169. A. W. Johnson, J., 1946, 1009.

170. J. B. Armitage, E. R. H. Jones, M. C. Whiting, J., 1951, 44.

171. H. Bader, L. C. Cross, I. Heilbron, E. R. H. Jones, J., 1949, 619.

172. "Documentation of Molecular Spectra",

Butterworth's Scientific Publications, London.

173. W. von E. Doering, L. H. Knox, J. Amer. Chem. Soc., 1957, 79, 352.

174. H. Plieninger, G. Ege, Angew. Chem., 1958, 70, 505.

175. W. von E. Doering, A. K. Hoffmann,

J. Amer. Chem. Soc., 1954, 76, 6162.

176. W. M. Wagner, Proc. Chem. Soc., 1959, 229.

177. D. Seyforth, R. J. Minasz, A. J. H. Treiber, J. M. Burlitch,

R. S. Dowd, J. Org. Chem., 1963, 28, 1163.

178. O. A. Reutor, A. N. Lovtsova,

Doklady Akad. Nauk. S.S.S.R., 1961, 139, 622.

Chem. Abs., 1962, 56, 1469a.

179. L. Skattebol, personal communication,

and J. Org. Chem., 1964, 29, 2951.

180. H. Gilman, J. W. Morton, Organic Reactions, Vol. VIII, p. 285.

181. L. F. Fieser, "Experiments in Organic Chemistry",

Heath and Co., Boston, 1955, chap. 10, p. 65.

182. Organic Syntheses, Coll. Vol. III, p. 74.

183. H. Takahashi, M. Yamaguchi, J. Org. Chem., 1963, 28, 1409.

184. G. Wittig, H. Eggers, P. Duffner, Annalen, 1958, 619, 10.

185. J. Sicher, J. Zavada, M. Svoboda,

Coll. Czech. Chem. Comm., 1962, 27, 1927.

186. "Interpretation of the Ultraviolet Spectra of Natural Products",

A. I. Soott, Pergamon Press, 1964, p. 48.

187. A. C. Cope, L. L. Estes, J. R. Emery, A. C. Haven,

J. Amer. Chem. Soc., 1951, 73, 1199.

188. C. S. Mervel, B. D. Wilson, J. Org. Chem., 1958, 23, 1483.

189. Kolthoff, Stender, "Volumetric Analysis" Vol. II,

Interscience Publishers Inc., New York, 1947, p. 250.

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497. *Rearrangement of Diacetylenes to Aromatic Compounds.*

By G. EGLINTON, R. A. RAPHAEL, R. G. WILLIS, and J. A. ZABKIEWICZ.

Hepta-1,6-diyne-4-carboxylic acid (I) readily undergoes base-catalysed aromatisation in high yield to *m*-toluic acid. The rearrangement has been extended to diacetylenic hydrocarbons of types (II) and (III) which give mixtures consisting mainly of the correspondingly *o*-disubstituted and monosubstituted benzenes.[1]

BY dehydrobromination and hydrolysis of diethyl di-(2-bromoallyl)malonate Perkin and Simonsen [2] isolated a crystalline acid, $C_8H_8O_2$, m. p. 47°, which they named "ψ-*m*-toluic acid." They assigned to it the plausible structure hepta-1,6-diyne-4-carboxylic acid (I), and reported that it underwent a remarkable isomerisation by treatment with hot mineral acid, or even by boiling with water, to give *m*-toluic acid. Attempted repetition of Perkin and Simonsen's route to this compound was uniformly unsuccessful in our hands. A preparation of authentic hepta-1,6-diyne-4-carboxylic acid, m. p. 45·5°, was carried out by dialkylation of diethyl malonate with prop-2-ynyl chloride followed by careful hydrolysis and decarboxylation.[3] This acid was substantially unaffected by boiling water and was only slowly attacked by mineral acid with the formation of lactonic products.[4] No indication could be found of the production of *m*-toluic acid or its derivatives under any of the conditions previously described.[2] However, when the diacetylenic acid was boiled with potassium hydroxide solution it was transformed virtually quantitatively into *m*-toluic acid.

