A Thesis

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"Macrocyclic Acetylenic Compounds"

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CONTENTS.

PART I

INTRODUCTION: MACROCYCLIC ACETYLENIC COMPOUNDS.

The chemistry of macrocyclic acetylenic compounds has excited considerable interest in recent years and the following introduction comprises a review of the work of this field since 1960 (a description of previous results before this date has been given by Behr[1]).

In 1960, the synthesis of the highly strained cyclic tatrayne (2) was reported[2,3,4]. The high dilution oxidative coupling of o-diethynylbenzene (1) furnished (2) as unstable canary yellow needles (decomp. ca. 80°) in 43% yield. The instability of this hydrocarbon is not surprising when consideration is given to its extraordinary strained structure with the acetylenic linkages "bowed" outwards. Under mild reducing conditions (Pd-C), the tetrayne (2) underwent extensive transannular interactions with the formation of (4) (3%) and (6) (38%). The expected reduction product (5) was obtained in 50% yield and could be dehydrogenated to (6) exclusively. Sodium-ammonia reduction of (2) produced (3) (70%) which could then be dehydrogenated to one of the catalytic reduction products (4).

Nakagawa[5], two years later, carried out a similar coupling on 9,10-diethynylphenanthrene (7) to test the generality of this cyclic dimerisation of compounds containing the o-diethynyl structure. The tetrayne (8) was obtained as orange needles (decomp. ca. 290° without melting) in 33% yield. Catalytic hydrogenation (Pd-C) of (8) gave a mixture from which the crystalline hydrocarbon (9)(25%) was isolated. The liquid component of the crude product was not examined but it may possibly have contained compounds which were formed by a transannular reaction during the reduction.

The synthesis and u.v. spectra of a series of diacetylenic macrolides (11, n = 3,4,5,7,) have been reported by Nakagawa.[6] Due to the inherent strain, when n = 2 or 3 2,2'-dibenzofuranyl (12) and related compounds were produced. For example, when the cyclic diyne (11, n = 3) was prepared from the diethynyl compound (10, n = 3) by oxidative coupling, the benzofuran (12) was formed as a by-product. This same by-product, together with the acid (14) was obtained in an attempted cyclisation of the terephthalatediyne (13). The mechanism of the formation of these benzofurans is obscure but Nakagawa has produced evidence that it does not involve ring fission of the expected cyclic diacetylene.

Nakagawa[7,8] has extended this type of investigation to an analogous system of strained cyclic ethers. Oxidative coupling of the diynediether (15, n = 1 to 6) furnished the cyclic diyne monomer(16) only when n = 3,4,5, or 6 and the cyclic tetrayne dimer (17) when n = 2 to 6, in the yields shown. The u.v. spectra of the diynes (16, n = 3,4,5, and 6) were compared with each other and with acyclic analogues. It was found that the bending of the diacetylenic linkage was progressively less in the series n = 3,4,5, and 6 and this was illustrated by a corresponding increase in the u.v. extinction coefficients. The 12 mμ shift to lower wave lengths of (16, n = 3) in comparison to (16, n = 5 and 6) was also attributed to the bent diacetylenic linkage of this smaller macrocycle. In the cyclic dimers (17, n = 2,3,4,5, and 6) when n is odd, (3 and 5) or large and even (6) the u.v. spectra do not depart from those of the open chain analogues. However, when n is even (2 and 4) anomalies in the u.v. spectra appear and these have been attributed to the

non-planar geometry of these molecules.

The cis and trans olefin diethers (18) were prepared by Nakagawa[7] and coupled to form the diynes (19, cis and trans). The u.v. spectrum of the trans diyne (19) showed anomalies which seemed to be associated with a transannular interaction between the π'-electrons of the double bond and the diyne unit. The diyne product (21) (8%) from the coupling of (20) showed a u.v. spectrum similar to that of the cis olefin (19) and from this it was concluded that both these cyclic diethers had equivalent ring strain and that transannular interaction between the phenylene group and the diyne unit was excluded. This latter conclusion was supported by molecular models. The cyclic dimer (22) was formed in 3% yield as a by-product of the coupling of the diyne (20). This tetrayne (22) showed no ring strain as evinced by its u.v. spectrum which was identical to that of the open chain analogue (23).

The cyclic triacetylene (25) was obtained in 3% yield from the oxidative coupling of (24). The large ring strain of this compound (25) and consequent deformation of the diacetylene linkage is illustrated by its u.v. spectrum which is shifted $8_{m\mu}$ to shorter wave lengths compared with its acyclic analogue (26). The cyclic diyne (27) (25%) was prepared from the diethynyl precursor (28) in order to investigate possible transannular interactions in more detail. Models of (27) showed it to be almost strain free. Comparison studies on the u.v. spectrum of (27) revealed anomalies

which were probably associated with a transannular interaction of the π-electrons in the bridging benzene ring with those of the diyne function. A proximity effect was also demonstrated by the i.r. spectrum of (27) in which the aromatic protons absorbed at a lower frequency (776 cm^{-1}; out-of-plane deformation) than the protons of the acyclic analogue (28) (814 and 796 cm^{-1}).

Nakagawa[9,10] has synthesised the acyclic diacetylene (30, n = 1) by the oxidative coupling of 1-ethynylanthracene (29, n = 1) and has used this substance (30, n = 1) as a model for the cyclic, unstrained tetraacetylene (32, n = 1) which was prepared similarly from 1,8-diethynylanthracene (31, n = 1). The tetrayne (32, n = 1) was obtained as stable orange crystals in high yield. Reduction with sodium in ammonia furnished a product which was tentatively assigned the structure (33). Catalytic hydrogenation of (33) partially reduced the remaining anthracene nulceus and formed the saturated aromatic hydrocarbon (34). The u.v. spectrum and the unusual stability of (32, n = 1) seemed to be attributable to an enhanced interaction of the π-electrons of the acetylenic bonds with those of the aromatic system.

This latter result prompted Nakagawa[11,12] to prepare higher acetylenic macrocycles. Once again he first prepared the model (30, n = 2) by the oxidative coupling of 1-butadiynylanthracene (29, n = 2). The best conditions for the Eglinton[3,4] coupling of the diethynyl compound (31, n = 2) were found to involve a reaction

time of one minute at 20° and the yield of the octaacetylene (32, n = 2) was only 17%; it was found that the cuprous salt of (31, n = 2) readily decomposed in pyridine. The octaacetylene (32, n = 2), obtained as deep red needles (decomp. ca.160°) was found to be a stable substance; surprisingly, for such a conjugated polyyne, the fine structure of its u.v. spectrum was very indistinct. Catalytic reduction of the octayne (32, n = 2) apparently produced (35) in which both the anthracene nuclei were partially reduced.

Sondheimer and his co-workers have produced an impressive body of work on monocyclic carbocyclic unsaturated systems. The results are summarised succinctly in the following pages in chronological order. Most noteworthy has been his use of intermolecular acetylenic coupling techniques and subsequent prototropic rearrangement and controlled catalytic hydrogenation to produce cyclic conjugated polyenes. The properties of these substances have been investigated to see if they conform to the prediction that aromatic properties are associated with a planar molecule of this kind containing a closed shell of $(4n + 2)$ π electrons (Hückel's rule). This series of reactions may be summarised in skeletal form as follows:

$$-CH_2-CH_2-C\equiv CH + HC\equiv C- \xrightarrow{\text{Coupling}} -CH_2-CH_2-C\equiv C-C\equiv C- \xrightarrow{KO^tBu}$$

$$-CH=CH-CH=CH-C\equiv C- \xrightarrow[H_2]{\text{Lindlar}} -CH=CH-CH=CH-CH=CH-$$

The hexayne (36) prepared[13] by the oxidative coupling of 1,5-hexadiyne, was rearranged with potassium t-butoxide in t-butanol to the hexaenetriyne (38) (50%) which is a planar molecule with three cis and three trans double bonds. A by-product of this rearrangement was triphenylene (37)(7%). The formation of this compound was rationalised via the intermediate production of the all-cis hexaene-triyne (39) which is sterically favourable for transannular rearrangement to triphenylene.

Cyclotetradecaheptaene (43) ([14]annulene) contains $(4n+2)$ π electrons ($n=3$) but it cannot exist in a planar form. It therefore complies with only one of the above two criteria which have been postulated for aromaticity in such systems.[30] Sondheimer[14] has synthesised [14] annulene (43) by the oxidative coupling and subsequent direct base rearrangement of the triyne (40). The intermediate (42) (2%) (two isomeric forms) still contained one triple bond which was partially reduced over Lindlar's catalyst to produce [14] annulene (43)(15%). The structure (43) shown, was later[26] confirmed by X-ray analysis. Because of the instability of this product, Sondheimer suggested that the condition of planarity for the existance of aromaticity is therefore an important one. However, later on, he states[20,22] that there is no theoretical justification for equating "aromaticity" with "stability". The importance of

planarity is better demonstrated by the n.m.r. spectrum of [14]-annulene which is discussed later.

A condensation between trans-1,4-dibromobut-2-ene and allenylmagnesium bromide was used by Sondheimer[18] to provide the starting material, trans-5-decene-1,9-diyne(44) (40%), for the attempted synthesis of the theoretically non-aromatic [20]-annulene (46) and the theoretically aromatic [30] annulene (48). However, while the oxidative cupric acetate-pyridine coupling of (44) produced the dimer (45) (7.3%), the trimer (47) (2.5%), the tetramer (2.3%) and the pentamer (0.9%) as analytically pure compounds, neither the dimer (45) nor the trimer (47) could be rearranged to produce the annulenes in a pure state. Only non-homogeneous oils were obtained. A different approach[24] to the [20] and [30] annulenes, from 1,5,9-decatriyne (49) was successful. The cyclic products from the oxidative coupling of this latter acetylene were the dimer (50) (6.2%) and the trimer (52) (5.2%). Prototropic rearrangement of the 1,5-diyne units in these cyclic compounds converted them to the corresponding dark brown-violet, crystalline, dehydro-annulenes (51) (16%) and (53) (10%) respectively. Lindlar partial hydrogenation of bisdehydro [20] annulene (51) gave the [20] annulene (e.g.46)(25%) as a yellow oil and similar treatment of the tridehydro [30] annulene (53) provided the [30]-annulene (e.g.48) which was not isolated but was shown to be present (6%) spectroscopically. None of the fully conjugated compounds showed any unusual stability although the dehydro-annulenes were more stable

than the corresponding annulenes.

The success of this approach to the [20] and [30] - annulenes was in keeping with Sondheimer's findings in the acyclic series that the isomerisation of linear 1,5-diynes to the conjugated polyen-ynes[17] with potassium t-butoxide proceeded more easily and in higher yield than the corresponding isomerisation of linear 1,5-enynes to the conjugated polyenes[16].

Monodehydro [20] annulene (56) has also been synthesised[19]. All trans-4,10,16-eicosatriene-1,7,13,19,-tetrayne (54) was produced in 3% yield by the reaction of trans-1,4-dibromobut-2-ene with an excess of ethynylmagnesium bromide. Cyclic coupling with cupric acetate-pyridine of (54) gave the colourless trienetetrayne (55)(18%) which could be rearranged with potassium t-butoxide to the monodehydro [20] annulene (56)(20%), a yellow oil which soon decomposed on standing either alone or in solution.

By the coupling and subsequent rearrangement of trans-4-octene-1,7-diyne (57), Sondheimer[23] has produced [16] annulene and dehydro [16] annulenes. Cuprous chloride-ammonium chloride coupling of the diyne (57) furnished the linear dimer (58) (25%) and the cyclic dimer (64) (3%). Rearrangement of this latter compound with potassium t-butoxide in t-butanol and benzene provided the bisdehydro [16] annulene (63) (5%) (or a steroisomer). A by-product of this reaction was the diphenylsuccindene (62) (15%) and this product could be obtained in better yield (50%) by ethanolic potassium hydroxide rearrangement of the tetrayne (64). The linear tetrayne (58) was cyclised by cupric acetate-pyridine coupling to

the bisdehydro [16] annulene (59) (1.5%), a highly unstable compound. In this coupling reaction rearrangement of (58) to an α,ω -diethynylhexaene must have occurred prior to the formation of the 1,3-diyne unit.

Partial hydrogenation of (59) over a Lindlar catalyst provided the moderately unstable monodehydro [16] annulene (60) (30%) and a low yield of an orange oil, [16] annulene (61).

[16] Annulene (61) could also be prepared by hydrogenation of (60).

By cyclic cupric acetate-pyridine coupling of 1,5-hexadiyne (65), Sondheimer[20,22] has prepared the [18] , [24] , and [30] annulenes via the intermediate dehydroannulenes. The cyclic trimer (66), tetramer (67), pentamer (68) and hexamer prepared by this means all possessed the easily rearrangeable 1,5-diyne unit. These cyclic products were separated by chromatography and individually rearranged to the corresponding polyenyne system by potassium t-butoxide. However, tridehydro [18] annulene (69), tetradehydro [24] annulene (70), pentadehydro [30] annulene (71) and hexadehydro [36] annulene were prepared more conveniently by the coupling of (65) followed by direct rearrangement, without isolation of the intermediates. (The spectroscopic yields of the first three based on (65) were 3.3,2 and 1% respectively.) Partial hydrogenation of tridehydro [18] annulene (69) provided [18] -annulene (72) as brown-red needles. The structure (72) shown for

this annulene has been proved by an X-ray analysis. Thus it appears that catalytic hydrogenation of the triple bonds in (69) has given predominantly trans double bonds. This rather exceptional reaction course is possibly due to steric control of the hydrogen addition which would occur in two steps. The half hydrogenated triple bond intermediate would be forced to adopt the energetically more stable configuration followed by addition of the second hydrogen atom to produce the trans double bond. [18]-Annulene is the first fully conjugated cyclopolyolefin after benzene for which aromatic character was predicted and indeed X-ray studies have revealed a lack of bond alternation, and an almost planar molecule. This annulene, although reasonably stable, showed no striking signs of stability. [18] Annulene underwent addition (conjugated polyene) rather than substitution (aromatic) reactions. However, very recently, [18] annulene was nitrated using a mild process involving copper nitrate in acetic anhydride. Sondheimer has pointed out that chemical reactivity is not a property of the ground state of a molecule whereas the delocalisation of the π-electrons around the ring is representative of this state. It is this latter property which functions as a criterion for aromaticity.

The [24] annulene (73) was similarly prepared from (70) and it proved to be a rather unstable compound. The u.v. spectrum favoured the almost planar structure (73) shown, and here again overall trans addition of hydrogen appears to have occurred. [24] Annulene does not obey Hückel's rule and was therefore not expected to exhibit

aromatic properties.

The same [30] annulene (48) was obtained and identified spectroscopically by partial hydrogenation of either the pentadehydro [30] annulene (71) or the tridehydro [30] annulene (53)[24], whereas a different isomer would have been expected. This suggests that the stereochemistry of an annulene does not necessarily conform exactly to the stereochemistry of the double bonds in its acetylenic precursor but that the most stable configuration is formed. [30] Annulene proved to be a highly unstable compound.

Tridehydro [18] annulene (69) was also prepared by cupric acetate - pyridine coupling of 1,5-hexadiyn-3-ol (77), followed by lithium aluminium hydride reduction and dehydration. No pure triol was isolated from the coupling as a wide scope for isomerism exists for the coupled products from an unsymmetrical α,ω -diacetylene such as (77). (Two possible positional isomers (78) and (79) are shown). Lithium aluminium hydride reduction is known to cause reduction of propargylic alcohols to the corresponding trans-allylic alcohols. Dehydration of (80) was carried out with potassium bisulphate in boiling acetic anhydride-acetic acid and since the same tridehydro [18] annulene (69) was produced by this means as by the previous method[20] (by the coupling of 1,5-hexadiyne (65) and rearranging the trimeric product) it was concluded that the intermediate triol must have the symmetrical structure (78).

Sondheimer[25] found that cuprous chloride -ammonium chloride coupling of 1,5-hexadiyne (65), when carried out in the usual manner but with the addition of benzene to keep the products in solution, furnished the cyclic dimer (74). This product was extremely unstable and it was not isolated. Direct prototropic rearrangement with potassium t-butoxide furnished two products, biphenylene (76) (25%) and bisdehydro [12] annulene (75) (2%). This latter product was not an intermediate of the biphenylene formation reaction as treatment of (75) with the same base gave no biphenylene. Bisdehydro [12] annulene (75) is an unstable, theoretically non-aromatic annulene.

In order to investigate the physical and chemical effects of substituents on annulenes and dehydroannulenes, Sondheimer[27] prepared and coupled (cupric acetate - pyridine) 3,4-dimethyl-1,5-hexadiyne. Direct rearrangement of the product, in the usual manner, gave a mixture of dehydro-annulenes from which the 18 membered compound (82) was isolated in pure form. (1%). Comparison of this compound with tridehydro [18] annulene (69) showed that the six methyl groups cause a bathochromic shift in the u.v. of ca. 7 mμ. The position of the methyl groups on the cis double bonds and outwith the ring were confirmed by the n.m.r. spectrum of (82) (τ = 7.40; deshielded methyl protons)(see later discussion). Lindlar partial hydrogenation of (82) gave a low yield (0.3%) of the hexamethyl [18] annulene (83), which proved, interestingly, to be less stable than the desmethyl analogue.

An extremely unusual aromatic compound 1,8-bisdehydro [14]-annulene (85) was discovered by Sondheimer[28] as a minor product in the oxidative coupling (cupric acetate - pyridine) of trans, trans-4,10-tetradecadiene-1,7,13-triyne (84); the main product was the dehydro [14] annulene (42). This minor product can only be represented by cumulene containing Kekulé resonance forms and its structure finds confirmation in its n.m.r. spectrum which shows the two protons inside the ring to be strongly shielded (τ = 15.54) and those outwith the ring to be deshielded (see later discussion). Further proof of its structure came from its X-ray analysis[29] which showed it to be planar. Apart from the two 'triple bond' values, the carbon-carbon bond lengths correspond to a π-bond order identical with that of benzene, and the internal hydrogen atoms, coplanar with the carbon framework, are under no steric strain. The structure proved to be unusually stable.

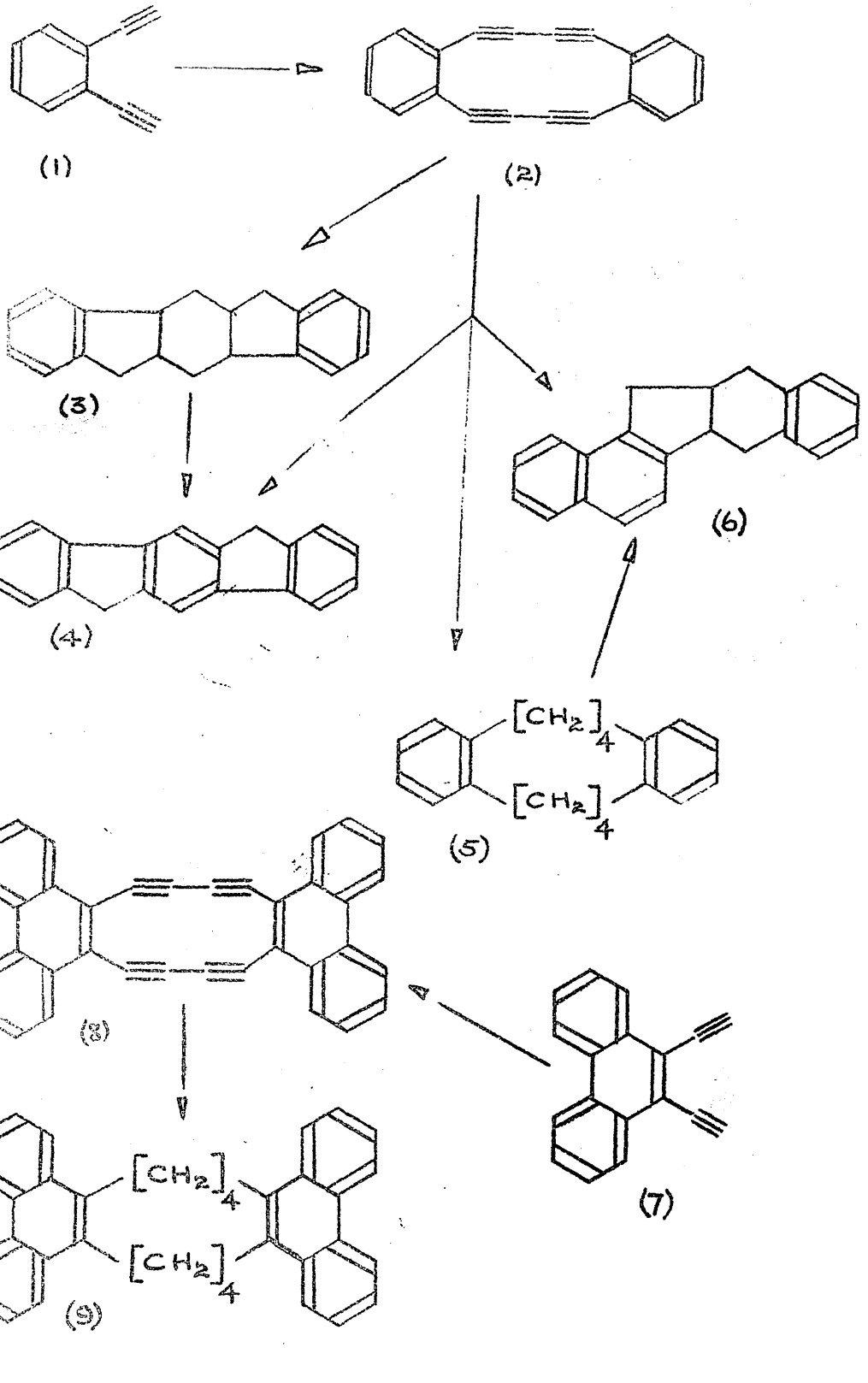
Sondheimer and Jackmann[26] have applied n.m.r. spectroscopy to a series of annulenes and dehydroannulenes in order to determine the extent of their aromaticity. A particular ground state property of an aromatic molecule is the ability of the closed shell system of π-electrons to sustain a magnetically induced ring current[31]. A manifestation of this effect will be shown by the chemical shifts of the ring protons, which, in annulenes and dehydro-annulenes, may be situated either inside or outside the ring. The protons inside the ring will therefore be shielded (unusually high fields) and those outside, deshielded (unusually low fields) if an

induced ring current is possible.

The n.m.r. spectrum of [14] annulene (43), a molecule which cannot be planar due to the overcrowding of the inner hydrogens, showed a singlet (τ = 4.42) very close in position to the olefinic protons of cyclooctatriene (τ = 4.26) and the non-aromatic cyclooctatetraene (τ = 4.31). In contrast, monodehydro [14] annulene (42) with the structure shown, can assume a near planar state by in-plane deformations of bond angles. The n.m.r. spectrum showed (42) to be aromatic with absorptions at τ = 1.2 - 2.7 (outer protons) and τ = 10.7 (inner protons).

Similar measurements on [18] annulene (72) and tridehydro [18] annulene (69), which obey Hückel's rule and are reasonably planar, show them both to be capable of sustaining an induced ring current. They are both, therefore, aromatic in terms of the above definition.

The absence of aromaticity in [24] annulene (73) (singlet, τ = 3.16) and tetradehydro [24] annulene (70) (τ = 1.8 and τ = 3.6 - 4.8) is expected on the basis of Hückel's rule.


(1)
(2)
(3)
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[CH2]4
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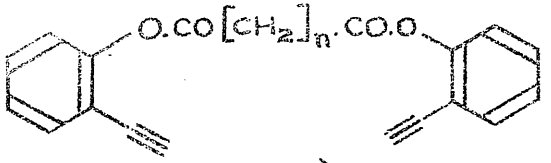
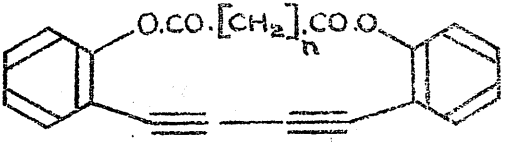


(10)

n = 3, 4, 5, 7.

(n = 3)



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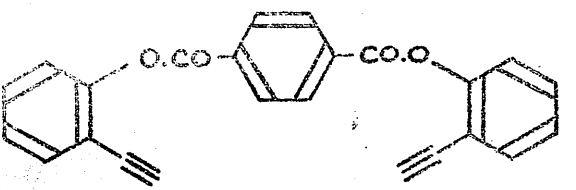
(12)



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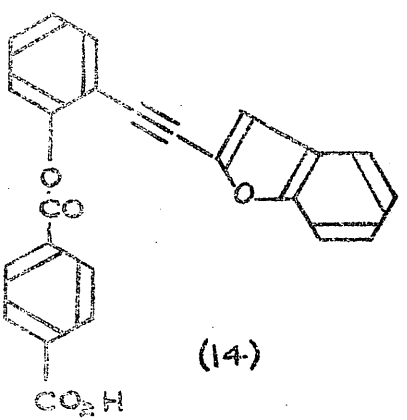

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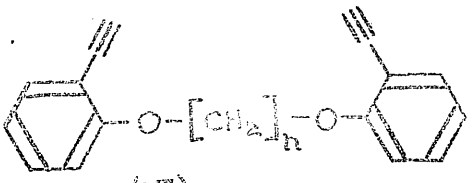
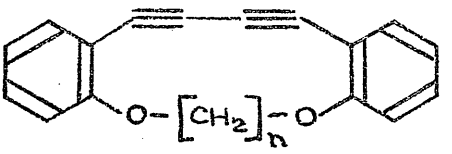


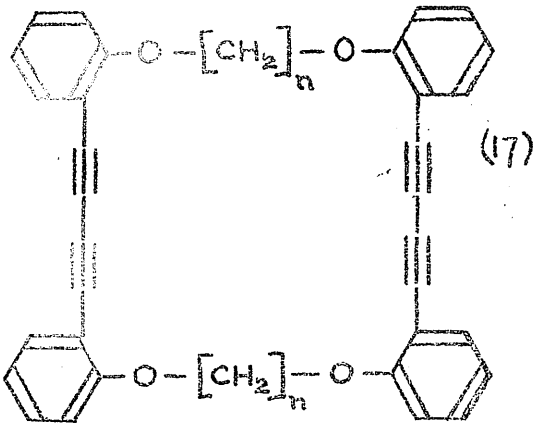
(15)

n = 1 to 6



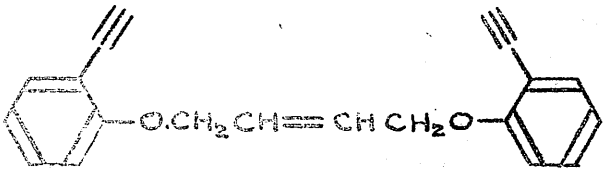
(16)

n = 3 (3%), 4 (40%), 5 (40%), 6 (40%).



(17)

n = 2 (2·5%), 3 (1%), 4 (2%), 5 (trace), 6 (10%).



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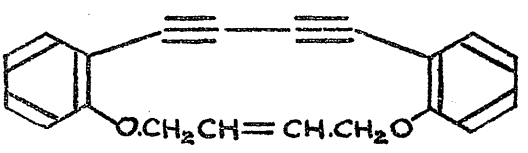
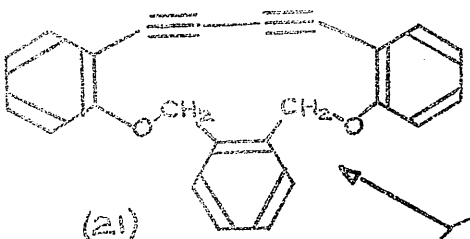


(19) cis and trans.



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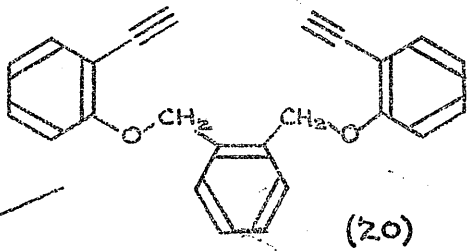

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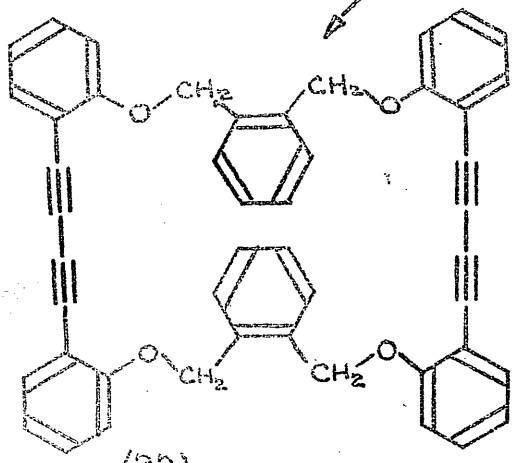

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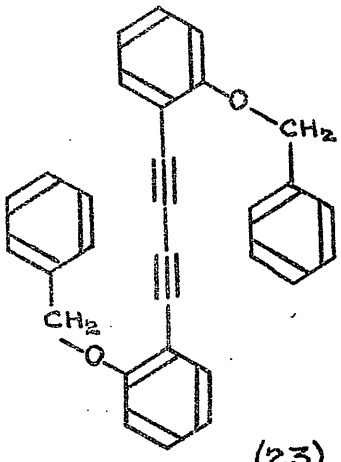

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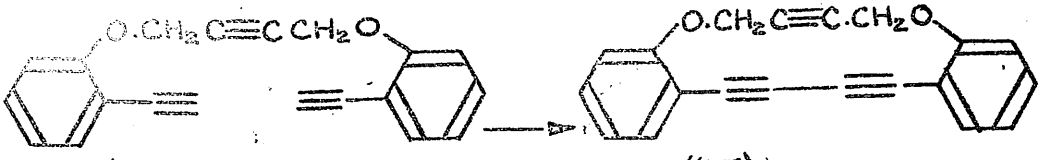
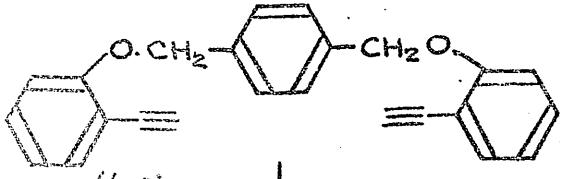


(24) (25)



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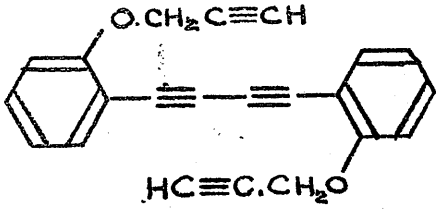

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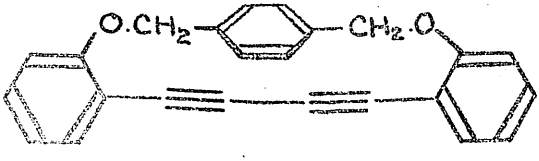

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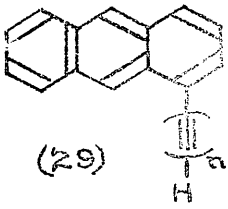

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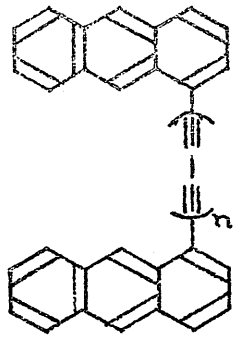

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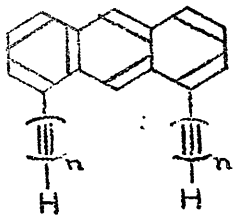

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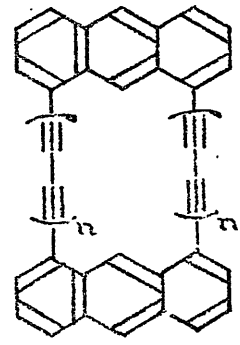

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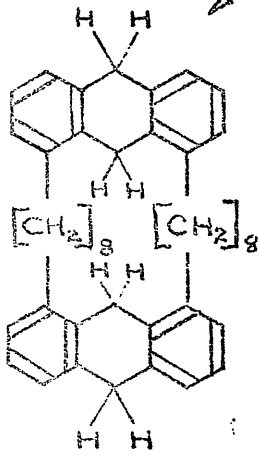

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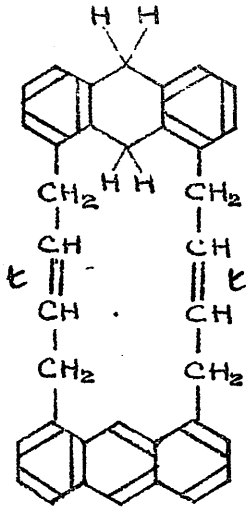

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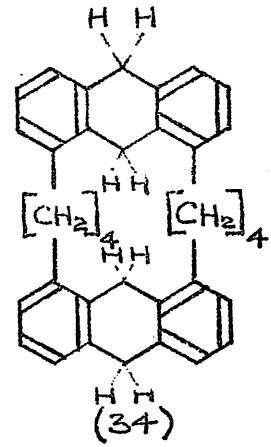

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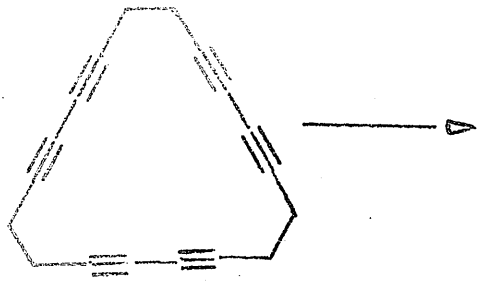

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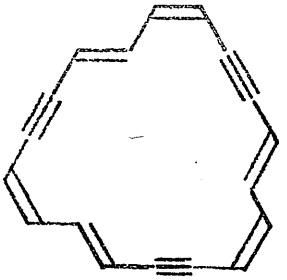

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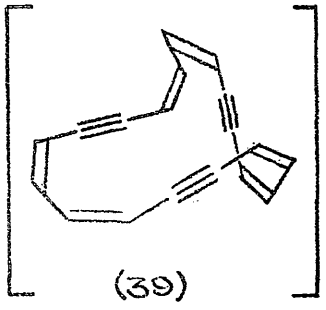

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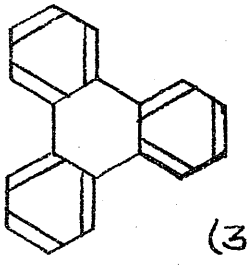

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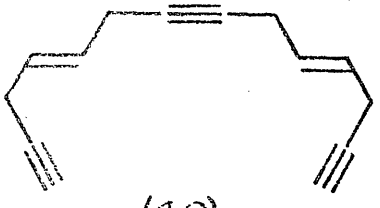

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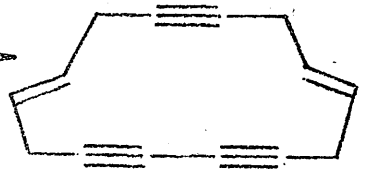

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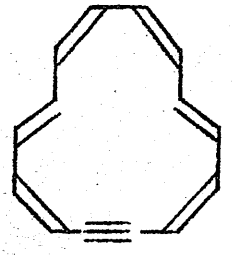

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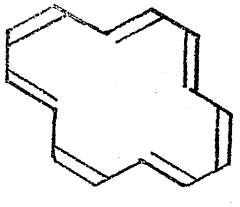