Perkin and Simonsen suggested an unlikely mechanism involving hydration of the two triple bonds of hepta-1,6-diyne-4-carboxylic acid and aldolisation of the resulting diketo-acid. This latter acid has now been prepared by hydration of acid (I) but, as expected,

$$\underset{\text{(I)}}{(HC\equiv C\cdot CH_2)_2\cdot CH\cdot CO_2H} \qquad \underset{\text{(II)}}{HC\equiv C\cdot[CH_2]_n\cdot C\equiv CH} \qquad \underset{\text{(III)}}{CH_3\cdot[CH_2]_n\cdot(C\equiv C)_2\cdot[CH_2]_n\cdot CH_3}$$

treatment with base produced only 3-methyl-5-oxocyclohex-3-ene-1-carboxylic acid,[4] with no trace of *m*-toluic acid. In order to examine the generality and structural requirements for this unusual rearrangement it was extended to a series of diacetylenic hydrocarbons. Preliminary experiments showed that potassium t-butoxide dispersed in boiling bis-(2-methoxyethyl) ether (diglyme) was a convenient basic medium. Treatment in this manner of the hydrocarbon most nearly related to (I), hepta-1,6-diyne (II; $n = 3$), rapidly caused substantial aromatisation to toluene. In a similar manner a variety of straight chain $\alpha\omega$-diacetylenes (II; $n = 4, 5, 6, 10, 17$) gave products consisting mainly of the isomeric *o*-dialkylbenzenes, the total conversion into aromatic compounds being in most cases around 65%. The rearrangement was not confined to terminal acetylenes; thus, nona-2,7-diyne gave the same proportions of n-propylbenzene and *o*-ethylmethylbenzene as did nona-1,8-diyne (II; $n = 5$). Conjugated diynes underwent the rearrangement with equal ease; thus, both octa-3,5-diyne and octa-1,7-diyne produced similar proportions of ethylbenzene and *o*-xylene.

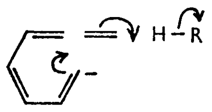
To study the reaction in more detail the isomeric pair, deca-1,9-diyne and deca-4,6-diyne, were investigated. Analysis using a high-resolution capillary gas chromatography column calibrated with known synthetic mixtures revealed similar proportions of the expected benzenoid isomers, n-butylbenzene, *o*-methyl-n-propylbenzene, and *o*-diethylbenzene, the last two isomers predominating. However, these were by no means the only peaks to appear; at least six further products were indicated on the traces from both diynes. The ethylenic nature of these "abnormal" constituents was clearly shown by the nuclear magnetic resonance (n.m.r.) spectra of the total product. That at least some of these olefins were conjugated was demonstrated by differential ultraviolet (u.v.)

spectroscopy. Infrared (i.r.) spectra showed strong indications of cyclic *cis*-double bonds (sharp band at 700 cm.$^{-1}$). These olefinic properties disappeared completely when the mixture was catalytically hydrogenated (under conditions which left the benzenoid constituents unscathed). The absence of n-decane, demonstrated by gas-liquid chromatography (g.l.c.) of the hydrogenated mixture, showed conclusively that these olefinic constituents were certainly not straight-chain compounds but were most likely cyclic in nature. Certain unassigned peaks on the traces did not shift on hydrogenation; these almost certainly could not have corresponded to ethylenic compounds and this point is discussed below in connection with the C_8 diyne.

In view of the large number of isomeric possibilities for these C_{10} by-products, detailed investigation of this aspect of the rearrangement was transferred to the C_8 system. Similar base-catalysed isomerisation of octa-1,7-diyne produced an eight-component mixture (capillary column). The expected ethylbenzene and *o*-xylene formed the two most important components of the mixture. As in the C_{10} series, the spectral data (u.v., n.m.r., i.r.) clearly indicated conjugated ethylenic unsaturation (*cis*-CH=CH), and these characteristics vanished on hydrogenation. Examination by analytical and preparative g.l.c. of the hydrogenated mixture showed, of course, that the peaks due to ethylbenzene and *o*-xylene had not altered their position. However, most unexpectedly, a partly resolved double peak was also unaltered in position after hydrogenation, strongly suggesting the presence of two further aromatic isomers; these were identified by g.l.c. as *m*- and *p*-xylene! Two further components of the hydrogenated product proved to be cyclo-octane and methylcycloheptane, identified by g.l.c. and n.m.r. Employment of milder rearrangement conditions (2% butoxide in diglyme for 2 hr.) gave a very similar product distribution, with the addition of two acyclic products tentatively identified as octa-1,3,5,7-tetraene and octa-2,6-diyne.