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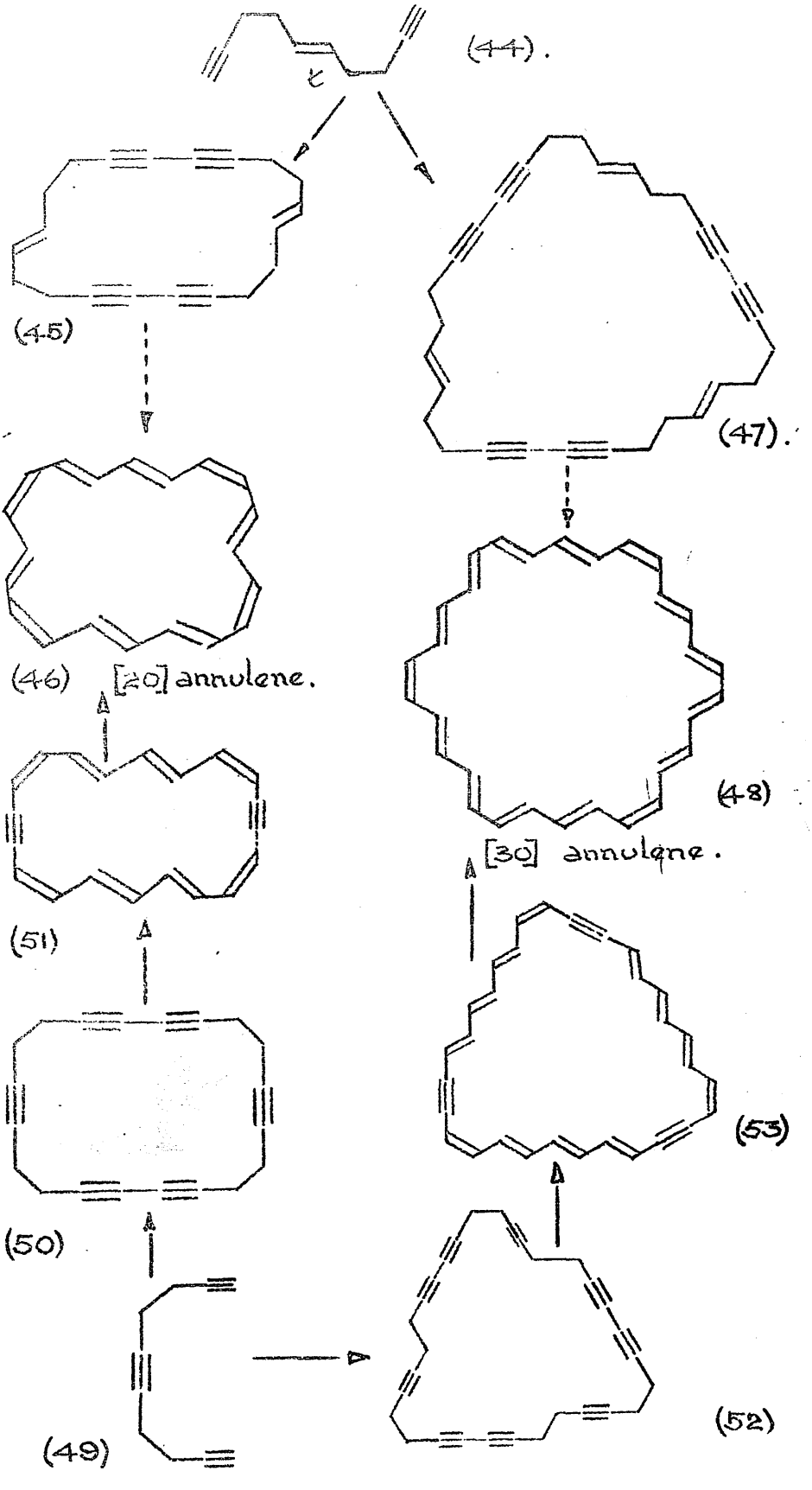
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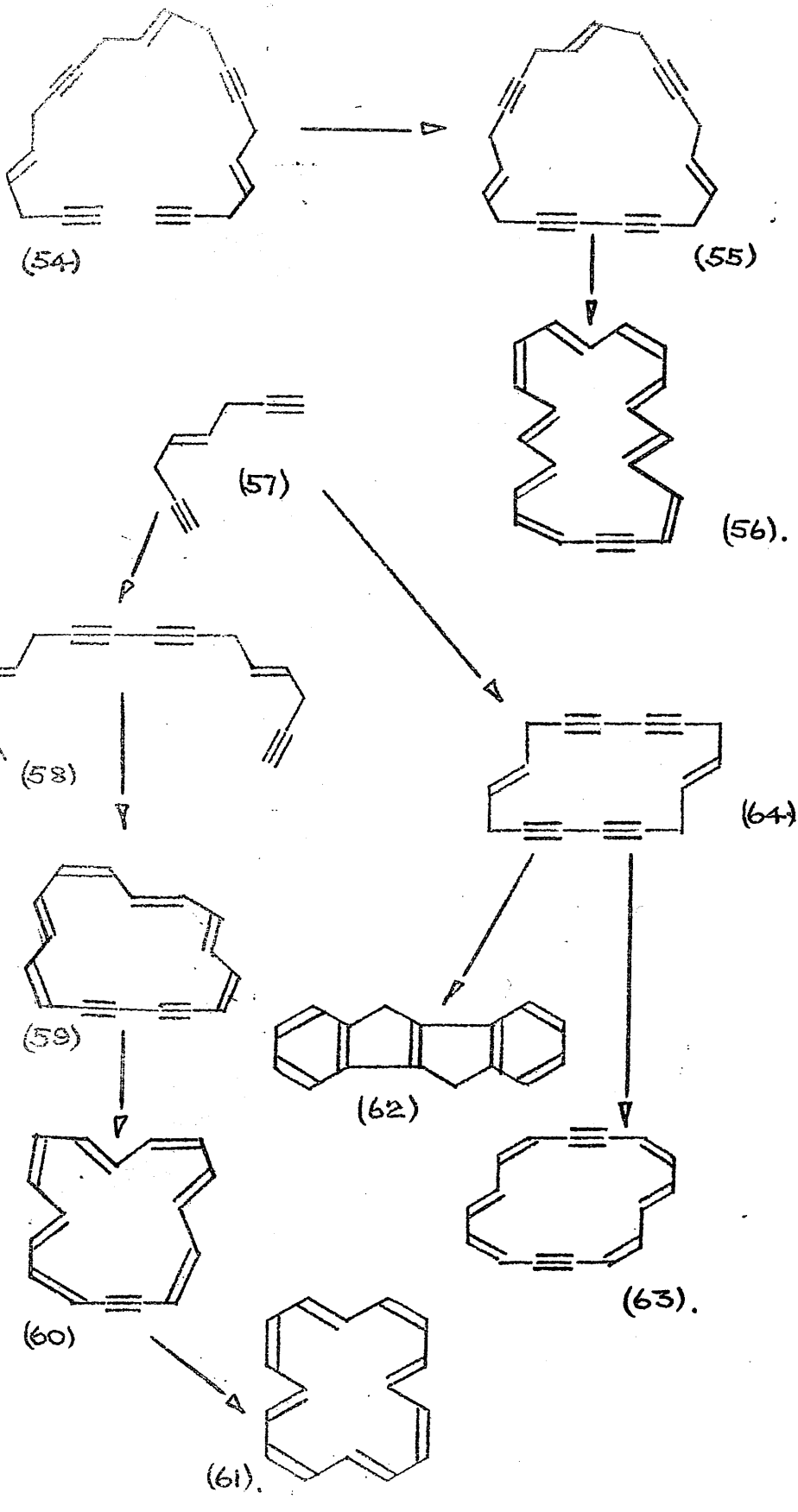
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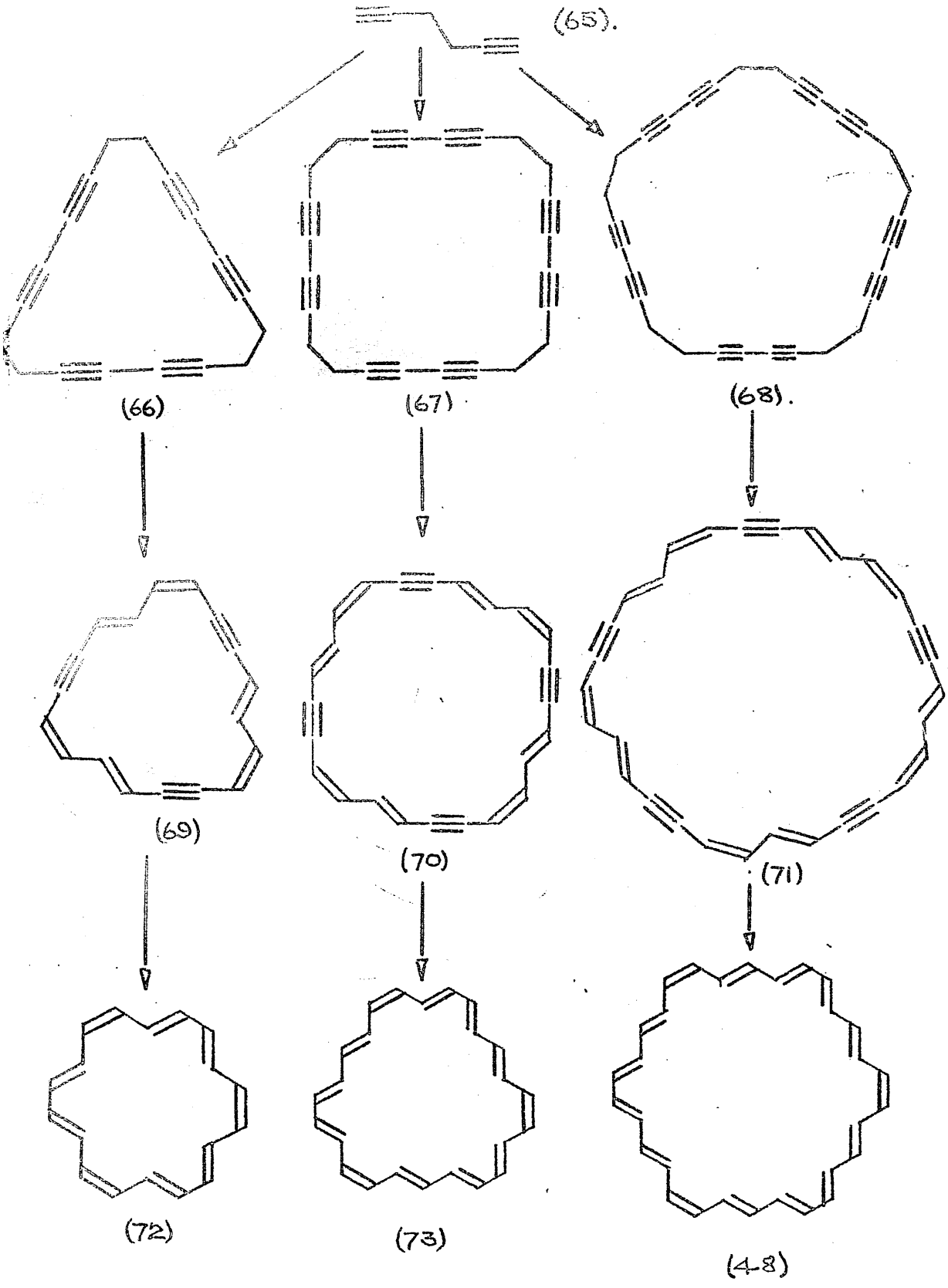
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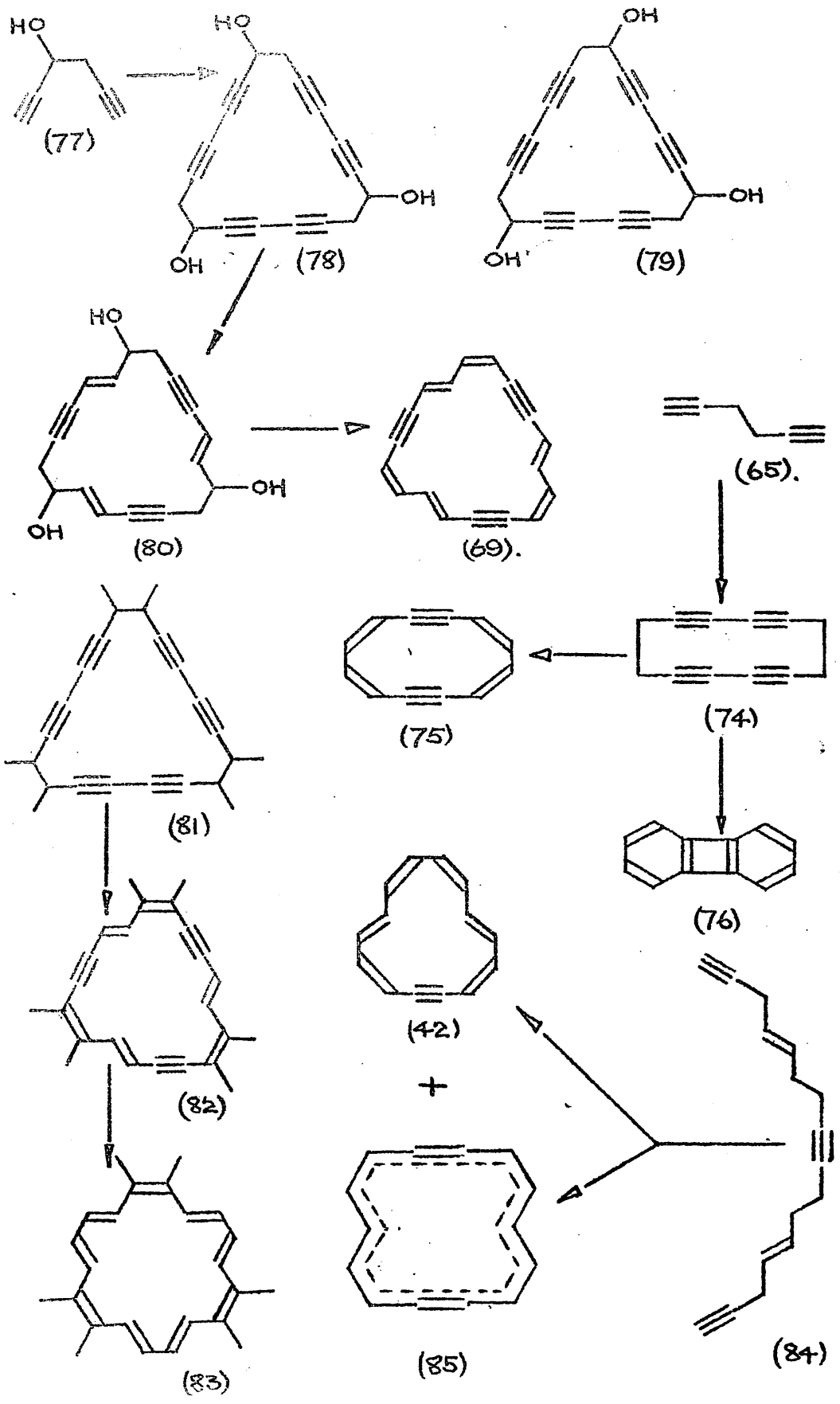
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STUDIES IN ACETYLENIC CARBOCYCLES

The surprising production of the highly strained dimer (2) from the oxidative coupling of o-diethynylbenzene (p.l.) prompted the investigation of the mechanism of formation of this unexpected compound. One reaction pathway to (2) could proceed via a stepwise sequence involving initial unilateral coupling of o-diethynylbenzene with the formation of the acyclic o,o'-diethynyl-1,4-diphenylbutadiyne (100) followed by intramolecular coupling of this compound to give the cyclic dimer (2). The following work describes the sythesis of this hypothetical intermediate (100) and the examination of its intramolecular coupling in order to confirm the practical feasibility of this process. A preliminary investigation of the problem had been carried out in this department,[1] but the whole project was re-examined in detail with extensive use of the powerful new tools of thin layer chromatography (t.l.c.), preparative scale gas liquid chromatography (g.l.c.) and n.m.r. spectroscopy.

The key compound for the production of the required intermediate was 1-ethynyl-2-(trans-2'-bromovinyl)benzene (88). This was obtained from o-di-(1'-2'-dibromoethyl)benzene (86) in the following manner.[1] It had already been shown that controlled dehydrobromination of this tetrabromide surprisingly produced an unsymmetrical dibromodiene of structure (87). Repitition of this process showed that the product was by no means homogeneous. T.l.c. examination showed one major spot accompanied by a spot of weaker intensity and lower R_f value. Bromine analysis gave values higher than

those expected for the pure dibromodiene (87).

The identity of this impurity as 1-(1'-bromovinyl)-2-(1',2'-dibromoethyl)benzene (91) was revealed in the following way. The n.m.r. spectrum (fig.1) of the starting tetrabromide (86) showed a triplet and a doublet in agreement with the presence of two 1',2'-dibromoethyl units. The n.m.r. spectrum (fig.1) of the impure dibromide (87) (n_D^{22} = 1.6340) showed a similar A$_2$B pattern. The presence of a -CHBr.CH_2Br structural unit in the impurity is thus demanded; however, t.l.c. examination excluded the presence of starting tetrabromide (86). Further, an infra-red spectrum showed no ethynyl absorption and the intensity of the 903 cm^{-1} band ($CBr=CH_2$) was greater than that of the 950 and 935 cm^{-1} band (trans $CH=CHBr$) (the infra-red spectrum of g.l.c. pure dibromide (87) (fig.2) has these two bands of equal intensity). Since the analysis was high in bromine, and since the total intensity of the n.m.r. absorption of the $CBr=CH_2$ group (two doublets) was appreciably greater than that of the $CH=CHBr$ trans group (an A.B. quartet) it was concluded that the impurity must have the structure (91).

It was decided to repeat the dehydrobromination of the tetrabromide (86) with an excess of potassium t-butoxide with the intention of reducing the concentration of the tribromide impurity (91). Two molecular equivalents of potassium t-butoxide were added at ice bath temperature in the usual manner[1,2] and a third molecular equivalent was added over 1 hour. Aliquots were removed at intervals

and examined by t.l.c. The spot corresponding to the tribromide (91) persisted under these conditions but on leaving the reaction overnight only a faint trace of the spot remained. Chromatography on alumina rendered the oily product colourless and g.l.c. examination of the oil showed it to be 93% (area of peak) pure with three other impurities of which one was shown to be (88), present to an extent of 1.3% (area of peak); none of the impurities was o-diethynylbenzene (89). The unexpected unsymmetrical structure of the dibromodiene (87) as 1-(1'-bromovinyl)-2-(trans-2'-bromovinyl)-benzene was conclusively demonstrated by the spectral properties of a sample rigorously purified by g.l.c. Thus the n.m.r. spectrum (fig.2) showed an AB quartet as two doublets centred on $\tau = 2.65$ and 3.35 ($J = 14$c.p.s.; trans $CH = CHBr$) and another pair of doublets centred on $\tau = 4.05$ and 4.25 ($J = 1$ c.p.s.; $CBr = CH_2$). This assignment was confirmed by the infra-red spectrum which showed diagnostic absorption at 950 m, 935 s (trans $CH = CHBr$) and 903 s cm^{-1} ($CBr = CH_2$).

A possible mechanism for the unexpected unsymmetrical dehydrobromination of the tetrabromide (86) to the dienedibromide (87) is indicated via a quinonoid intermediate of type (95). In a similar instance, to account for two dimeric products obtained[33] from the potassium t-butoxide treatment of 1,1,1',1'-tetrabromo-o-xylene, Cava and Muth[34] postulated the formation of the tribromide (97).

In an analogous example the reaction of 1,1'-diiodo-o-diethylbenzene (98) with sodium iodide was shown to involve a vinylogous 1,4-diiodide elimination with the formation of the intermediate (99), whose quinonoid structure was verified [35] by its reaction with maleic anhydride to form a stable adduct.

The unsymmetrical nature of the dibromodiene (87) gave good hopes of its subjection to a mono-dehydrobromination process to give the required bromovinylacetylene (88); only in the 1'-bromovinyl grouping ($-CBr = CH_2$) of (87) is there a trans alignment of hydrogen and bromine atoms. In the event treatment of the substantially pure dibromodiene (87) with one mol. of potassium t-butoxide effected the expected elimination in high yield with the formation of the hoped-for bromovinylacetylene (88). The spectra of a g.l.c. purified sample of this compound fully supported its structure as (88). Thus the n.m.r. spectrum (fig.2) showed the appropriate singlet at $\tau = 6.75$ ($\equiv CH$) and the AB quartet centred on $\tau = 2.45$ and 3.18 ($J = 14$ c.p.s.)(trans-$CH = CHBr$); the infra-red spectrum showed the expected bands at 3300 ($\equiv CH$) and 950 and 938 cm^{-1} (trans $-CH = CHBr$).

It is interesting to note the deshielding effect of the triple bond on the protons of the trans-$CH = CHBr$ group. (table 1). In the n.m.r. of (92) and (88) the protons of this group absorb at 0.15 to 0.20 ppm. less than the protons of this group when it is situated in a non-acetylenic environment such as in compound (87).

Dreiding models of (88) and (92) show that by simple bond rotation, both protons of the trans CH=CHBr group can be located outwith the shielding cones of the carbon to carbon triple bond. These protons are therefore deshielded. (The shielding cones of the acetylene bond extend from each end and lie with their axes along the carbon to carbon triple bond [36(a)]).

The complexities that ensued if the starting dibromodiene (87) were not relatively pure are graphically illustrated by the range of products that were obtained from this dehydrobromination using (87) made according to the previous directions [1]. Separation by g.l.c. (fig.3) showed no fewer than nine components of which one (retention time 9.4 min) proved to be the bromovinylacetylene (88) and another (R.T. = 26.0 min) the starting dibromodiene (87). Two further pure g.l.c. fractions (R.T.'s = 13.6 and 54 min) were tentatively assigned structures (93) and (94) on infra-red evidence as sufficient quantities were not obtained for n.m.r. examination. The remaining five components could not be purified further and were not examined in detail.

Further dehydrobromination of the bromovinylacetylene (88) to o-diethynylbenzene (89) was readily effected in high yield by further treatment with potassium t-butoxide. The quality of the product (89) was considerably better than that obtained [1,2] by the one-step double dehydrobromination of the dibromodiene (87).

The pure bromovinylacetylene (88) was then subjected to

the standard coupling conditions which furnished the desired dibromovinyldiacetylene (92) as a readily purified crystalline solid in 30% yield with spectral properties concordant with the expected structure. From (92) the desired tetrayne intermediate (100) was obtained by double dehydrobromination as a pale yellow crystalline solid. Subjection of this product (100) to intramolecular oxidative coupling (cupric acetate; pyridine) indeed produced the cyclic tetrayne (2); the yield of (2) produced by the coupling of o-diethynylbenzene under exactly similar conditions proved to be comparable. This result strongly suggested that the acyclic tetrayne (100) could certainly function as an intermediary in the transformation of o-diethynylbenzene to the cyclic tetrayne (2). Accordingly an attempt was made to detect this intermediate (100) by subjecting o-diethynylbenzene to a coupling process using oxygen and cuprous chloride, a procedure which sometimes favours linear coupling. Again however, the cyclic tetrayne was the predominant product.

The successful conversion of o-diethynylbenzene to the cyclic tetrayne (2) prompted the extension of this type of reaction to 1,2-diethynylcyclohexanes. In particular such a product (103) derived from the coupling of 1,2-diethynylcyclohexan-1,2-diol (101) would have fruitful potentialities for further conversion by periodate fission to a twenty membered tetraketonic tetra-acetylenic carbocycle. The required (101) had already been reported by two authors as preparable by interaction of cyclohexan-1,2-dione (104) and sodium acetylide but the quoted melting points were very discordant (McEntee[40] claimed m.p. 82°C and Riod and Schmidt[39] recorded m.p. 105°C). The structure of McEntee's product was confirmed by periodate fission and hydrogenation to the known decan-3,8-dione.

In this work interaction of cyclohexan-1,2-dione and sodium acetylide produced a solid diol of wide m.p. range (m.p.85-102°C) a result compatible with the production of the two expected stereoisomers. This was supported by t.l.c. evidence which showed two very closely spaced spots. To enhance this separation the preparation of derivatives was attempted. The corresponding acetates showed no wider separation on t.l.c. Selective acetonide formation was then attempted (it was presumed that only the cis-diol would form such a derivative (102)). Treatment of the diol mixture with acetone in the presence of anhydrous copper sulphate furnished a high yield of pure sharply melting diol m.p. 79-81°C which showed

only one spot on t.l.c.; this was presumed to be the trans-diol. The mother liquors showed two spots on t.l.c. and were not further investigated. The pure trans-diol was oxidatively coupled under high dilution conditions. The product was a high-melting gummy solid which gave five closely-spaced spots on t.l.c. This result is promising but the complexity of the product and the small differences in R_f value between the components precluded a more detailed investigation in the time available.

EXPERIMENTAL

General.

Melting points were recorded on a Kofler microscope hot stage and are uncorrected. Infra-red spectra were recorded on Unicam S.P.100, Perkin Elmer 137B and 237 spectrophotometers, and ultra-violet spectra on a Perkin Elmer 137 UV spectrophotometer. N.M.R. (in CCl_4 solution unless otherwise stated and with $SiMe_4$ as internal standard) and mass spectral measurements were made with A.E.I. spectrometers RS2 (60 megacycles) and MS2 respectively. Gas-liquid chromatographic data were recorded with a Pye 'Argon' Chromatograph equipped with a ^{90}Sr detector. Thin layer chromatography (t.l.c.) was carried out with Kieselgel G silica.

EXPERIMENTAL PART I.

1-(1'-Bromovinyl)-2-(trans-2'-bromovinyl)benzene (87)

(a) Two molar equivalents of potassium t-butoxide.

Potassium (3.93 g; 0.1 mol.) was dissolved in t-butanol (250 ml.), dioxan (20 ml) added, and the solution cooled to ca.15°. This solution was added dropwise to a stirred, ice-cooled solution of the tetrabromide (86) (23.5 g.; 52 m.mol.) in dioxan (50 ml), the temperature being kept below 7°. A pale brown precipitate formed almost immediately. The solvents were then removed under reduced pressure under nitrogen (bath temperature 25-30°.). The residue was treated with dilute (1.8%) hydrochloric acid, and thoroughly extracted with ether. The ether extracts were then washed and dried (sodium sulphate) and the ether removed under reduced pressure to furnish the dibromodiene (87) (14.7 g) as an orange oil. The product was distilled (100° (bath)/0.2 mm) to give an oil n_D^{22} = 1.6340 (Behr [1,2] n_D^{22} = 1.6385; Deluchat [32] n_D^{22} = 1.6370). (Found: C,38.75; H. 2.95; Br, 58.25. $C_{10}H_8Br_2$ requires C, 41.70; H, 2.80; Br, 55.50%). T.l.c. (silica; benzene : petrol, (10:90)) showed one major spot and a second spot, less intense and of lower R_f value. (Neither spot corresponded to the tetrabromide (86)). ν_{max} (film) no ethynyl absorption, 903 ($CBr=CH_2$) of greater relative intensity than 950 and 935 cm^{-1} (trans $CH=CHBr$). The n.m.r. spectrum (fig.1) showed a triplet (τ = 4.35,4.50, 4.62; J = 9.0 and 7.2c.p.s. respectively) and a doublet (τ = 5.85, 5.97; J = 7.2 c.p.s.) for

the CHBr.CH Br group, (cf. n.m.r. of the tetrabromide (86), table 1)
2
and two doublets (τ = 4.04, 4.08; J = 2.4 c.p.s. and τ
= 4.25, 4.28; J = 1.8 c.p.s.) of greater total intensity
36(b)
than the AB quartet (τ = 2.50, 2.74; J = 14.4 c.p.s. and
τ = 3.19, 3.43; J = 14.4 c.p.s.) of the CH=CHBr trans
36(b)
group. From the above data it was concluded (see discussion) that the product contained an impurity in the form of the tribromide, 1-(1'-bromovinyl)-2-(1',2'-dibromoethyl)benzene (91).