At this point it was found that a drastic simplification of this product complexity could be achieved by using carefully filtered butoxide solutions in diglyme. Even though the solution was extremely dilute (~0·2% butoxide), it effected very rapid and clean-cut isomerisation of octa-1,7-diyne to a 9 : 5 mixture of *o*-xylene and ethylbenzene with the formation of less than 1% of by-products. It would therefore seem at first sight that the formation of anomalous side-products in the isomerisation is associated with the presence of solid butoxide; this point is being further examined.

The simplest conception to account for the production of monoalkyl- and *o*-dialkylbenzenes from diacetylenes would seem to be a multiple prototropic rearrangement to a *cis*-allene diene of the type shown, followed by either an intramolecular Diels–Alder reaction [1,5] or internal attack on the allene by a terminal carbanion [6] as depicted. Such a mechanism would imply the necessary involvement of at least a seven-carbon chain and it is interesting to note that base-catalysed rearrangement of hexa-1,5-diyne under the above and other conditions [7] furnishes no detectable trace of benzene. Since the original announcement [1] of this aromatisation a number of allied base-catalysed transformations have been reported, *e.g.*, cyclo-octatetraene to benzocyclobutene,[8] non-conjugated macrocyclic diynes to 1,2-polymethylenebenzenes,[9] cyclododeca-1,3,7,9-tetrayne to biphenylene,[10] cyclohexadeca-1,9-dien-4,6,12,14-tetrayne to 10-diphenylsuccindene,[11] *cis*-oct-4-en-1,7-diyne to two dimers of *o*-dimethylenequinone,[12] cyclo-octadeca-1,3,7,9,13,15-hexayne to triphenylene,[13] and 1,6-dithiacyclodeca-3,8-diyne to 4,9-dithiabicyclo[5,3,0]deca-1(10)2,7-triene.[14]



Suggested mechanisms for the production of alicyclic products and *m*- and *p*-dialkylbenzenes in the non-homogeneous reactions would be premature at this stage. Certainly alkyl- and *o*-dialkyl-benzenes remain unaffected under these conditions and therefore cannot be the source of the unexpected compounds. Further experiments are in hand to clarify these findings.

EXPERIMENTAL

Light petroleum had b. p. 30—40°. Diglyme [bis-(2-methoxyethyl) ether] was purified by heating under reflux over sodium and subsequent distillation. The g.l.c. studies were made with a Pye Argon chromatograph (packed columns) equipped with a strontium-90 detector and a Perkin-Elmer model 451 fractometer (50 m. Apiezon L capillary column and 2 m. packed columns) equipped with a flame-ionisation detector. The packed columns were also used for small-scale preparative separations, using a hot-wire detector. Peak areas were measured by means of a planimeter and standard solutions of the various aromatic hydrocarbons, singly and as mixtures, were used to evaluate the possible differing response of the detector; in practice these differences were found to be negligible.

Quantitative i.r. measurements were obtained with a Unicam S.P. 130 grating spectrophotometer and survey spectra with either a Perkin-Elmer 137 or 237 instrument. The u.v. spectra were measured with a Perkin-Elmer model 137 UV and with a Unicam S.P. 500 spectrophotometer. An Associated Electrical Industries model RS2 (60 megacycles) instrument was employed for the n.m.r. spectra, with tetramethylsilane as internal standard.

Diethyl Di-(2-bromoallyl)malonate.—The original method [2] from 1,2,3-tribromopropane was repeated but a much better yield was obtained by using 2,3-dibromoprop-1-ene as follows. The dibromopropene [15] (67 g.) was added dropwise to a stirred suspension of diethyl sodiomalonate [from sodium (7·8 g.) and diethyl malonate (29 g.)] in ethanol (125 ml.) at 60°, and the mixture heated under reflux for 30 min. The bulk of the solvent was removed under reduced pressure and the resulting suspension poured into dilute sulphuric acid. Isolation with ether and distillation, gave the ester as an oil (43 g.), b. p. 122—123°/0·1 mm., n_D^{20} 1·5010 (lit.,[2] b. p. 191°/11 mm.), which solidified to long needles, m. p. 7° (Found: C, 40·5; H, 4·6; Br, 39·3. Calc. for $C_{13}H_{18}Br_2O_4$: C, 39·3; H, 4·6; Br, 40·2%); $\nu_{max.}$ (film) 1735s, 1616s, 1200s, and 855s cm.$^{-1}$. All attempts to convert this ester into "ψ-*m*-toluic acid" by the reported method [2] failed. It was noteworthy, however, that drastic alkaline treatment produced excellent yields of *m*-toluic acid.

Hepta-1,6-*diyne*-4,4-*dicarboylic Acid.*—Dimethylhepta-1,6-diyne-4,4-dicarboxylate, m. p. 46°, was prepared in high yield by the dialkylation of diethyl malonate with prop-2-ynyl chloride [4] or bromide. This ester (7·5 g.), in methanol (20 ml.), was added to a warm solution of potassium hydroxide (5 g.) in 80% aqueous methanol (20 ml.). The resultant suspension was heated for 2 hr. on a steam-bath and diluted with methanol (20 ml.), the precipitated salt was collected, dissolved in water, and acidified, and the crude free acid was extracted; it (4·2 g.) had m. p. 139—140° [benzene–light petroleum (3 : 1)] (lit.,[16] 140°).

Hepta-1,6-*diyne*-4-*carboxylic Acid* (I).—The dicarboxylic acid (2·2 g.) was dissolved in pyridine (15 ml.), the solution heated under reflux for 90 min., and the solvent removed *in vacuo.* The residue was treated with dilute sulphuric acid (100 ml.); the resulting acid crystallised from light petroleum in large prisms (1·4 g.), m. p. 45·5° (lit.,[16] 45°).

Isomerisation of Acid (I) *to* m-*Toluic Acid.*[17,18]—The action of boiling water, hot dilute sulphuric acid (10%), or hot potassium carbonate solution on the acid (I) produced no *m*-toluic acid, as indicated by the absence of its characteristic spectral properties. Successful isomerisation was carried out as follows. A solution of the acid (I) (590 mg.) in 10% aqueous potassium hydroxide (50 ml.) was heated under reflux for 4 hr. Acidification, and crystallisation of the product from water gave *m*-toluic acid (420 mg.), m. p. 111—112°, identical with an authentic sample.

2,6-*Dioxoheptane*-4-*carboxylic Acid.*[7]—A solution of the acid (I) (2·8 g.) in water (200 ml.) was heated under reflux with mercury-impregnated Amberlite IR-120 H resin (2·8 g.) for 30 min.[19] Isolation by means of ether yielded the *dioxo-acid* (2·6 g.) as needles, m. p. 72·5° (from ethyl acetate–light petroleum) (Found: C, 56·0; H, 6·8. $C_8H_{12}O_4$ requires C, 55·8; H, 7·0%). Base treatment of this compound gave no *m*-toluic acid, but the product showed spectral properties in accord with the expected 3-methyl-5-oxocyclohex-3-ene-1-carboxylic acid.

Preparation of Diacetylenes.—Hexa-1,5-diyne,[20] hepta-1,6-diyne,[21] octa-1,7-diyne,[22] nona-1,8-diyne,[23,24] deca-1,9-diyne,[23] nona-2,7-diyne,[25] octa-3,5-diyne,[26] deca-4,6-diyne,[26] tetradeca-1,13-diyne [27] were prepared by standard literature methods.