(b) Three molar equivalents of potassium t-butoxide.

Two molar equivalents of potassium t-butoxide were added under the same conditions as in (a) above to the tetrabromide (86). A further molar equivalent of potassium t-butoxide was added portionwise over 1 hour at 0° and an aliquot showed, on t.l.c. examination, that the impurity (91) was still present in the same proportion as in (a) above. The reaction was allowed to come to room temperature and stirred for 18 hours. The oily product now showed only a faint trace of impurity. After passage through alumina (benzene: petrol, (15:85)) the eluate was evaporated to give 1-(1'-bromovinyl)-2-(trans-2'-bromovinyl)benzene (87) as a colourless oil which was shown by g.l.c. (10% Apiezon,L, 150°) to be 93% pure (area of peak) (RT = 25.8 mins.). Of the three other components present (RT = 4.5, 9.4 and 13.6 min), one (RT = 9.4 min) was shown to be (88) (1.3%); none of the impurities was o-diethynylbenzene (89) (RT = 1.36 min). A sample of the dibromodiene (87)

was rigorously purified by preparitive g.l.c. (see p. 28) and had ν max. (film) (fig. 5) no ethynyl absorption, 950m, 937 s, (trans CH = CHBr), 902 s, (CBr_2 = CH). The n.m.r. spectrum (fig.2) of this sample showed a quartet of two doublets(τ = 2.54, 2.77; J = 13.8 c.p.s. and τ = 3.20, 3.44; J = 14.4 c.p.s.) corresponding to the trans CH = CHBr group and two doublets (τ = 4.05, 4.06; J = 0.6 c.p.s. and τ = 4.25, 4.26; J = 0.6 c.p.s.) expected for the CBr_2 = CH group.

1-Ethynyl-2-(trans-2'-bromovinyl)benzene(88)

The dibromodiene (87) (11.53 g; 40 m.mol) was dissolved in dioxan (20ml) and a solution of potassium t-butoxide (4.4 g; 40 m.mol) in t-butanol (80 ml) was added. After 15 minutes reflux the reaction mixture was worked up with dilute (HCl; 6N) and extracted with ether. The extracts were washed, dried and evaporated to provide the bromovinylacetylene (88) as a dark red oil (7.89 g; 95%). Distillation of a portion provided a fraction of b.p. 65-66° /0.05 mm. and n_D^{25} = 1.6225 (Behr n_D^{25} = 1.6218). (Found C, 57.75; H, 3.70; Br, 38.5. $C_{10}H_7Br$ requires C, 58.0; H, 3.40; Br, 38.50%). G.l.c. purified bromovinylacetylene (88) (see p. 27) had ν max (film) (fig. 4) 3300 s, (≡CH), 950 m, 938 s, (trans CH = CHBr), and λ max (ethanol) 237, 245, 268 (sh), 274 and 283 mμ (log ε = 4.27, 4.17, 4.06, 4.08 and 3.92) and λ min 243 and 252 mμ (log ε = 4.16 and 3.89). The n.m.r. spectrum (fig.2) of this compound was in conformity with the structure (88) proposed and showed an AB quartet

(τ = 2.38, 2.63; J = 15 c.p.s. and τ = 3.06, 3.29; J = 13.8 c.p.s.) corresponding to the trans CH = CHBr group and a singlet (τ = 6.75) expected for the acetylenic proton.

Preparative g.l.c. investigation of the dehydrobromination

When the above dehydrobromination was carried out on an impure sample of the dibromodiene (87), prepared according to the previous directions[1], (with two moles of potassium t-butoxide), a highly complex product ensued. Analytical g.l.c. (Pye Argon; 10% Apiezon.L on Embacil; 4' x $\frac{1}{4}$" column; 150°; 38 ml / min) showed the presence of approximately nine components in this product (fig.3). Samples (30 µl) of the mixture were separated on a preparative g.l.c. column (Pye Argon; 10% Apiezon.L on Embacil; 4' x $\frac{1}{2}$" column; 145°; preheat 165°; exit temperature 145°; 300 ml / min) and fractions 4,5,6,7, and 9 were collected separately in spiral traps cooled to -80°. An analytical g.l.c. of each showed them to be relatively pure (fig.3). In this respect fraction 5 was exceptional in showing a twin peak (RT = 9.2 and 9.6 min) (cf. fraction 4, RT = 9.4 min). It did not correspond to fraction 5 (RT = 10.4 min.) in the original product mixture. Fraction 4 (RT = 9.4 min) was the pure bromovinylacetylene (88). Fraction 5 (RT = 9.2 and 9.6 min) was apparently two compounds. ν max (film)(fig.4) identical to that for fraction 4 but for the absence of two weak absorptions at 2910 and 2850 cm^{-1}. Fraction 6 (RT = 13.6 min) had ν max (fig.5) 900 s. cm^{-1}, (CHBr = CH), and no 950 or 937 cm^{-1} absorptions

corresponding to the trans CH = CHBr group. On this evidence alone, there being insufficient for an n.m.r., it was assigned the o-di(1'-bromovinyl)benzene structure (93). Fraction 7 (RT = 26.0 min) was the pure dibromodiene (87). Fraction 9 (RT = 54.0 min) had ν max (fig.5) 950 and 932 cm^{-1} (CH = CHBr trans) and neither (≡CH) nor (CHBr = CH_2) absorptions. This compound was tentatively assigned the o-di(trans-2'-bromovinyl)benzene structure (94).

o-Diethynylbenzene (89).

Potassium (1.44g) was dissolved in t-butanol and the excess solvent removed under vacuum. The residual potassium t-butoxide was then dissolved, with stirring, under reflux, in benzene (100 ml). The bromovinylacetylene (88)(4.0g), in benzene (20 ml) was added dropwise to the opalescent solution and the mixture heated under reflux for 3 hours. Acidification (HCl, 6N) and ether extraction furnished the neutral fraction as a brown oil (3.17g) which was then distilled (90°(bath)/0.1 mm.) into a chilled (CCl_4/solid CO_2) receiver. The o-diethynylbenzene was obtained as a very pale yellow oil (1.96g; 80%)(n_D^{20} = 1.5904) with spectral properties indistinguishable from those already recorded[2], viz., ν max 3310, (≡CH), 2105 w, (C ≡ C) and 750 cm^{-1} (aromatic).

o,o'-Di-(trans-2'-bromovinyl)-1,4-diphenylbutadiyne (92).

The bromovinylacetylene (88)(10 g) in methanol (60 ml) was added to a solution of copper acetate (17.4g) in pyridine: methanol (1:1)(400 ml) and the resulting solution heated under reflux to 100° for 6 minutes. After cooling to room temperature the reaction mixture was acidified (HCl, 6N) and extracted with ether (x2). The ether extracts were treated with a solution of silver nitrate (5 g) in ethanol (100 ml) and left at 0° overnight. The ethereal solution was decanted from the precipitated silver salts and washed with water, dried and evaporated to give a red oil (9.52g). ν max no ethynyl absoprtion. The oil crystallised on cooling to -12° overnight and recrystallisation from methanol (x2) furnished the dibromovinyldiacetylene (92) as colourless needles (3.06 g; 30%) m.p. 107-108°. (Behr[1] obtained a 50% yield; a mixed m.p. determination with a sample of Behr's product was underpressed (107-108°)). ν max (nujol) (fig. 4) no ethynyl absorption, 1604m, 1593 m, 949 m and 936 s (trans CH = CHBr). λ max (ethanol) 249, 262 (sh), 273 (sh), 308, 328, and 351 mu (log ε = 4.70, 4.65, 4.57, 4,36 and 4,31) λ min 298, 318, 342 mu (log ε = 4.25, 4.29 and 4,20.) The n.m.r. spectrum (fig.2) showed, together with complex aromatic absorptions, the AB quartet of the trans CH = CHBr group (τ = 2.41, 2.64, J = 13.8 c.p.s. and τ = 3.02, 3.26, J = 14.4 c.p.s.).

o,o'-Diethynyl-1,4-diphenylbutadiyne (100)

The dibromovinyldiacetylene (92)(446 mg) was dissolved in dioxan (10 ml) and a solution of potassium t-butoxide (500 mg) in t-butanol (20 ml) added. The mixture was refluxed for 1.5 hours (the reflux period of 15 min. recommended by Behr[1] was found insufficient). Acidification (HCl, 6N) and ether extraction provided a brown solid (277 mg), which after treatment with animal charcoal in chloroform, and recrystallisation from light petroleum (b.p. 60-80°), gave the tetrayne (100) as pale yellow needles (164 mg; 62%) m.p.123-125°. (Behr[1], 80% and 124-124.5°). $\nu_{max.}^{(CCl_4)}$ 3280, (≡CH), 3050, 2220, 2110, 950 cm^{-1}.

1,2:7,8-Dibenzocyclododeca-1,7-diene-3,5,9,11-tetrayne (2) by the coupling of:

(a) o,o'-Diethynyl-1,4-diphenylbutadiyne (100) (Intramolecular)

The tetrayne (100) (36mg) in pyridine (5 ml), methanol (5 ml) and ether (40 ml) were added dropwise over 2 hours to a stirred solution of cupric acetate (120 mg) in pyridine (10 ml) and methanol (10 ml). After 1 hour's reflux the reaction was acidified (HCl,6N) and extracted with ether to furnish the crude product as a discoloured solid (44 mg)(grease contamination). Chromatography (Woelm alumina, grade 1, (6.0g); benzene elution) furnished a fast moving yellow band which provided the cyclic tetrayne (2) as yellow needles (24 mg; 65%) decomp. p. ca.80°. $\nu_{max}^{(CCl_4)}$ no ethynyl absorption, 2190w, 2115w, (C≡C), 1950w, 1920w, 1890w, 1850w, 1815w cm^{-1}. (Behr[1] quotes similar values).

(b) o-Diethynylbenzene (89) (Intermolecular).

o-Diethynylbenzene (89) (390 mg) in pyridine (50 ml) and methanol (50 ml) was added with stirring to a solution of cupric acetate (2.4 g) in pyridine (125 ml), methanol (125 ml) and ether (125 ml) over 3 hours. After 2 hours reflux the reaction was worked up by pouring it into a mixture of concentrated sulphuric acid (100 ml), water (100 ml), ice (200 g) and ether (200 ml). Ether extraction, washing of the extracts with dilute sulphuric acid, water, dilute sodium carbonate and water, and drying over sodium sulphate afforded the product as a brown solid (369 mg). Purification as in (a) above, furnished the cyclic tetrayne (2) as yellow needles (107 mg; 27%), decomp. p.ca. 80°. ν_{max} as in (a) above. (Behr[1] obtained a yield of 43% determined spectroscopically).

(c) Linear coupling of o-diethynylbenzene (89).

To a stirred solution of cuprous chloride (170 mg), ammonium chloride (270 mg) and concentrated hydrochloric acid (one drop) in water (5 ml), o-diethynylbenzene (81 mg) in ethanol (1 ml) was added over 10 minutes. A yellow participate, presumably the copper salt of the acetylene, was deposited. The colour changed from yellow to orange on passing oxygen through the solution, heated to 50°. After 6 hours stirring at this temperature, ammonia was added and the reaction mixture extracted with ether. The product, a brown oil, was examined by t.l.c. (silica; benzene: petrol, (10:90))

which showed five components. No starting material was present. One spot corresponded to the cyclic tetrayne (2) and another to the desired acyclic tetrayne (100) but the latter was of very low intensity compared to the former. The other three components were unidentified.

A satisfactory yield of the tetrayne (100) was therefore unobtainable by this method. An attempt to separate the components of the product mixture by thick layer chromatography was unsuccessful.

Cis-trans mixture of 1,2-diethynylcyclohexan-1,2-diol (101)

Cyclohexanone (105) was oxidised (SeO_2) to cyclohexane-1,2-dione (104) by the method of Rauh, Smith, Banks and Diehle[38].

The conditions used by Ried and Schmidt[39] for the treatment of the dione (104) with sodium acetylide were followed exactly. 1,2-Diethynylcyclohexan-1,2-diol (101) was obtained as an oil (b.p. 74°/0.15 mm) which crystallised from benzene:pyridine (80:20) as colourless prisms m.p. 85-102° (Ried and Schmidt[39], m.p. 105°; McEntree[40] m.p.82°). ν_{max} (CCl_4)(Unicam) ca.3605 w, (broad shoulder)(free OH), 3574 m, (bonded OH), 3308 s cm^{-1} (C ≡ CH). T.l.c. (silica; methanol: chloroform, (4:96)) showed two spots, one large, the other, of slightly greater R_f, much smaller (ca.20% of the large spot).

Pure trans-1,2-diethynylcyclohexan-1,2-diol (101).

The cis-trans mixture of the diol (101) (m.p.85-102°) (1.78 g) was shaken for 100 hours with copper sulphate monohydrate (10.0 g) in dry acetone (200 ml). The solution was filtered and the inorganic salts washed with more acetone. The solvent was removed from the filtrate to leave a sticky colourless solid which recrystallised from carbontetrachloride to give trans-1,2-diethynylcyclohexan-1,2-diol (101) as colourless prisms (1.38 g ; 77%) n.p. 79-81°. (Found: C,73.35; H, 7.30. $C_{10}H_{12}O_2$ requires C, 73.15; H, 7.35%). ν_{max} (CCl_4) (Unicam) ca. 3605 w, (broad shoulder)(free OH), 3574 m, (bonded OH), 3308 s cm^{-1} ($C\equiv CH$). i.e. identical in this region to the corresponding i.r. of the original cis-trans mixture. Comparison of the whole i.r. (nujol) spectra of the cis-trans mixture with the pure trans compound showed them to be similar but not identical. T.l.c. (silica; methanol:chloroform, (8:92)) showed a single spot which corresponded in R_f to the larger of the two spots found for the cis-trans mixture.

Evaporation of the mother liquors furnished an oil (100 mg; 6%) whose t.l.c. (as above) showed two spots of comparable R_f to the trans diol (101). ν_{max} (film) showed OH and $C\equiv CH$ and no distinct band attributable to an acetonide. This oil was not investigated further.

Notes. over/...

(1) Acetylation of the cis-trans mixture of the diol (101) (Acetic anhydride; pyridine) furnished the corresponding acetates whose t.l.c. separation was no greater than the separation of the original diols.

(2) Bromination[37] and chorination[41] of the cis-trans mixture of the diol (101) were unsuccessful, starting material being recovered unchanged.

High dilution coupling of trans-1,2-diethynylcyclohexan-1,2-diol (101)

The diol (101) (670 mg) in methanol:pyridine (1:1; 100 ml) was added over 5 hours to a stirred refluxing solution of cupric acetate (4.0 g) in the same solvent (100 ml). After a further 1 hour at reflux temperature the reaction mixture was left 2 days at room temperature and worked up by acidification and constant ether extraction (48 hours). The product, a brown gum (357 mg), was extracted with boiling carbontetrachloride to provide a gummy solid m.p.185-195°C whose t.l.c. (silica; methanol:chloroform, (4:96)) indicated five intense spots and a sixth weak spot which corresponded to the diol (101). The five products were poorly separated and all had R_f values less than the diol (101). No further attempt was made to separate these components.

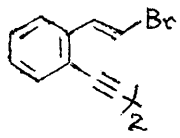
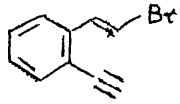
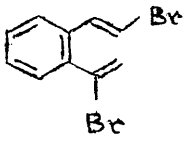
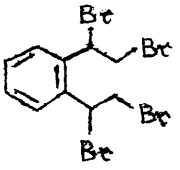
COMPOUND	τ VALUE OF PROTONS		
 (92)	$-C\left]\right[=CHBr$	$-CH=C\left]\right[Br$	$-CBr=C\left]\right[_2$
	2.41, 2.64	3.02, 3.26.	
	J = 14.1 c.p.s. average		
 (88)	2.38, 2.63	3.06, 3.29.	
	J = 14.4 c.p.s. average		
 (87)	2.54, 2.77	3.20, 3.44.	4.05, 4.06 J = 0.6 c.p.s.
	J = 14.1 c.p.s. average		4.25, 4.26 J = 0.6 c.p.s.
 (86)	$-C\left]\right[Br-CH\ Br_2$	$-CHBr-C\left]\right[_2\ Br$	
	4.35, 4.50, 4.62.	5.85, 5.97.	
	J = 7.6 c.p.s. average		

TABLE I.

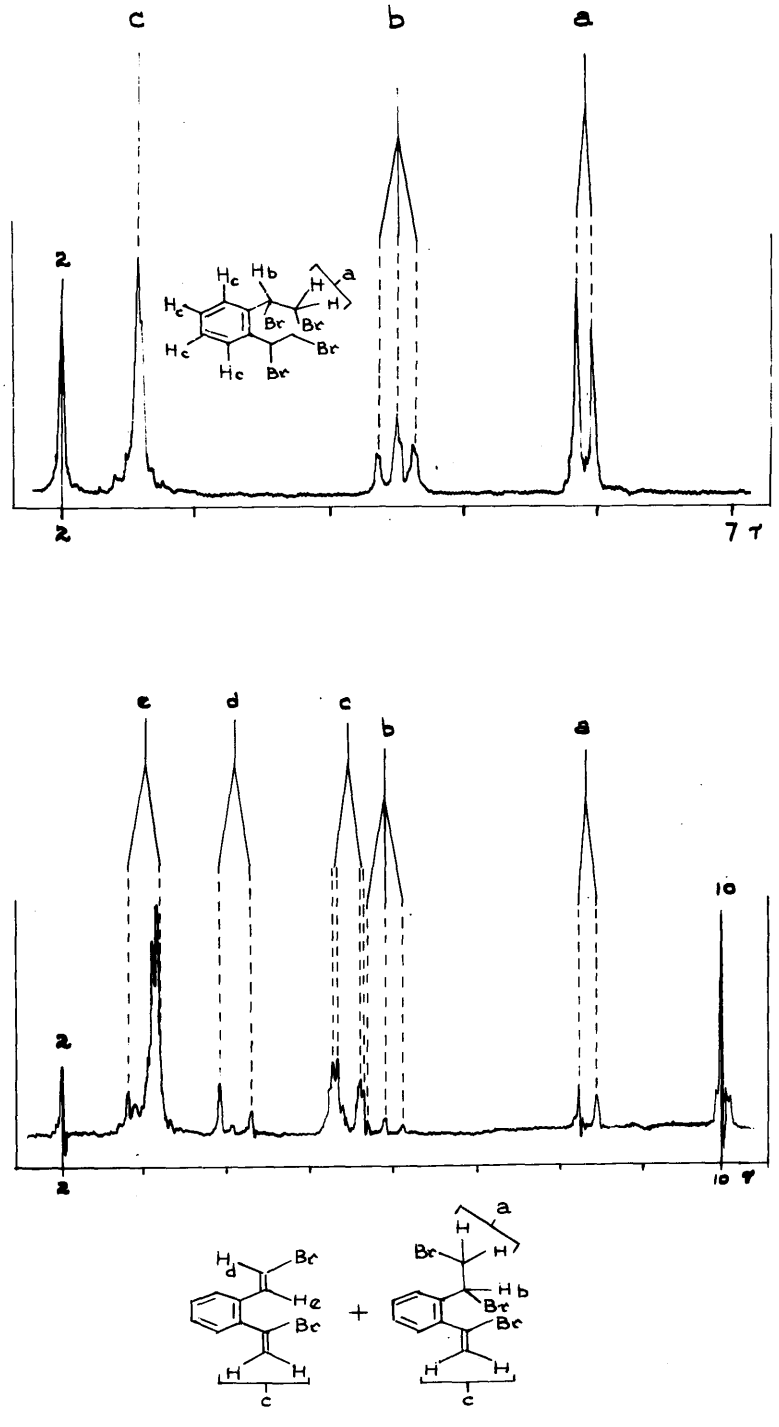

c
b
a
2
Hc
Hb
H
a
Br
Hc
Hc
Br
Hc
Br
2
7 τ
e
d
c
b
a
10
2
10 τ
Hd
Br
He
Br
H
H
c
+
a
H
Br
H
Hb
Br
Br
H
H
c