Heneicosa-1,20-diyne was obtained as follows. Undeca-10-yn-1-yl chloride [28] (17·3 g.) in benzene (250 ml.) was treated with triethylamine (11 g.), set aside overnight at room temperature, then acidified with dilute sulphuric acid, and the diketen isolated with ether. The residue after removal of solvent was dissolved in aqueous ethanolic potassium hydroxide [potassium hydroxide (13 g.) water (10 ml.), ethanol (125 ml.)], set aside for 48 hr., and refluxed for 4 hr. The *heneicosa*-1,20-*diyn*-11-*one* (13·6 g.) separated from the cooled solution in plates, m. p. 46—47° (from aqueous methanol) (Found: C, 83·4; H, 11·0. $C_{21}H_{34}O$ requires C, 83·4; H, 11·3%); $\nu_{\max.}$ (film) 3270, 2110 (–C≡C–H), and 1700 cm.$^{-1}$. A mixture of the ketone (500 mg.), dioxan (10 ml.), water (20 ml.), concentrated hydrochloric acid, and zinc amalgam (10 g.) was heated under reflux for 6 hr., during which time a further quantity of acid (5 ml.) was added. Isolation by light petroleum and chromatography on alumina (grade V) gave *heneicosa*-1,20-*diyne* as a waxy solid, m. p. 47—48° (from methanol) (single peak on g.l.c.) (Found: C, 87·3; H, 12·6. $C_{21}H_{36}$ requires C, 87·4; H, 12·6%); $\nu_{\max.}$ (film) 3300, 2110, and 725 cm.$^{-1}$.

Aromatisation of Diynes (*General Method*).—The basic medium was prepared just before use, as an opalescent dispersion, by refluxing freshly-prepared potassium t-butoxide (previously heated at 160° under reduced pressure until sublimation started) with ten times its weight of diglyme. The diyne (500 mg.) and this reagent (3 g. of butoxide in 30 ml. of solvent) were refluxed under nitrogen for the requisite period (4—15 hr.). The mixture was diluted with water and extracted with pentane. Repeated washing with water, drying ($MgSO_4$), and evaporation of the extract gave the hydrocarbons.

The aromatic products were detected by the absorption bands, γ(CH), near 750 and 690 cm.$^{-1}$ due to *o*-disubstituted and monosubstituted benzenes, respectively; by permanganate oxidation to phthalic and benzoic acids, respectively, and by comparative g.l.c. studies with authentic alkylbenzenes where feasible.

Diacetylene	Main benzenoid products
Hexa-1,5-diyne (II; $n = 2$)	—
Hepta-1,6-diyne (II; $n = 3$)	Toluene
Octa-1,7-diyne (II; $n = 4$) Octa-3,5-diyne (III; $n = 1$)	Ethylbenzene and *o*-xylene
Nona-1,8-diyne (II; $n = 5$) Nona-2,7-diyne	n-Propylbenzene and *o*-ethyltoluene
Deca-1,9-diyne (II; $n = 6$) Deca-4,6-diyne (III; $n = 2$)	n-Butylbenzene, *o*-n-propyltoluene, and *o*-diethylbenzene
Tetradeca-1,13-diyne (II; $n = 10$) Heneicosa-1,20-diyne (II; $n = 17$)	Complex mixture of isomeric *o*-dialkylbenzenes

Deca-1,9-*diyne and Deca*-4,6-*diyne*.—The relevant hydrocarbon was heated under reflux as above for 8 hr., and the product examined by capillary g.l.c. and n.m.r., i.r., and u.v. spectroscopy. (A time study of the progress of the reaction of deca-4,6-diyne showed that no diyne was detectable after 1 hr.; after 25 hr. the g.l.c. pattern was essentially similar.) The product of hydrogenation with 10% palladium–charcoal in ethyl acetate was examined in exactly the same manner.

The " before " and " after " results for deca-1,9-diyne are illustrated in the Figure. The g.l.c. trace of the primary product showed a nine-component mixture, of which the three peaks indicated corresponded to n-butylbenzene, *o*-diethylbenzene, and *o*-n-propyltoluene in

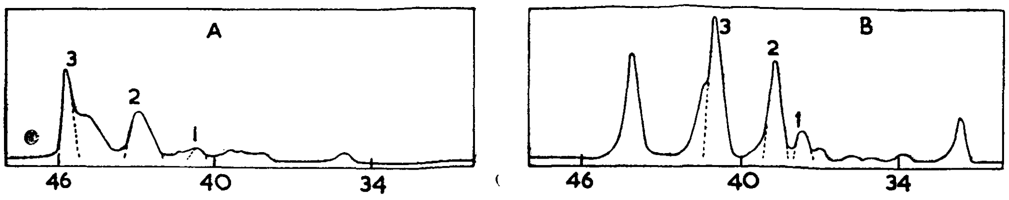
Physical properties of aromatic reaction products.