FIG. 1

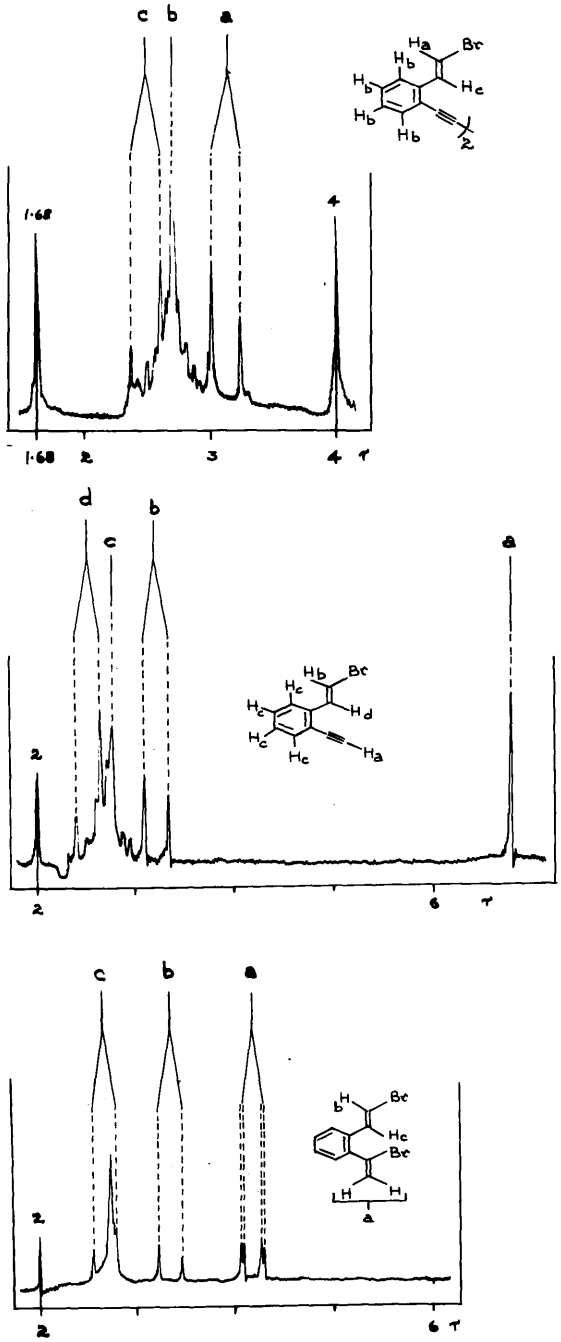

c b a
Ha Br
Hb
Hb Hc
Hb
Hb
2
1·68
4
1·68 2 3 4 τ
d c b a
Hb Br
Hc
Hc Hd
Hc
Hc Ha
2
2 6 τ
c b a
Br
Hb
Hc
Br
H H
H
a
2
2 6 τ

FIG. 2

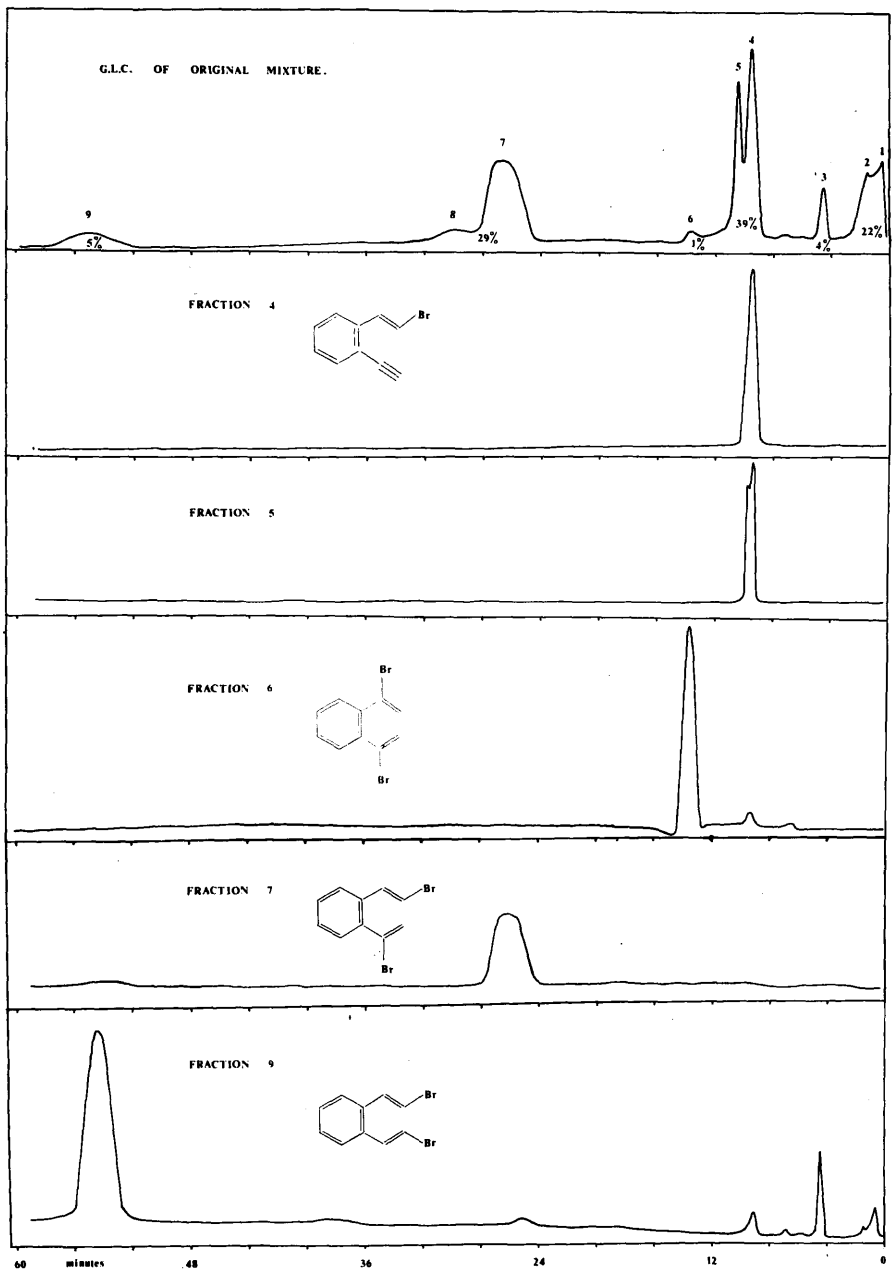

G.L.C. OF ORIGINAL MIXTURE.
9
5%
8
7
29%
6
3%
5
4
39%
3
4%
2
1
22%
FRACTION 4
Br
FRACTION 5
FRACTION 6
Br
Br
FRACTION 7
Br
Br
FRACTION 9
Br
Br
60
minutes
48
36
24
12
0

FIG. 3

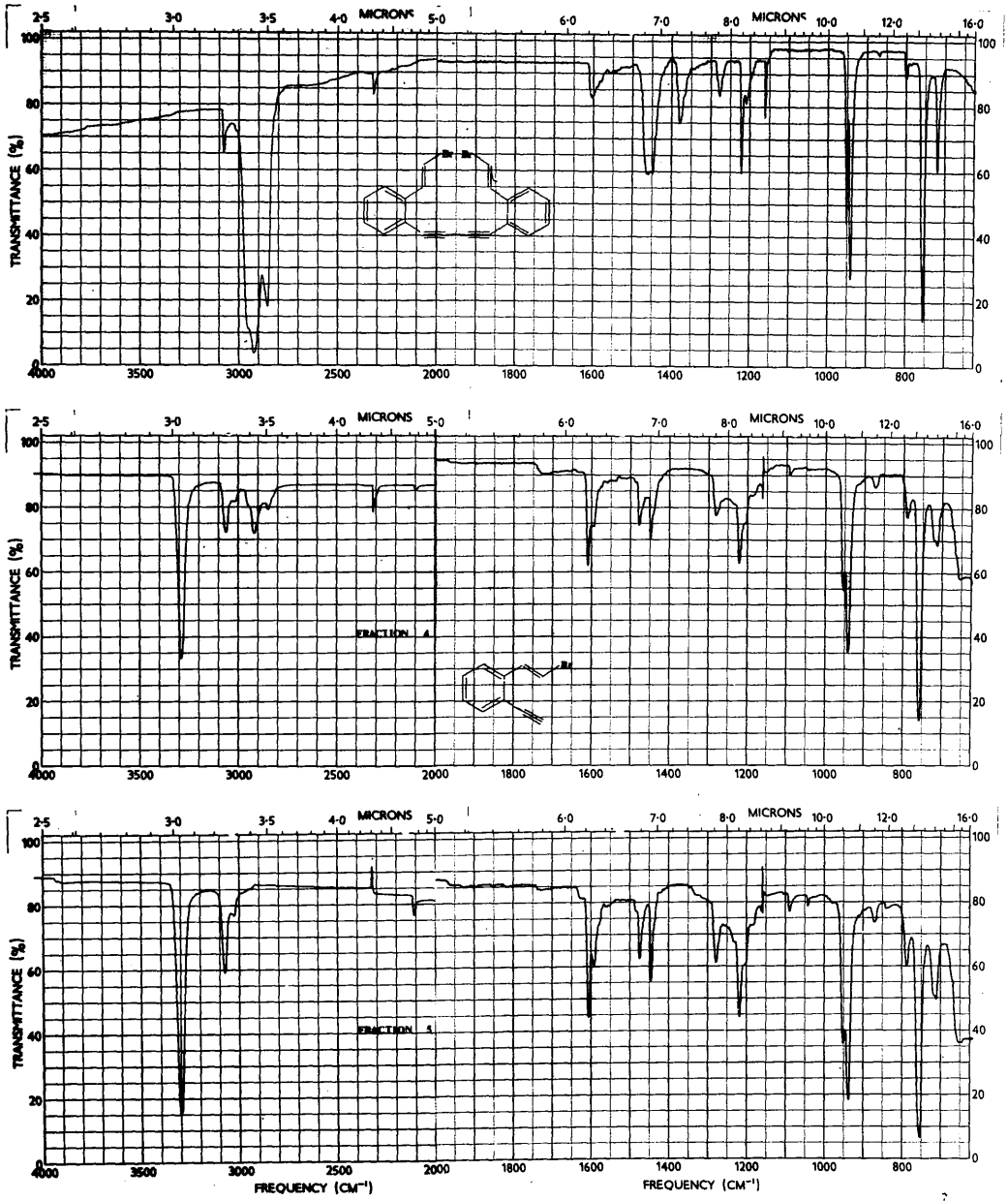

MICRONS
TRANSMITTANCE (%)
FRACTION 4
FRACTION 5
FREQUENCY (CM⁻¹)

FIG. 4

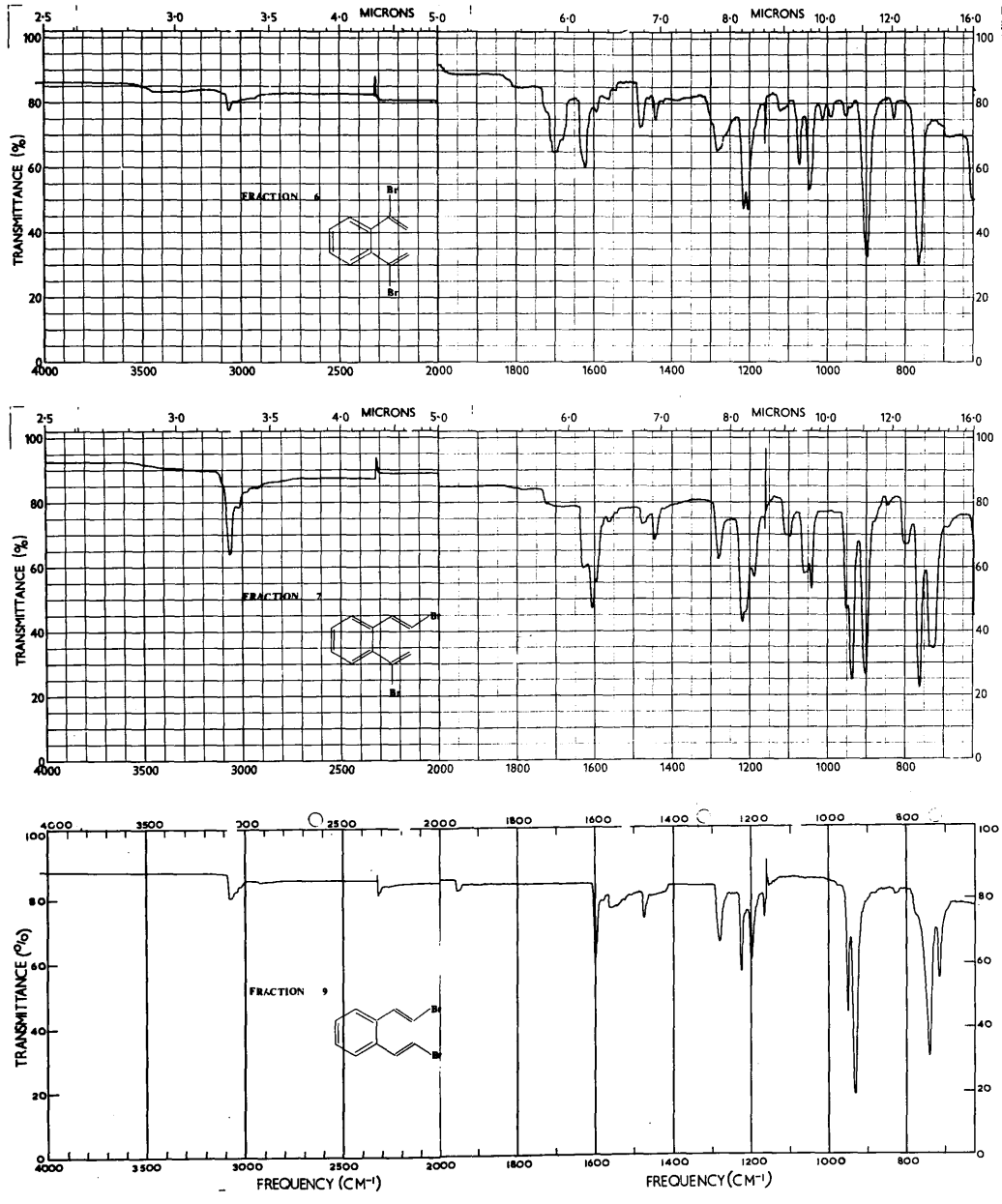
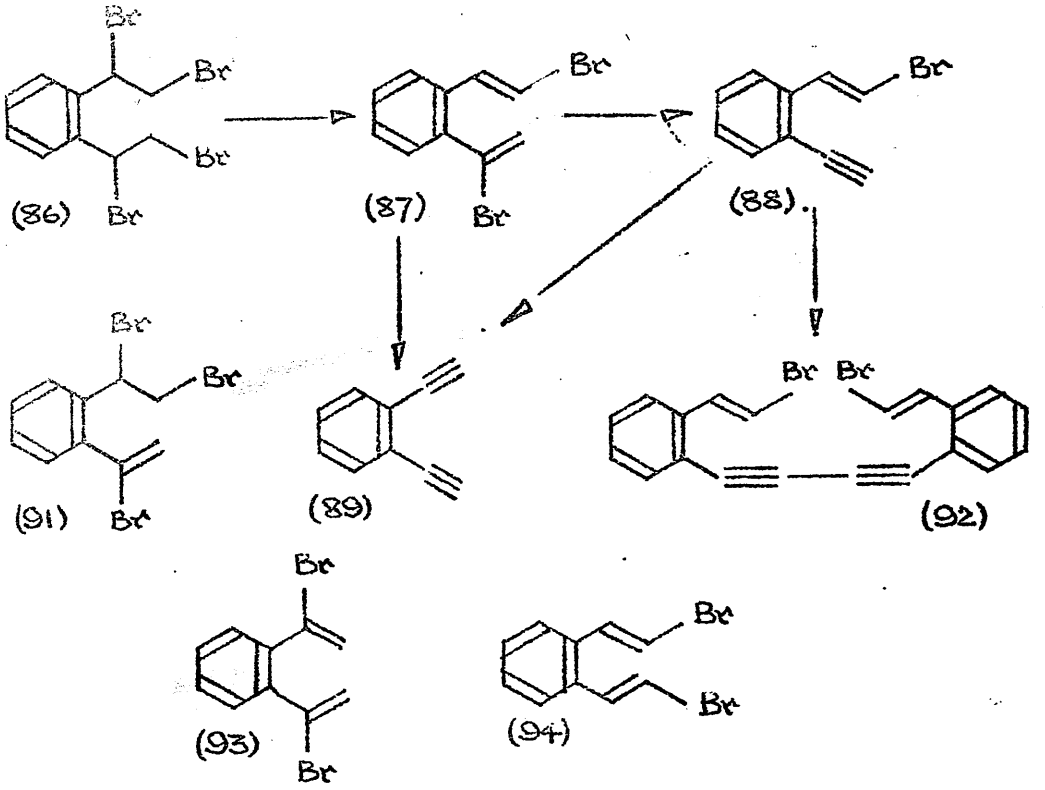
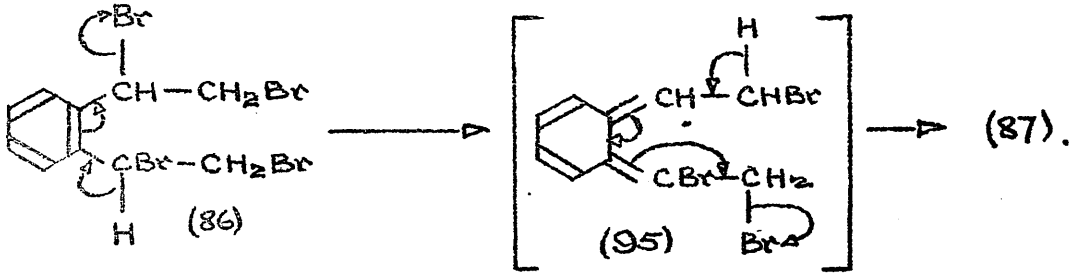
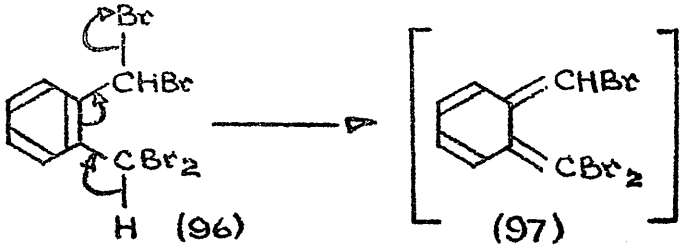
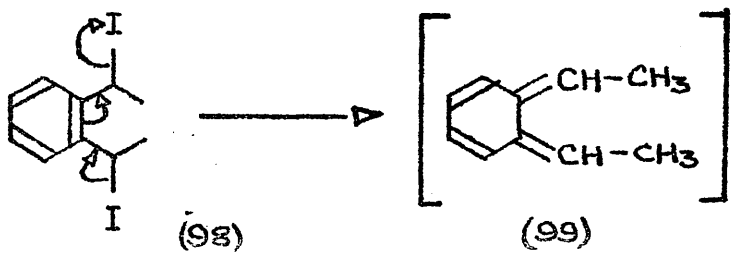

MICRONS
TRANSMITTANCE (%)
FRACTION 6
FRACTION 7
FRACTION 9
FREQUENCY (CM⁻¹)
Br

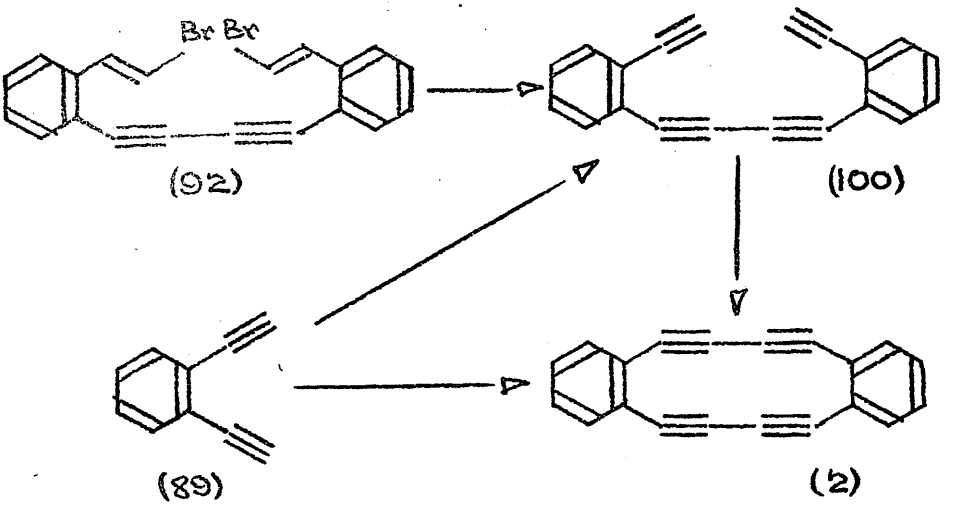
FIG. 5

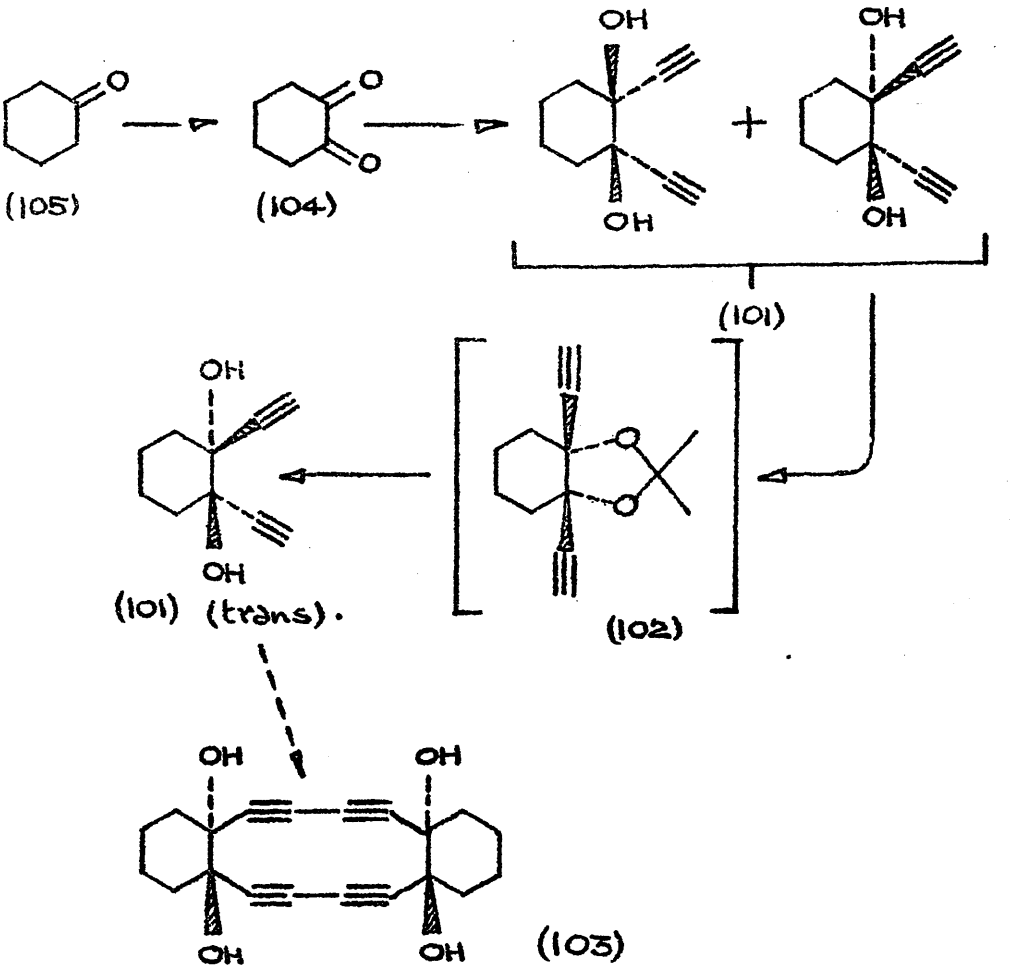

Br
Br
Br
Br
(86)
(87)
(88)
(91)
(89)
(92)
(93)
(94)


CH—CH2Br
CBr—CH2Br
H
(86)
(95)
(87).


CHBr
CBr2
H
(96)
(97)


I
I
(98)
CH—CH3
CH—CH3
(99)


Br Br
(92)
(100)
(89)
(2)


(105)
(104)
OH
OH
OH
OH
(101)
OH
OH
(101) (trans).
(102)
OH
OH
OH
OH
(103)

PART II

NITROGENOUS BY-PRODUCTS IN THE CADIOT-CHODKIEWICZ REACTION

The Cadiot-Chodkiewicz coupling reaction, developed in 1957, provides a means of preparation of unsymmetrical conjugated acetylenes. The fundamental reactions involved are as follows:

$$RC{\equiv}CH + Cu^{+} \longrightarrow RC{\equiv}CCu + H^{+} \quad \text{.....(a)}$$

$$RC{\equiv}CCu + BrC{\equiv}CR' \longrightarrow RC{\equiv}C\text{-}C{\equiv}CR' + CuBr \quad \text{.....(b)}$$

As reaction (b) regenerates the cuprous ion, it need only be present in a catalytic amount (1-2%). Indeed, this is a prime necessity as oxidation of the cuprous ion by the bromoacetylene, reaction (c), gives rise to the undesired cuprous acetylide which can couple with the bromoacetylene, reaction (d), and so furnish the unwanted symmetrical conjugated acetylene.

$$R'C{\equiv}CBr + 3Cu^{+} \longrightarrow R'C{\equiv}CCu + Br^{-} + 2Cu^{++} \quad \text{.....(c)}$$

$$R'C{\equiv}CBr \quad R'C{\equiv}CCu \quad R'C{\equiv}C\text{-}C{\equiv}CR' + CuBr \quad \text{.....(d)}$$

To avoid this secondary reaction the coupling is carried out under nitrogen and hydroxylamine hydrochloride (or hydrazine hydrochloride) is added as required to maintain the copper in the cuprous state. The bromoacetylene is added dropwise to the well stirred reaction medium. The addition of base, preferably a primary amine, (to the extent of 1.8 moles per mole of acetylene), facilitates the reaction by removing the librated acid. It also helps to diminish the oxidisability of the cuprous acetylide and the cuprous ions and to assist the formation of the cuprous acetylide possibly

by complexing with it. Chodkiewicz recommends the use of water, alcohol, ether and tetrahydrofuran as solvents for this reaction; for very insoluble components, dimethylformamide or N-methylpyrrolidone have been used.

Behr[1] found that during the normal Chodkiewicz conditions o-diethynylbenzene (89) gave an insoluble canary yellow precipitate which appeared quite unreactive towards the bromoacetylene component of the coupling. This solubility difficulty was overcome by changing the solvent-base mixture to n-butylamine:ethanol (4:1); thus a 60% yield of the tetrayne (107) was achieved by a mixed coupling between o-diethynylbenzene (89) and 1-bromophenylacetylene (106) in this homogeneous solvent system. However when the bromoacetylene component was altered to 1-(2'-bromoethynyl)-2-(2'-trans-bromovinyl)benzene (108) no coupled product could be isolated. Infra-red examination of the product showed diminished bromoethynyl absorption and undiminished ethynyl absorption; this strongly suggested that the bromoacetylene component was reacting with the solvent. This was confirmed by reaction of (108) alone with these reagents i.e. 1% cuprous chloride, n-butylamine:ethanol (4:1), and hydroxylamine hydrochloride, whereupon a crystalline hydrochloride $C_{18}H_{27}N_2Br.HCl$ was isolated in 44% yield. Tentative assignment of its structure as the amidine (109) was made on the basis of its analytical data and general characteristics. To test the generality of this unexpected reaction the simpler analogue

1-bromophenylacetylene was treated alone with the above reagent mixture. In this case two products were isolated as their hydrochlorides. The first, $C_{12}H_{18}ON_2$, was conclusively shown to be the amidoxime (110) by a synthesis involving interaction of N-n-butylphenylthioacetamide (113) and hydroxylamine. This amidoxime (110) could also be produced by the interaction of 1-bromophenylacetylene, n-butylamine and hydroxylamine in the absence of cuprous chloride. The second product was stated to possess the molecular formula $C_{16}H_{26}N_2O$; it was produced exclusively when hydrazine was used as reducing agent in place of hydroxylamine in the reaction mixture. Acid hydroysis gave phenylacetic acid while mild alkaline treatment produced N-n-butyphenylacetamide (114). On the basis of these reactions this second product was assigned the amidine N-oxide structure shown (112).

Such a structure type has not yet been recorded in the vast literature on amidines[58] and related compounds[43] and it was obviously desirable to confirm this novel structure by synthesis. The obvious mode of approach seemed to involve interaction of N-n-butylphenylthioacetamide and the hitherto unknown N-n-butyl-hydroxylamine. Attempted preparation of this latter compound by reduction of 1-nitro-n-butane by Beckmann's[44] method (zinc and ammonium chloride) gave poor results but controlled catalytic hydrogenation furnished an excellent yield of N-n-butylhydroxylamine

as its crystalline oxalate. A wide variety of conditions was then tried to effect condensation between this base and both N-n-butylphenylthioacetamide (113) and N-n-butylphenylacetamide (114) to produce a compound of structure (112) but all proved abortive.

At this juncture suspicions were aroused as to the authenticity of the structural assignment (112). To re-examine the problem the compound in question was re-prepared from 1-bromophenylacetylene by Behr's[1] procedure; significantly the same compound was produced by reaction of 1-bromophenylacetylene and n-butylamine alone and this latter reaction was markedly catalysed by trace quantities of cupric acetate (fig.8). The resulting hydrochloride was converted into the corresponding free base which was purified by distillation. Elementary analysis on this product and its derived hydrochloride surprisingly showed them to be oxygen free and corresponded to the molecular formula $C_{16}H_{26}N_2$. This formula strongly suggested the simple amidine structure (111) for this product, a suggestion borne out by its spectral characteristics. As firm confirmation of this assignment authentic N,N'-di(n-butyl)phenylacetamidine (111) was prepared by interaction of N-n-butylphenylacetamidochloride (115) (obtained from N-n-butylphenylacetamide and phorphorus pentachloride) and n-butylamine. The resulting amidine and its hydrochloride were identical in all respects with the product from 1-bromophenylacetylene. The explanation for Behr's misleading analysis can possibly be

assigned to contamination with the corresponding hydrobromide. Attempts to extend the reaction between 1-bromophenylacetylene and other bases such as analine and o-phenylenediamine were unseccessful.

Normally these side reactions do not occur to any extent in Cadiot-Chodkiewicz couplings because of the great speed of this latter process and the fact that relatively small amounts of reactive amine and of hydroxylamine hydrochloride are employed. However, it is clear that complications of the above type should be borne in mind whenever a sluggish bromoacetylene component is being used or modified reaction conditions employed. Related conversions of ethoxyacetylene[45] and of bromopropiolic acid[46] into amidines have been reported, while more recently, 1-bromophenylacetylene has been found to give 2,2-di(diethylamino)-styrene on treatment with diethylamine[47]. It is evident from these results, the present work, and from very recent studies[48], that 1-bromoacetylenes are not so inert to nucleophilic substitution as had been believed.

EXPERIMENTAL PART II.

1-Nitro-n-butane

n-Butylbromide (41 g; 0.3 mol) was added to a stirred mixture of sodium nitrite (36 g; 0.52 mol) in dimethlformamide (600 ml) in a water bath at room temperature (cf.50). After 6 hours stirring the reaction mixture was poured into ice-water (1.5 l) and light petroleum (b.p. 40-60°; 100 ml) and thoroughly extracted with light petroleum (100 ml x 4). The petrol extracts were dried ($MgSO_4$) and evaporated under vacuum (20 mm). The 1-nitro-n-butane was collected at 74-80°/20 mm (14.0 g; 45%) (Zublin[49] b.p. 151-2°/760 mm). ν max (film) 1560-1530 s, (NO_2) and 1340 m cm^{-1} (NO_2).

Attempted preparation of N-n-butylhydroxylamine hydrochloride

Zinc powder (12.3 g; 0.19 mol) was added slowly to a stirred ice-cooled mixture of 1-nitro-n-butane (7.6 g; 0.074 mol) and ammonium chloride (2.7 g; 0.051 mol) in water (36 ml) and the stirring was continued for 3 hours (cf. 44). The reaction mixture was then filtered and the filtrate acidified (HCl, 6N) and evaporated to dryness. Final traces of water were removed by azeotropic distillation with benzene. The residue was dissolved in ethanol and the inorganic salts were filtered off. On addition

of ether no product was precipitated. The solvents were then removed to furnish a viscous oil (6.7 g), ν max (film) 3400 to 2450 cm^{-1} as a broad poorly resolved band; the pattern of absorption was similar to that of an authentic sample of N-methylhydroxylamine[44]. The product gave a red-purple colouration when treated with an alkaline solution of triphenyltetrazonium chloride[62]; it is likely therefore, that it contained the required hydroxylamine, but the procedure obviously possessed little preparative value.

N-n-Butylhydroxylamine oxalate

A solution of 1-nitro-n-butane (5.15 g; 0.05 mol) and oxalic acid (3.15 g; 0.029 mol) in water (40 ml) was hydrogenated over a 10% palladium charcoal catalyst (0.5 g) (cf. 51). The theoretical uptake of hydrogen was observed (2.24 l). Filtration of the catalyst and removal of the water by rotary evaporation gave large colourless plates which after recrystallisation from n-butanol gave N-n-butylhydroxylamine oxalate as colourless plates (3.81 g; 30%) m.p. 116.5-118.5°. (Found: C, 44.75; H, 8.70; N, 10.10. $C_{10}H_{24}O_6N_2$ requires C, 44.75; H, 9.00; N, 10.45%). ν max (mujol) 3500 to 2000 (extensive hydrogen bonding) and 1550 cm^{-1} (RCO_2^-). The oxalate on treatment with sodium carbonate solution and ether extraction furnished the free base, N-n-butylhydroxylamine, as colourless needles m.p. 49-50°, which rapidly deteriorated on exposure to the atmosphere; ν max (film) 3275 s, 3140 s, and 2975 to

2700 cm^{-1} (broad band). Neither the oxalate nor the free base formed derivatives with sodium picrate or picric acid respectively.

Attempted preparation of N,N'-di(n-butyl)phenylacetamidine-N-oxide(112) by reaction between :

(a) N-n-Butylphenylthioacetamide[1] (113) and crude N-n-butylhydroxylamine hydrochloride

The thioacetamide (113) (1.09 g; 5.3 m.mol) and the oil which was presumably the N-n-butylhydroxylamine hydrochloride (0.66 g; 5.3 m.mol) were refluxed in methanol (20 ml) with sodium carbonate (0.56 g; 5.3 m.mol) for 27 hours. The solvent was removed under vacuum (20mm) and the residue was treated with sodium carbonate solution (4N, 10 ml) and extracted with ether. The ether extracts were extracted with acid (HCl,6N) and acid layer basified (solid sodium carbonate) and re-extracted with ether. The ether solution after thorough drying ($MgSO_4$) was treated with hydrochloric acid gas. No solid was precipitated and the solvent was removed to furnish a viscous oil (0.87 g) showing i.r. absorption identical to the starting hydroxylamine hydrochloride.

Repitition of this experiment in the absence of solvent and under a carbon dioxide atmosphere gave the same result.

(b) /...

/(b) N-n-Butylphenylthioacetamide (113) and N-n-butylhydroxylamine oxalate

The thioacetamide (113) (414 mg; 2.0 m.mol), and the hydroxylamine oxalate (268 mg; 1.0 m.mol) were refluxed in methanol (20 ml) in the presence of sodium carbonate (212 mg; 2.0 m.mol) for 72 hours. The reaction was worked up as in (a) and treatment of the ethereal solution of the basic components with hydrochloric acid gas deposited an oil which could not be induced to solidify. Treatment of this product with sodium carbonate solution and ether extraction provided a yellow oil with an i.r. spectrum not at all similar to that recorded[1] for the postulated amidine-N-oxide base (112).

Various modification of this reaction were attempted; it was conducted in an atmosphere of carbon dioxide to prevent any possible autoxidation of the hydroxylamine[52]; the reactants were heated in the absence of solvent to 130° for 14 hours; an attempt was made to catalyse the reaction by the addition of mercuric chloride[42]; finally dimethylformamide was used as the solvent. In no instance was a solid obtained and the i.r. spectrum of the product was always poorly resolved.

(c)/...

/ (c) N-n-Butylphenylacetamide[1] (114) and N-n-butylhydroxylamine oxalate

The acetamide (114) (380 mg; 2.0 m.mol) and the hydroxylamine oxalate (270 mg; 1.0 m.mol) were refluxed in ethanol (15 ml) in the presence of sodium carbonate (210 mg; 2.0 m.mol) for 7 days. The solvent was then removed by evaporation (20 mm), saturated sodium carbonate solution added, and the resulting solution extracted with ether. The ethereal extracts were then extracted with acid (HCl, 6N) and the acid solution neutralised with solid sodium carbonate. Colourless needles (151 mg.) m.p. 49-50° rose to the surface. A mixed melting point determination and the i.r. spectrum showed this product to be simply the N-n-butylhydroxylamine free base. Ether extraction of the basic aqueous solution afforded no further material.

Preparation of the so-called "N,N'-di(n-buty)phenylacetamidine-N-oxide"[1] (112) by Behr's method.

Cuprous chloride (18 mg) was added to stirred solution of n-butylamine:ethanol (4:1; 42 ml) under nitrogen. The resulting blue colouration was removed by the addition of hydrazine hydrochloride (ca. 100 mg). After cooling the solution to -5°, 1-bromophenylacetylene (1.8 g) in ether (10 ml) was added dropwise over 15 minutes. Stirring was continued for 1 hour at room temperature, and the reaction was then evaporated (1.0 mm) at the same temperature. The residue was acidified (HCl, 6N), and extracted

with ether; the ether layer was set aside. The aqueous layer was neutralised with solid sodium carbonate, whereupon a brown oil separated. (No blue colouration, found by Behr, was detected at this point). Chloroform extraction provided a very viscous oil which crystallised on trituration. Recrystallisation from ethanol: ether at -80° gave the anidine-N-oxide hydrochloride (112) as colourless microprisms (1.6 g; 54%) m.p.83-84° (Behr m.p.84-85°) A mixed melting point with Behr's product was undepressed. (Found: C, 65.75; H, 8.95; N, 11.60; O, 0.34. $C_{16}H_{26}N_2O.HCl$. (112) requires C, 64.4; H, 9.1; N, 9.4; O, 5.35%)

A sample of the hydrochloride (112) was neutralised with saturated sodium carbonate solution and the free base extracted with ether. Removal of the ether furnished an oil which was distilled (118°/0.15mm) to give the free base as a colourless oil $n_D^{20} = 1.5180$. (Found: C,77.55; H, 10.4; N, 11.1. $C_{16}H_{26}N_2O$ (112) requires C,73.2; H, 10.05; N, 10.7%. However, $C_{16}H_{26}N_2$ (111) requires C, 77.9; H, 10.65; N, 11.4%). The free base was dissolved in ether and extracted with acid (HCl, 6N). Chloroform extraction of the acid layer gave the hydrochloride which solidified on removal of all traces of solvent (0.15 mm). Recrystallisation (x4) from ethanol:ether at -80° provided the pure hydrochloride as colourless microprisms m.p. 86-87°. (Found: C, 67.8; H, 9.75; N, 10.1. $C_{16}H_{26}N_2O.HCl$ (112) requires C,64.4; H, 9.1; N, 9.4%

However $C_{16}H_{26}N_2 \cdot HCl$ (111) requires C, 67.9; H, 9.6; N, 9.9%.)
The analytical data for the free base and the regenerated hydrochloride necessitate a reassignment of an amidine structure $C_{16}H_{26}N_2$ (111) for this product.

Attempted reduction of the postulated "N,N'-di(n-butyl)phenylacetamidine -N-oxide" (112)

(a) Sulphur dioxide[53]

The "amidine-N-oxide" hydrochloride (112)(250 mg) was dissolved in chloroform (60 ml) and sulphur dioxide gas bubbled through the solution. Aliquots (15 ml) were removed at time intervals up to 10 days but the i.r. spectrum of each showed only unchanged starting material.

(b) Lithium aluminium hydride[54].

The "amidine-N-oxide" (112)(723 mg) was stirred at room temperature in anhydrous ether (20 ml) and lithium aluminium hydride (210 mg; 4 mol excess) added. No evolution of heat was observed and the solution was refluxed for 18 hours and then cooled in an ice-bath. The excess hydride was decomposed with water (0.25 ml), sodium hydroxide solution (15%; 0.25 ml) and a further quantity of water (0.75 ml). The reaction mixture was filtered, the salt residues washed with warm ether, and the ethereal solution dried ($MgSO_4$). Removal of the ether provided a colourless oil (660 mg; 91%) possessing an i.r. spectrum identical to that of the starting material.

Synthesis of N,N'-di(n-butyl)phenylacetamidine (111)

Phosphorus pentachloride (450 mg; 2.17 m.mol) was refluxed in benzene (30 ml) till the evolution of hydrochloric acid gas had ceased (cf.55). N-n-butylphenylacetamide (382 mg; 2.0 m.mol) was added to the cooled solution and n-butylamine (146 mg; 2.0 m.mol) in benzene (5 ml) added immediately the amide was dissolved. After 3 hours reflux, the solvent was evaporated, and a minimal volume of ethanol was added to dissolve the residue. The resulting solution was treated with ammonium hydroxide (0.880) and extracted with ether. Treatment of the thoroughly dried ether extracts with hydrochloric acid gas furnished the crude hydrochloride as an oil which was dried by azeotropic distillation with benzene. Trituration rendered the oil solid and recrystallisation from ethanol:ether at -80° gave the amidine hydrochloride (111) as a colourless microcrystalline powder (57 mg; 20%) m.p. 83-84°. This product was identical (mixed melting point undepressed; i.r. spectrum) to that isolated from the reaction of 1-bromophenylacetylene (106) with the Cadiot-Chodkiewicz coupling reagent.

Attempts to synthesise this amidine (111) by the interaction of N-n-butylphenyacetamide (116) and n-butylamine hydrochloride[59] or N-n-butylphenylthioacetamide (113) and n-butylamine[60] were not successful, the starting materials being recovered unchanged.

Phenylureide of the Amidine (111): (cf 61)

A dry ethereal solution of the amidine (111) (184 mg; 0.75 m.mol) and phenylisocyanate (59 mg; 0.75 m.mol) was held at room temperature overnight. Removal of the ether left a pale orange oil (230 mg) which solidified at ~80°. Recrystallisation (x5) from aqueous acetone provided the phenylureide as off-white needles (30 mg) m.p.238-244° whose melt indicated the presence of a brown crystalline impurity. Sublimation (170°/0.07 mm) provided a sample m.p. 241-244°, which was still impure. (Found: C,73.9; H, 5.65; N, 13.5. $C_{23}H_{31}N_3O$ requires C, 75.9; H, 8.55; N, 11.5%).