		Bands in 800—650 cm.$^{-1}$ region (CS$_2$; 0·51 mm. cell)				R_{RT}	$\lambda_{\max.}$ (mμ) (cyclohexane)	ε
o-Diethylbenzene	γCH	753						
	$\Delta\nu\frac{1}{2}$	8				1·00	265	175
	ε^a	160						
o-n-Propyltoluene	γCH		745					
	$\Delta\nu\frac{1}{2}$		14			1·06	265	265
	ε^a		150					
n-Butylbenzene	γCH		744		696			
	$\Delta\nu\frac{1}{2}$		18		7	0·94	262	215
	ε^a		95		195			
Primary product from deca-1,9-diyne	γCH	753	742	707		0·95		
	$\Delta\nu\frac{1}{2}$	sh	~18	10		1·00	264	1905
	ε^a	~65	100	80		1·06		
Hydrogenated product from deca-1,9-diyne	γCH	753	742		697	0·97		
	$\Delta\nu\frac{1}{2}$	sh	~8		~7	1·00	264	115
	ε^a	55	90		5	1·06		

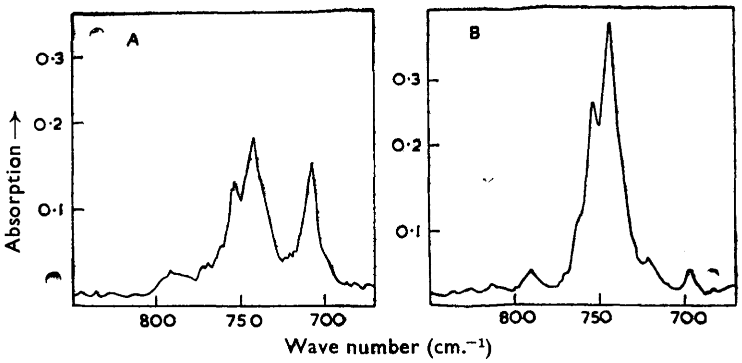
R_{RT} = Retention time relative to *o*-diethylbenzene (for conditions see Figure).

approximate proportions of 2 : 5 : 6; these identifications were made by direct comparison with authentic samples (see Table). The hydrogenated product also showed the expected peaks for these aromatic isomers in the same proportions. Seven other components were detectable in the hydrogenation product but n-decane was not present.

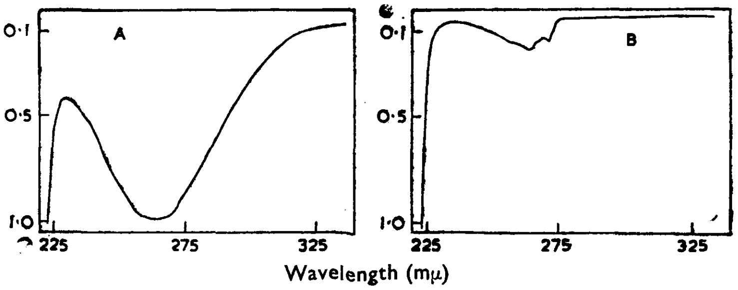
The n.m.r. spectrum of the primary product clearly showed the presence of ethylenic compounds (vinylic proton absorption over the region τ 3·5—4·9) as well as aromatic products (τ 2·8—3). This was confirmed by the disappearance of the former absorption in the n.m.r. spectrum of the hydrogenated product. The i.r. absorption of the primary product clearly



Apiezon L capillary column with flame-ionisation detector; 50 m.; 81°; 50 and 110 ml./min., respectively (total flow). 1. n-Butylbenzene. 2. *o*-n-Propyltoluene. 3. *o*-Diethylbenzene.