No picrate or oxalate derivative of the amidine could be made.

Investigation of the copper ion catalysis of the amidine formation.

(a) Non-catalysed reaction:

1-Bromophenylacetylene (106)(1.8g; 10 m.mol) was dissolved in n-butylamine (50 ml) and aliquots (10; 5 ml) were removed at intervals. The aliquots were worked up by evaporation, addition of ether and extraction (x2) with dilute nitric acid. Standard silver nitrate solution was added and the excess was titrated against standard potassium thiocyanate solution using a ferric alum indicator. (Ferric ammonium sulphate (5 g) in water (50 ml) and concentrated nitric acid (5 ml), boiled vigorously to remove oxides

of nitrogen). The titres are recorded below.

Repetition of this reaction without removal of aliquots and with the usual work up furnished, after a reaction period of 24 hours, 25% of unchanged 1-bromophenylacetylene and 70% of an oil from which the pure amidine (111) hydrochloride was isolated in 25% yield.

t (mins)	KSCN titre v. 20 ml $AgNO_3$ (ml)	Vol. of $AgNO_3$ reacted (as KSCN vol.) (ml)	Vol. of $AgNO_3$ reacted (ml)
0	20.30	1.00	0.94
35	19.47	1.83	1.72
56	18.76	2.54	2.38
138	17.66	3.64	3.41
198	16.90	4.40	4.13
258	16.01	5.29	4.96
303	15.29	6.01	5.65
1248	7.90	13.40	12.60
1458	6.90	14.40	13.51
2800	0.04	21.26	20.00

(10.65 ml KSCN soln. = 10.00 ml $AgNO_3$ soln.)

(b) /...

/(b) Cupric ion catalysed reaction :

The experiment was repeated as in (a) with the addition of cupric acetate (30 mg; ca. 2% per mole of bromoacetylene). The acetate ion does not interfere with the estimation of the bromide ion liberated.

t (mins)	KSCN titre v. 25 ml $AgNO_3$ (ml)	Vol. of $AgNO_3$ reacted (as KSCN vol.) (ml)	Vol. of $AgNO_3$ reacted. (ml)
0	24.09	2.36	2.24
45	20.07	6.38	6.03
60	19.77	6.68	6.31
120	15.72	10.73	10.18
180	9.33	17.12	10.21
240	5.37	21.08	20.00
305	4.55	21.90	20.70
340	4.71	21.74	20.60
1260	1.15	25.30	24.00

(10.58 ml KSCN soln. = 10.00 ml $AgNO_3$ soln.)

These results are illustrated graphically (fig.8). It is evident that the addition of cupric ion has a marked catalytic effect on the formation of the amidine.

Attempted amidine formation from aniline and 1-bromophenylacetylene

1-Bromophenylacetylene (1.8 g) and aniline (50 ml) were mixed and left at room temperature for 5 days. Basification with sodium carbonate solution followed by ether extraction and removal of the solvent and excess aniline (flame distillation) gave a black glass (570 mg), showing no absorption between 1700-1600 cm^{-1} ($C \equiv N$). Treatment of an ethereal solution of the product with hydrochloric acid gas gave only aniline hydrochloride.

Attempted amidine formation from o-phenylenediamine and 1-bromophenylacetylene.

1-Bromophenylacetylene (3.6 g) in ethanol (5 ml) was added to a solution of o-phenylenediamine (2.15 g) and cupric acetate (72 mg) in ethanol (30 ml). After 24 hours at room temperature the reaction was acidified (HCl, 6N) and ether extraction furnished unreacted 1-bromophenylacetylene (2.4 g). Neutralisation of the acid layer with solid sodium carbonate and ether extraction furnished only o-phenylenediamine (1.9 g)

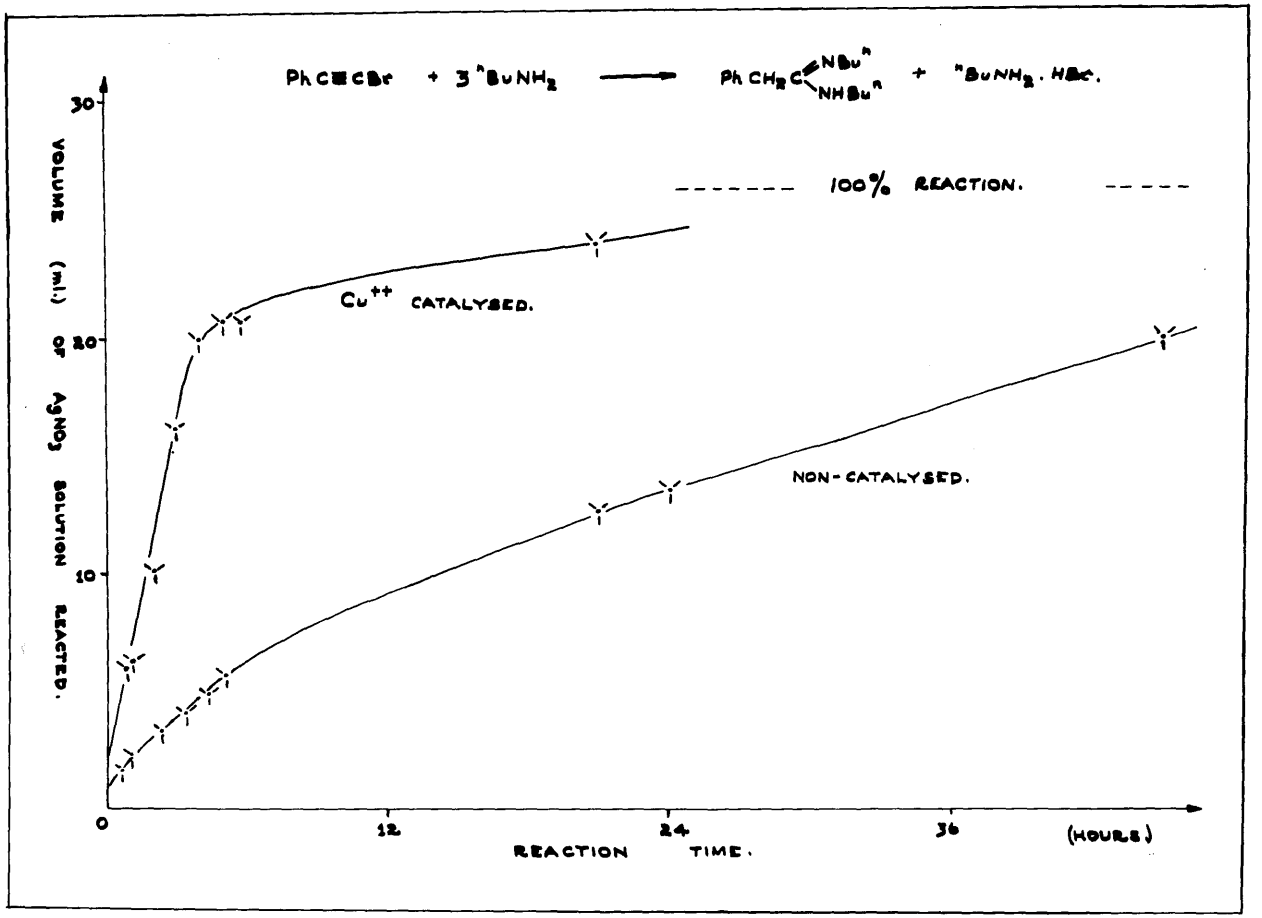
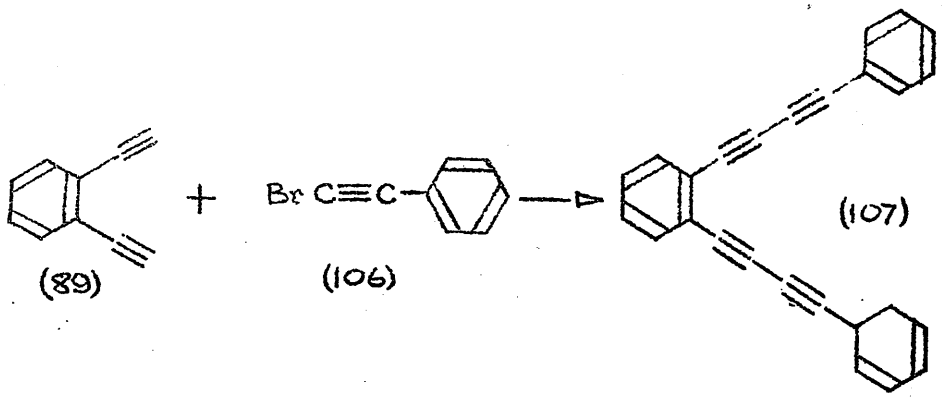
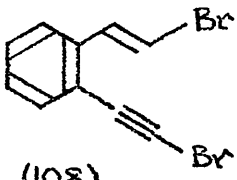


FIG. 8 : COPPER ION CATALYSIS OF AMIDINE FORMATION.



(89) (106) (107)



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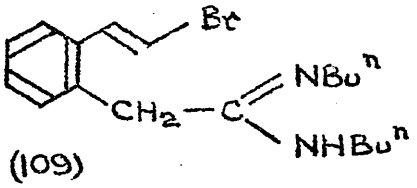

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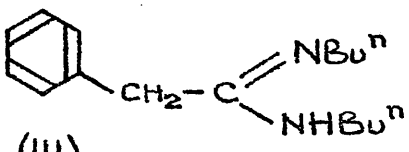
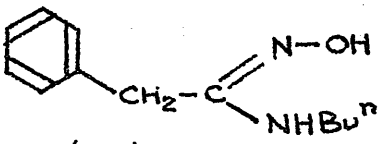


(111).



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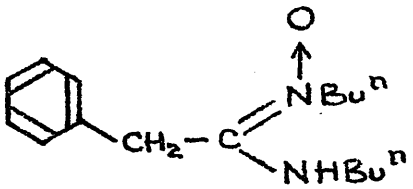

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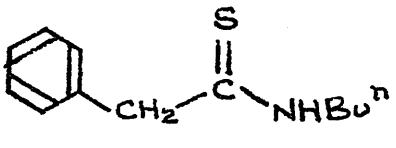
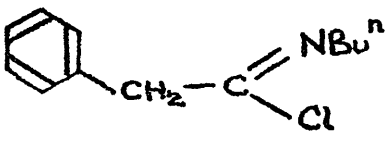


(113).



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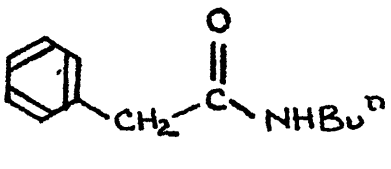


(114)

PART III.

STUDIES IN ACETYLENIC HETEROCYCLES

It is well known that there is a very close similarity in physical and chemical properties between aromatic hydrocarbons and the corresponding sulphur compounds in which the grouping $-CH=CH-$ is replaced by formally bivalent sulphur. The simplest example of this occurs with benzene and thiophene and their derivatives.[63 (a)] The similarity of the electronic structure of thiophene and benzene has been examined by Schomaker and Pauling[64] from the valence bond viewpoint and Longuet-Higgins[65] using the techniques of molecular orbital theory. The former investigators have postulated that structure such as (116), (116 a) and (116 b) contribute to an extent of about 10% to the thiophene resonance hybrid. Such structures involve the sulphur atom in a decet of electrons and the participation of sulphur d orbitals has thus been invoked. Longuet-Higgins has shown that, if this participation of the sulphur 3d orbitals is taken into account, the atomic and molecular orbitals of the π-electrons in a thiophene derivative correspond closely with those of the analogous benzene derivative. While the π-molecular orbitals of benzene can be derived from six ethylene molecular orbitals[66] (the two types (117) and (117 a) are shown), the π-molecular orbitals of thiophene can be constructed by substituting for two of the six ethylene orbitals (one of each type) sulphur orbitals, of similar symmetry, dimensions, and binding energy.

Hybridisation of a sulphur p_z orbital (118), a d_{xz} orbital (119) and a d_{yz} orbital produces three pd^2 hybrid orbitals which have the correct symmetry and energy to interact with the p_z orbitals of the ring carbon atoms. This is illustrated in the thiophene structure (120) shown where the non-bonding orbital (dotted) of the sulphur atom is vacant.

A further striking example of this effect of the substitution of a sulphur atom occurs in cyclopenta-[c]-thiapyran (121)[67] which is iso-π-electronic with azulene and shows ultra-violet and visible light absorption very similar to this hydrocarbon. Two even more esoteric illustrations of this principle are provide by the unexpected degree of stability shown by the four-membered sulphur-containing systems (121 a)[87] and (121 b)[88].

This possibility of d orbital interaction possessed by the sulphur heteroatom, coupled with the properties of the Hückel-type hydrocarbon 18-annulene (72) (discussed in Part I) prompted an attempt to sythesise the iso-π-electronic 1,6,11-trithiacyclopentadeca-2,4,7,9,12,14-hexaene (122). An obvious starting material for this compound would be the isomeric triacetylene 1,6,11-trithiacyclopentadeca-3,8,13-triyne (123) from which the production of (122) may be envisaged by a multiple base-catalysed prototropic rearrangement of the type used by Sondheimer.

The reaction between 1,4-dichlorobut-2-yne and sodium sulphide was therefore explored in the hope that the desired triacetylene (123)

would be at least one of the products formed. In the event much polymeric material was encountered but a crystalline high-melting sparingly-soluble product was isolated in low yield (0.2%) with the expected empirical formula C_4H_4S. This yield was improved considerably (21.5%) by the use of aqueous ammonium sulphide. A conventional molecular weight determination was precluded by the low solubility of the compound, which also negated n.m.r. examination. However, mass spectrometry measurements showed no peak higher than a mass number of 167 corresponding to a molecular ion, $C_8H_7S_2^+$; this immediately suggested a molecular formula of $C_8H_8S_2$ for the product which in turn pointed to the structure (124) as a possible representation of the compound. This indication was fully confirmed by an X-ray crystal analysis carried out by Dr. G.A. Sim. The crystal was found to be monoclinic with lattice parameters $\underline{a}$ 7.38, $\underline{b}$ 4.44, $\underline{c}$ 13.25 Å, $\beta = 109^\circ 30'$ and the space group is $P2_1/\underline{c}$. The sharpened Patterson projection on (010) was interpreted by a superposition method[89], and gave a direct determination of the molecular structure. There are two molecules in the unit cell and as there are four equivalent positions in the space group $P2_1/\underline{c}$ the molecule is required to be centrosymmetric; thus it cannot possess a boat-like conformation but must be either flat or, much more probably, chair-like. The atomic coordinates were refined by several cycles of structure-factor and Fourier calculations and the value of $\underline{R}$, the average discrepancy between measured and calculated structure factors, is now 17%. The electron-density projection

along the b axis is shown in figure 6.

It is noteworthy that an early claim[68] to have obtained the oxygen analogue of (124) in minute yield by interaction of acetylenedimagnesium bromide and dichlorodimethyl ether has recently been substantiated by Sondheimer[15]; the two heterocycles have very similar melting points. The crystallographic data reported for the oxygen analogue show that it is not isomorphous with the sulphur compound but both heterocycles have the same space group $P2_1/c$ and a chair conformation. Our own attempts to prepare the oxygen analogue (125) either by the condensation of 1,4-dichloro-but-2-yne with 1,4-dihydroxybut-2-yne or by the bimolecular cyclic dehydration of this latter compound were entirely unsuccessful. Sondheimer[15] was also able to isolate the fifteen-membered trioxa-compound, although the yield (0.5%) was much lower than that (2%) of the ten-membered dioxa-compound (125). In our own case the relatively high yield of (124) may reflect the favourable effect which the rigid chains of four carbon atoms may exercise in bringing about cyclisation once the probable intermediate, $(ClCH_2C{\equiv}CCH_2)_2S$, has been formed. This would seem especially plausible in view of the relatively high concentrations and the inhomogeneous conditions employed.

The diyne (124) presents interesting possibilities for ligand formation involving the π-orbitals of the triple bond and the d orbitals of the sulphur atoms and indeed metallic derivatives

were readily obtained. With silver nitrate a sparingly soluble complex (decomp. above 170°) was formed. Mercuric chloride formed a 1:1 complex (m.p. 148-150°) with the diyne (124) and the complex with dipotassium tetrachloropalladate was a black amorphous powder. No complex was formed with either nickel chloride or nickel bromide and the diyne was recovered unchanged after treatment with a tetrahydrofuran solution of iron pentacarbonyl and an n-heptane solution of iron enneacarbonyl.

Treatment of the diyne (124) in acetonitrile solution with methyl iodide, 1,4-dichlorobut-2-yne, or benzyl chloride did not appear to produce the corresponding sulphonium salts.

Hydrogen peroxide in acetic acid at room temperature oxidised the diyne (124) to the disulphoxide (126) and excess of this reagent over three days produced the disulphone (127). Both these oxidation products were sparingly soluble crystalline solids, which decomposed slowly at high temperatures without melting. On continued heating above 220° the disulphone (127) sublimed and did not lose sulphur dioxide to form cyclo-octatetraene as might have been expected (cf.86). Attempted base catalysed rearrangement of the disulphone (127) with potassium t-butoxide was ineffective.

The proximity in space of the two triple bonds on opposite sides of the molecule of (124) suggested that some transannular interaction between them might be effected by light activation. In the event the diyne (124) was unaffected by ultra-violet irradiation

either in the solid state or when in solution in light petroleum or benzene.

Further confirmation of the structure of the diyne disulphide as (124) was achieved by reductive desulphurisation with Raney nickel in diglyme when n-butane, identified by g.l.c., was produced. Most unexpectedly for a sulphide the diyne (124) underwent smooth catalytic hydrogenation in the presence of even the readily-poisoned palladium-charcoal to give the cis,cis-diene, 1,6-dithiacyclodeca-3,-8-diene (128); even vigorous conditions failed to reduce this diene further to the completely saturated heterocycle. The structure of (128) was capable of confirmation by n.m.r. spectroscopy as it proved to be much more soluble than the starting diyne (124). Thus the n.m.r. spectrum (fig 7) showed the eight methylene protons as a doublet centred on $\tau = 6.83$ and the four olefinic protons as a triplet centred on $\tau = 4.52$ ($J = 6$ c.p.s.). Sodium in ammonia reduction of the diyne (124) provided a low yield of a volatile malodorous oil which g.l.c. examination proved to be too complex for further examination in the time available. An attempt to synthesise the diene (128) from cis-1,4-dichlorobut-2-ene and ammonium sulphide produced only malodorous oils.

The diene (128) formed a bis mercuric chloride complex but was recovered unchanged from an n-hexane solution of molybdenum hexacarbonyl. It has been shown[90] that ultra-violet irradiation of cis,cis-cycloocta-1,5-diene produces the saturated hydrocarbon tricyclo-$[3,3,0,0^{3}]$-octane. The somewhat analogous heterocyclic

diene (128) was therefore irradiated in a like manner to see whether an analogous transannular bond formation took place; it proved to be unaffected by the treatment. Oxidation of the diene (128) with hydrogen peroxide in acetic acid furnished the diene-disulphone (129) as highly insoluble colourless needles (decomp. p. 300°). Prolonged refluxing of the diene (128) with potassium t-butoxide in t-butanol did not cause rearrangement of the double bonds so that they became conjugated with the sulphur atoms.[69]

Base catalysed prototropic rearrangement of the diyne (124) to the fully conjugated tetraene was then attempted. Treatment with potassium t-butoxide in t-butanol caused a rapid transformation into an isometric low-melting substance with a naphthalene-like odour. This product gave a violet colouration with isatin-sulphuric acid indicating the presence of a thiophene nucleus.[63 (b)] More detailed identification of this product came from its spectral properties. The n.m.r. spectrum (fig 7) showed (a) four methylenic protons as a quartet (τ = 7.05, 6.75) (b) two cis vinyl protons as an AB quartet (τ = 4.2, 3.54; J = 11 c.p.s.) and (c) two thiophene α-protons as two doublets. (τ = 3.27 and 3.1; J = 3 c.p.s.). The mass spectrum showed prominent peaks at 168 (parent molecular ion), 153 (loss of CH_2) and 140 (loss of $-CH_2-CH_2-$). The infra-red spectrum showed absorptions at 3096 (thiophene =CH), 3010 (cis HC = CH), 797 and 788 (thiophene α-protons), 745 cm^{-1} (cis HC = CH). In the ultra-violet region the product showed end

absorption and λ max = 290 mu (ε = 15,800). All these properties were fully compatible with the structure 4,9-dithiabicyclo-[5,3,0]$^{(10)}$-deca-1,2,7-triene (130) proposed for this rearrangement product.

The conditions of the rearrangement reaction were studied carefully and it was found that the yield reached a maximum (64%) when the diyne (124) was treated with an excess of freshly prepared potassium t-butoxide in t-butanol for 15 minutes at 60°. A poor yield (8%) was obtained with ethanolic potassium hydroxide and no reaction occurred with triethylamine, potassium hydroxide (pellets) in petrol, grade (H) alumina, potassium t-butoxide in benzene or sodium methoxide in methanol.