Cell path 0·51 cm.; concentrations 4·6 and 11·1 mg./ml., respectively, in carbon disulphide.



Cell paths 0·1 and 0·2 cm., respectively; concentrations 0·64 and 0·79 mg./ml., respectively, in cyclohexane.

G.l.c., i.r., and u.v. characteristics of the primary product (A) and the hydrogenated product (B) from the rearrangement of deca-1,9-diyne.

showed the presence of *o*-dialkylbenzenes (Table). The strong band at 707 cm.$^{-1}$ was found to be due predominantly to *cis*-ethylenic absorption, its sharpness being indicative of an endocyclic ethylene. This band vanished completely in the hydrogenation product revealing a small residual absorption at 697 cm.$^{-1}$ due to n-butylbenzene. The presence of conjugated ethylenic unsaturation in the primary product was revealed by the u.v. spectrum. In the hydrogenated product this band collapsed to reveal the weak absorption in the 260 mμ region characteristic of alkyl-benzenes.

The cognate rearrangement of deca-4,6-diyne gave substantially the same products (g.l.c., n.m.r., i.r., and u.v.). The relative proportions of the aromatic hydrocarbons were essentially the same, but there was a greater preponderance of ethylenic consitituents.

From these results it would seem that the main products from these two isomeric diynes were the three expected aromatic isomers. At least some of the remaining unassigned g.l.c. peaks must correspond to a range of unsaturated conjugated cyclic hydrocarbons. As the isomeric possibilities for such structures of molecular formula $C_{10}H_{14}$ are very numerous it was decided to obtain further insight into these by-products by obtaining analogous compounds from a hydrocarbon of lower molecular weight.

*Rearrangement of Octa-*1,7-*diyne.*—(*a*) The conditions of the preceding experiment were used; no further isomerisation could be detected after 2 hr. In these circumstances octa-1,7-diyne gave a primary product separated into eight components by capillary g.l.c. (Apiezon L; 50 m.; 81°; total flow rate 55 ml./min.). The two main components were identified as the expected *o*-xylene and ethylbenzene in a proportion of 5 : 3 (by direct area comparison).

However, most unexpectedly, a partly resolved double peak was present, which appeared to be due to *m*- and *p*-xylene. Preparative g.l.c. [poly(ethylene glycol) column, 20%; 2 m., 85°; 20 p.s.i. pressure] furnished a fraction which was shown by i.r. and analytical g.l.c. (20% of 7,8-benzoquinoline column; 2 m.; 80°; 65 ml./min.) to contain *m*- and *p*-xylene. The total aromatic constituents were shown to be present in the proportions of *o*-xylene : ethylbenzene : *m*-xylene + *p*-xylene = 5 : 3 : 2 (by peak area). The i.r. (film; γCH, $cm.^{-1}$) and g.l.c. (retention time; min.) identification data for the aromatic constituents were as follows. Product: 795w, 790w, 743vs, 707s, 697s; R_t 17·85, 19·10, 20·35, 25·70. Ethylbenzene: 790vw, 772w, 697vs; R_t 17·80. *m*-Xylene: 770vs, 695s; R_t 19·00. *p*-Xylene: 795vs; R_t 20·30. *o*-Xylene: 743vs; R_t 25·65. The possibility that the *m*- and the *p*-isomer had arisen by isomerisation of *o*-xylene or ethylbenzene under these conditions was disproved by direct trial.

Examination of the primary product, using g.l.c., and n.m.r., i.r., and u.v. spectroscopy, showed the presence of conjugated ethylenic carbocycles. Hydrogenation of the primary product and g.l.c. (capillary column) showed the four aromatic peaks due to ethylbenzene and the three xylenes. Apart from these, four further peaks were obtained; the two predominant ones were isolated by preparative g.l.c. in the following manner. A poly(ethylene glycol) column (20% stationary phase; 2 m.; 80°; and 18 p.s.i. pressure) was used for the initial separation of the non-aromatic fraction, which was then subjected to further separation on an Apiezon L column (20% stationary phase; 2 m.; 85°; and 18 p.s.i. pressure). The two predominant fractions were collected and identified as cyclo-octane and methylcycloheptane by direct comparison (g.l.c., n.m.r.) with authentic samples.

(*b*) The use of a 2% butoxide dispersion for 2 hr. gave a similar spread of products with the addition of two further components. One was detected in the mixture by its strong absorption at 269 (ε 400), 280 (ε 400), 293 (ε 45), and 306 mμ (ε 305) (cyclohexane); this suggested the presence of a small percentage of the acyclic octa-1,3,5,7-tetraene [$\lambda_{max.}$ (iso-octane) 267, 278, 290, and 304 mμ].[7]

A second acyclic component, isolated by preparative g.l.c. [20% poly(ethylene glycol); 2 m.; 90°; and 18 p.s.i. pressure], possessed properties compatible with its tentative formulation as octa-2,6-diyne [29] (u.v., end absorption only) $\nu_{max.}$ (film) 2338w, 2235w, 2050w, 1435s, 1375w, 1340m $cm.^{-1}$. Hydrogenation with 10% palladium–charcoal gave a product identified by analytical g.l.c. as n-octane.

(*c*) A hot dispersion of 2% butoxide in diglyme was carefully filtered through a sintered-glass filter under nitrogen. Use of this filtrate for the isomerisation (2 hr.) gave a two-component mixture of *o*-xylene and ethylbenzene, as shown by g.l.c., with only traces of other components.

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[1] Eglinton, Raphael, and Willis, *Proc. Chem. Soc.*, 1960, 247.
[2] Perkin and Simonsen, *J.*, 1907, 816, 840, 848.
[3] Schulte and Reiss, *Chem. Ber.*, 1954, **87**, 964.
[4] Schulte and Nimke, *Arch. Pharm.*, 1957, **290**, 597; Schulte, Mleinek, and Schär, *ibid.*, 1958, **291**, 227.
[5] Alder and Brachel, *Annalen*, 1957, **608**, 195.
[6] Skatteböl and Sörensen, *Acta Chem. Scand.*, 1959, **13**, 2101.
[7] Sondheimer, Ben-Efraim, and Wolovsky, *J. Amer. Chem. Soc.*, 1961, **83**, 1675.
[8] Eglinton, Raphael, and Willis, *Proc. Chem. Soc.*, 1962, 334.
[9] Dale, Hubert, and King, 1963, 73.
[10] Wolovsky and Sondheimer, *J. Amer. Chem. Soc.*, 1962, **84**, 2844.
[11] Sondheimer and Gaoni, *J. Amer. Chem. Soc.*, 1961, **83**, 4863.
[12] Ben-Efraim and Sondheimer, *Tetrahedron Letters*, 1963, 313.
[13] Amiel and Sondheimer, *Chem. and Ind.*, 1960, 1162.
[14] Eglinton, Lardy, Raphael, and Sim, *J.*, 1964, 1154.
[15] Lespieau and Bourguel, *Org. Synth.*, Coll. Vol. I, 209.
[16] Gaudemar, *Compt. rend.*, 1953, **237**, 71.
[17] Harkin, B.Sc. Thesis, Glasgow University, 1955.
[18] Rosenfeld, B.Sc. Thesis, Glasgow University, 1959.
[19] Newman, *J. Amer. Chem. Soc.*, 1953, **75**, 4740.
[20] Raphael and Sondheimer, *J.*, 1950, 120.
[21] Kamm and Marvel, *Org. Synth.*, Coll. Vol. I, 25.
[22] Bader, Cross, Heilbron, and Jones, *J.*, 1949, 619.
[23] Everett and Kon, *J.*, 1950, 3131.
[24] Lespieau and Journaud, *Compt. rend.*, 1929, **188**, 1410.
[25] Henne and Greenlee, *J. Amer. Chem. Soc.*, 1945, **67**, 484.
[26] Armitage, Jones, and Whiting, *J.*, 1951, 44.
[27] Eglinton and Galbraith, *J.*, 1959, 889.
[28] Sauer, *J. Amer. Chem. Soc.*, 1947, **69**, 2444.
[29] Sheppard and Simpson, *Quart. Rev.*, 1952, **6**, 1.

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