A tentative mechanistic proposal for this rearrangement reaction would involve the prototropic generation of the diallene (131) followed by carbonion-induced transannular bond formation as shown. The formation of a thiophene ring certainly provides a powerful driving force for this transformation.

The thiophene (130) did not form a complex with mercuric chloride. Raney nickel desulphurisation of the thiophene (130) gave no gaseous product and attempts to isolate the expected product, 3,4-dimethylhexane by ether extraction were completely unsuccessful; cold trap isolation of the product gave an oil which was not identified. Its infra-red spectrum was not similar to that recorded for 3,4-dimethylhexane.

No definite product could be isolated from the oxidation of the thiophene (130) with alkaline potassium permanganate, potassium permanganate in acetone, or performic acid at 70°. This result was not unexpected in view of previous reports[63(c)] that no attempt to isolate a 3,4-dicarboxythiophene from oxidation of a 3,4-dialkylthiophene had yet succeeded. The thiophene was treated with N-bromosuccinimide in the hope that introduction of a further double bond would be accompanied by sulphur extrusion to give 8-thiabicyclo-[4,3,0]-nona-1(9),2,4,6-tetraene (132) which is a known compound[85]. However no trace of (132) could be detected by this procedure. Equally unsuccessful was the attempt to dehydrogenate the thiophene (130) with 10% palladium-charcoal.

Catalytic hydrogenation of the thiophene (130) proceeded rapidly with the uptake of one molecular equivalent of hydrogen to give the saturated thiophene (133). The spectral properties of this product were consistent with the β,β'-disubstituted thiophene structure (133) proposed. Thus the ultra-violet spectrum showed end absorption and λ max $\simeq$ 244 mμ with a shoulder at 250 mμ and the n.m.r. spectrum (fig 7) showed the eight methylene protons of the seven membered ring as two quartets centred on $\tau \simeq 7.35$ (adjacent to S) and $\tau = 6.80$ (adjacent to the thiophene ring), and the two thiophene α-protons as a singlet at $\tau \simeq 3.17$.

The saturated thiophene (133) was recovered unchanged after attempts at selective desulphurisation of the seven-membered ring

either with Raney nickel in acetone under reflux[70] or with alkaline hydrazine hydrate in triethylene glycol at 160° for 5 hours[71].

The interesting reactions of the diyne (124) prompted an attempt to prepare the higher ring homologue 1,8-dithiacyclotetradeca-3,5,10,12-tetrayne (134) by an analogous route. However treatment of 1,6-dichlorohexa-2,4-diyne with ammonium sulphide produced only a high yield of solid polymer from which no crystalline material could be isolated. An alternative route to the tetrayne (134) involving the cyclic coupling of dipropargyl sulphide with cupric acetate in pyridine was therefore tried. However it soon became apparent that the copper salt was complexing with the sulphide (cf.72) and the direct use of this latter in the reaction was therefore impossible. It was therefore decided to use dipropargyl sulphone (135) in the hope that the cyclic sulphone obtained by acetylenic coupling of this derivative could be reduced to the desired cyclic sulphide (134) by lithium aluminium hydride. Dipropargyl sulphone (135), prepared from the sulphide by oxidation with hydrogen peroxide in acetic acid for three days at room temperature, was subjected to a variety of coupling conditions. As tertiary bases were found to form highly coloured insoluble complexes with the diynesulphone (135), the use of the conventional cupric acetate-pyridine reagent[3,4] was precluded. A Glaser coupling[e.g. 73,74,75] of the diynesulphone (135) with an aqueous ethanolic solution of cuprous chloride and ammonium chloride

in an atmosphere of oxygen and at a variety of pH values of < 3, 7 and 8-9 resulted in the rearrangement of the propargyl groups to allenyl groups with the formation of diallenyl sulphone (136). The diynesulphone (135) was recovered unchanged after treatment with cuprous chloride and tetramethylethylenediamine[76] in the presence of oxygen. Oxidative coupling (cupric chloride) of the preformed cuprous salt of the diynesulphone (135) produced a complex product with strong allenic absorption in the infra-red.

It was felt that the extraordinary facile rearrangement of the diynesulphone (135) merited a more detailed investigation. The diynesulphone was therefore treated with a catalytic amount of potassium t-butoxide in t-butanol. The product was an oil whose spectral properties indicated the presence of diallenylsulphone (136) contaminated by the starting diynesulphone (135). Purification of the crude diallene (136) by sublimation was unsuccessful; it would not form an addition product with either cyclopentadiene or dibromocarbene. Silver nitrate was found to complex equally well with both the diallene (136) and the diynesulphone (135).

In another attempt to obtain a pure sample of the diallenyl sulphone (136) by milder basic treatment the dipropargyl sulphone (135) was heated with saturated sodium carbonate solution. In these circumstances it was rapidly converted in high yield to a crystalline product (m.p.167-168°) of molecular formula $C_6H_8SO_3$. Its structure was clearly indicated as 2,6-dimethyl-1,4-oxathiin-4,4-dioxide (137) by the following spectroscopic properties. The n.m.r.

spectrum showed a methyl group singlet (τ = 7.8) three times the total intensity of the doublet corresponding to the olefinic protons centred on τ = 3.95; the infra-red spectrum showed a strong absorption at 1673 cm^{-1} in accord with the stretching frequency expected for the double bond in (137). Hydrogenation of the oxathiin (137) over palladium-charcoal gave as main product the crystalline oxathiane (138)(m.p.104-105°) whose structure was confirmed by its n.m.r. spectrum which showed a broad multiplet centred on τ = 5.93 (two methine protons adjacent to an ethereal oxygen), a broad singlet τ = 7.11 (the four methylene protons), and the two methyl groups as a doublet at τ = 8.61 and 8.72. This oxathiane (138) has been previously prepared in a number of ways[79,80,81] e.g. by treatment of di(β-chloroisopropyl)ether with sodium sulphide followed by oxidation of the product, but its reported melting point has fluctuated between 101° and 107°. The oxathiin (137) itself had already been reported in the literature[77,78] but the quoted melting point of 119° was quite different from our finding (m.p. 167-168°). The quoted method of preparation involved the dehydration of the diketone (139) obtained by the ozonisation of 3,4-dimethylbutadienesulphone. This suggested that the supposed 'oxathiin' obtained by these authors was in fact the isomeric conjugated ketone (140) obtained by normal intramolecular aldol condensation of the diketone (139). To confirm this suspicion dipropargyl sulphone was hydrated by mercuric acetate to the diketone (139); either base or acid treatment of this product gave a

crystalline conjugated ketone (140) melting at exactly the temperature (118-119°) recorded for the supposed 'oxathiin'. No trace of the authentic oxathiin could be detected. The structure of the conjugated enone ketone (140) was confirmed by its spectral properties. The infra-red spectrum showed absorptions at 3015 ($\equiv$CH), 1692 (C=O) and 1636 cm^{-1} (C=C) and the ultra-violet spectrum had a λ max = 236 mμ (ε = 10,900). The n.m.r. spectrum showed a broad singlet at τ = 3.75 corresponding to the single vinyl proton, a doublet centred on τ = 6.08 for the four methylene protons and a singlet at τ = 7.71 for the methyl group protons. The conjugated ketone (140) formed an orange 2,4-dinitrophenylhydrazone.

The readiness of these rearrangements of dipropargyl sulphone (135) obviously stems from the powerful electron-attracting nature of the sulphone grouping which aids the removal of adjacent hydrogen atoms as protons. It would appear that under anhydrous basic conditions prototropic rearrangement takes place and an equilibrium mixture of the diynesulphone (135) and the diallenylsulphone (136) is formed. In the presence of water, it would seem that rearrangement to the diallenylsulphone (136) is followed by unilateral hydration and subsequent intramolecular cyclisation with the formation of the oxathiin (137). An analogous reaction has been reported[81] with diallylsulphone; which on treatment with mild base formed the oxathiane (138). It is certain that the formation of the oxathiin

(137) from the diynesulphone (135) does not proceed via the diketone (139) which gives the aldol condensation product (140) on similar base treatment as reported above.

Finally the synthesis of the nitrogen analogue of the diyne (124) was attempted. Following the procedure of Müller[82], a cyclic condensation between 1,4-dichlorobut-2-yne and p-toluenesulphonamide to give the bis-tosyl derivative of the diazadiyne (141), could not be achieved under either mild or vigorous reaction conditions. An alternative route to the diazadiyne (141) involved a reaction between 1,4-ditosylaminobut-2-yne (142) and 1,4-dichlorobut-2-yne, by analogy with the work of Stetter and Roos[83]. The preparation of the former compound involved the tosylation of 1,4-diaminobut-2-yne previously prepared[108] in low yield by interaction of 1,4-dichlorobut-2-yne and ammonia. To try and develop an improved route to this diamine the hydrolysis of the readily available 1,4-diphthalimidobut-2-yne was investigated. Acid hydrolysis gave phthalic acid and a product from which tosylation gave a low yield of crystalline product; however analysis showed that this was not the desired compound (142).

Hydrolysis of the 1,4-diphalimidobut-2-yne with a milder reagent, hydrazine hydrate, was therefore tried. In water or dimethylformamide as solvent the starting material was recovered unchanged. In N-methylpyrrolidone, however, the required by-product phthalhydrazide was obtained. Subsequent tosylation gave colourless

needles (m.p. 229-230°) which however proved to be the known di-p-toluenesulphonylhydrazine (m.p.[84] 219-220°). Lack of time precluded any further work on this point.

EXPERIMENTAL

1,6-Dithiacyclodeca-3,8-diyne (124).

1,4-Dichlorobut-2-yne[91] (18.0 g; 0.146 mol) was added to a stirred solution of ammonium sulphide (600 ml) prepared by saturating ammonium hydroxide solution (0.880; 300 ml) with hydrogen sulphide and adding an equal volume of ammonium hydroxide to the resulting solution. After stirring for 18 hours the reaction mixture was extracted with chloroform (× 2), and the extracts washed with water and dried ($MgSO_4$). The solvent was partially removed under vacuum (20 mm) and the solution was set aside to allow crystallisation to take place. The crude diyne (124) was obtained as almost colourless needles (3.51 g; 28.5%) which were recrystallised from a very large volume of light petroleum (b.p. 100-120°) to give 1,6-dithiacyclodeca-3,8-diyne (124) as colourless needles (2.64 g; 21.5%), decomp. above 200° without melting; m.p. 200° when placed on the block preheated to 190°. (Found: C,57.0; H, 4.65. $C_8H_8S_2$ requires C, 57.1 H, 4.8%). The mass spectrum showed predominant peaks at 167 (parent molecular ion $C_8H_7S_2^+$), 153 (loss of CH_2), 135 (loss of S), 122 (loss of CHS), 110, 91, 84, 70, 69, 58, 51, 45, 39. λ max (ethanol) end absorption (210-200 mμ) (ε = 4,800). ν max (Unicam)(KCl disc) 2225 (C ≡ C), 1404 cm^{-1} (CH_2 lowered in frequency by the adjacent sulphur atom[92]). The diyne (124) was not found sufficiently soluble in deuterochloroform, acetonitrile,

trifluoracetic acid, or liquid sulphur dioxide for n.m.r. measurements. An X-ray analysis (see discussion) was carried out by Dr. G.A. Sim.

For calculations on the Glasgow University DEUCE computer, programmes[93] devised by Dr. J.S. Rollet and Dr. J.G. Sime were employed. The electron density projection along the b axis of the diyne (124) is shown (fig. 6).

Notes

1. Chromatography over alumina of the concentrated mother liquors was not successful in providing any further pure component as t.l.c. examination of each fraction indicated the presence of a complex mixture.

2. Reaction of 1,4-dichlorobut-2-yne with 2 moles of sodium sulphide nonahydrate in N-methylpyrrolidone for 2 hours at 40° then 3 hours at room temperature furnished, with the work up described above, the diyne (124) in 0.2% yield.

3. A mixture of 1,4-dichlorobut-2-yne and sodium sulphide nonahydrate in water: ether (4:1) was vibromixed for 18 hours to produce the diyne (124) in 1.8% yield.

4. 1,4-Dichlorobut-2-yne in petrol (b.p. 60-80°) was allowed to react with ammonium sulphide solution without agitation of the two layers. The diyne (124) was isolated in 6.5% yield.

Complex formation from 1,6-dithiacyclodeca -3,8-diyne (124).

Mercuric chloride complex

A solution of mercuric chloride (35.6 mg; 0.131 m.mol) in ethanol (2 ml) was added to a hot solution of the diyne (124) (22 mg; 0.131 m.mol) in ethanol (15 ml). On cooling the mercuric chloride complex was deposited as small colourless rods (51 mg; 91%) m.p. 148-150°. (Found: C, 21.7; H, 1.7; Cl, 11.3. $C_8H_8S_2HgCl_2$ requires C, 21.85; H, 1.85; Cl, 16.1%). ν max (Unicam)(KCl disc) 1390 cm^{-1} (CH_2).

Silver nitrate complex

The diyne (124)(14 mg; 0.083 m.mol) in hot ethanol (10 ml) was added to a solution of silver nitrate (20 mg; 0.113 m.mol) in the same solvent (10 ml). A colourless precipitate (18 mg) settled immediately, decomp. without melting from 170° onwards. ν max 1360 s and 810 w cm^{-1} (NO_3^-). The insolubility of the complex precluded its further purification.

Palladium chloride complex

Dipotassium tetrachloropalladate (29 mg; 0.0895 m.mol) in hot dimethylsulphoxide (5 ml) was added to a hot solution of the diyne (124)(15 mg; 0.0895 m.mol) in the same solvent (5 ml). Addition of a few drops of water turned the solution cloudy and after three days at room temperature a black amorphous powder (49 mg) (decomp. without melting at high temperatures ca. 300°) was isolated by

centrifugation. The complex was sparingly soluble in the common organic solvents; it dissolved in warm dimethylsulphoxide but it would not recrystallise from this solvent.

Attempted complex formation between the diyne (124) and either nickel bromide or chloride gave only unchanged diyne (124).

Attempted complex formation between 1,6-dithiacyclodeca-3,8-diyne (124) and iron pentacarbonyl.

The diyne (124)(81 mg; 0.48 m.mol) in dry tetrahydrofuran (10 ml) and iron pentacarbonyl (95 mg; 0.48 m.mol) in the same solvent (10 ml) were added to a three necked flask fitted with a mercury gas-seal and condenser, and previously flushed for 2 hours with oxygen-free nitrogen. After refluxing under nitrogen for 15 hours, the solution was filtered through celite and the solvent removed at low temperatures by rotary evaporation (20 mm) to furnish yellow needles (125 mg) subliming at 195-200° without melting as found for the starting material (124). Sublimation (100°/0.1 mm) provided the pure diyne (124)(73 mg; 90%) with an infra-red spectrum identical to the starting material.

Similar treatment of the diyne (124) with a nitrogen-saturated n-heptane solution of iron enneacarbonyl gave only unchanged diyne (124).

Attempted sulphonium salt formation between 1,6-dithiacyclodeca-3,8-diyne (124) and alkyl halides

Methyl iodide:

The diyne (124)(42 mg; 0.25 m.mol) and methyl iodide (128 mg; 0.9 m.mol) in acetonitrile (ca. 5 ml) were sealed in a Carius tube and heated at 60° for 18 hours. Removal of the solvent from the resulting red solution furnished a brown oil (81 mg) which was only slightly soluble in water. Attempts to render this oil solid were unsuccessful and less vigorous reaction conditions of 3 weeks at room temperature gave a similar brown oil.

Benzyl chloride:

A solution of the diyne (124)(24 mg; 0.143 m.mol) and benzyl chloride (54 mg; 0.43 m.mol) in acetonitrile (10 ml) was left at room temperature for 6 weeks. On evaporation the diyne (124) was recovered unchanged (i.r.; m.p. properties).

1,4-Dichlorobut-2-yne:

A solution of the diyne (124)(24 mg; 0.143 m.mol) and 1,4-dichlorobut-2-yne (17.6 mg; 0.143 m.mol) in acetonitrile (5 ml) was refluxed for 12 hours. Removal of the solvent furnished the unaltered diyne (124)(i.r; m.p. properties).

1,6-Dithiacyclodeca-3,8-diyne-1,6-dioxide (126).

The diyne (124)(61 mg) was dissolved in acetic acid (60 ml) and hydrogen peroxide (30%; 0.2 ml) added. After 14 hours at room

temperature the solvent was removed to leave the disulphoxide (126) as a colourless microcrystalline solid (76 mg) in quantitative yield. ν max (Unicam)(KCl disc) 1408 m, (CH_2), 1045 vs cm^{-1} (S=O) and no sulphone bands. Recrystallisation from dimethylsulphoxide and a small amount of water gave the disulphoxide (126) as colourless microprisms, slow decomp. without melting at high temperatures (ca. 300°). (Found: C, 47.7; H, 4.75. $C_8H_8S_2O_2$ requires C, 48.0; H, 4.05%). The disulphoxide (126) was highly insoluble in the more common solvents.

1,6-Dithiacyclodeca-3,8-diyne-1,1,6,6-tetroxide (127).

The diyne (124)(202 mg) was dissolved in hot acetic acid (200 ml) and hydrogen peroxide (30%; 5 ml) added when the solution was cool. After 3 days at room temperature the disulphone (127) was found deposited as large colourless dendritic prisms (188 mg; 93%), slow decomp. without melting 240-300°. The disulphone was dissolved in hot dimethylsulphoxide and recrystallised by the addition of acetic acid. (Found: C, 41.65; H, 3.55. $C_8H_8S_2O_4$ requires C, 41.35; H, 3.45%). ν max (Unicam)(KCl disc) 2250 w (C $\equiv$ C), 1326 and 1310 s (twin) (SO_2), 1120 s cm^{-1} (SO_2).

Attempted pyrolysis of 1,6-dithiacyclodeca-3,8-diyne-1,1,6,6-tetroxide (127).

The disulphone (127)(36 mg) was pyrolysed at 225° in a U-shaped sublimation tube with liquid-air cooling at the U-bend. After

10 minutes colourless microcrystals of unchanged disulphone (127) had collected in the trap and the residual solid was black and completely decomposed.

Attempted base catalysed rearrangement of 1,6-dithiacyclodeca-3,8-diyne-1,1,6,6-tetroxide (127)

(a) The disulphone (127)(35 mg) was dissolved in dimethylsulphoxide (15 ml) and a solution of potassium t-butoxide (2.0 g) in the same solvent (2 ml) added. The solution rapidly developed a pink colouration. After 20 hours at room temperature half the reaction mixture was acidified (HCl; 6N) and extracted with chloroform (× 3) but no product was isolated. The other half was treated with ether (15 ml) but no product was precipitated. Complete evaporation of the solvent using a rotary evaporator and oil pump vacuum left a brown oil whose infra-red spectrum was poorly resolved. Attempts to extract a clean product from this sparingly soluble oil with various solvents were not successful.

(b) A solution-suspension of the disulphone (127)(62 mg) and potassium t-butoxide (3 mg) in t-butanol (20 ml) was left at 30° for 20 hours and worked up by direct evaporation of the solvent. The product, a pale brown solid, was recrystallised from dimethylsulphoxide-acetic acid to provide unchanged disulphone (127) (i.r.).

Attempted photoisomerisation of 1,6-dithiacyclodeca-3,8-diyne (124).

(a) The diyne (124)(25 mg) in light petroleum (b.p.60-80°; 100 ml) was irradiated under nitrogen, with air cooling, for 4 hours. Ultra-violet irradiation of wavelength 254 mμ was used. The product was shown to be composed solely of the diyne (124) starting material by i.r. and t.l.c. evidence.

(b) The same result as found in (a) was achieved by similar irradiation in benzene solution for 21 hours.

(c) The diyne (124) was ground to a powder and spread as a thin layer on the wall of the irradiation tube. After 18 hours, no change (i.r.; t.l.c.) was observed.

Reductive desulphurisation of 1,6-dithiacyclodeca-3,8-diyne (124)

Raney nickel[94] (prepared from nickel-aluminium alloy with reaction conditions of 1 hour at 50°) as a settled suspension (0.3 ml) in 2,2'-dimethoxydiethyl ether (2.5 ml) was placed in a test tube fitted with a gas inlet and outlet. The diyne (124)(7.2 mg) was held magnetically above the reagent in a steel capsule until the reaction vessel had been thoroughly flushed with carbon dioxide which was then absorbed by the potassium hydroxide solution (50%) of an azotometer attached to the outlet. The diyne (124) was then dropped into the Raney nickel and the reaction heated for 1 hour at 80° and the liberated gas (4.7 ml) collected in the azotometer. (Theoretical volume of n-butane, 0.96 ml; a blank showed the liberation of 4.0 ml of hydrogen from the Raney nickel in the absence of the diyne (124)). G.l.c. of

the product gas (Pye Argon analytical; 25% Apiezon L on celite; 20°) showed one peak (R.T. = 83 secs.). An authentic sample of n-butane had the same retention time and a mixture of the two samples showed only one peak (R.T. = 83 secs.). From this it was concluded that the product gas was n-butane.

Cis,cis-1,6-dithiacyclodeca-3,8-diene (128).

1,6-Dithiacyclodeca-3,8-diyne (124)(67 mg; 0.4m.mol) in ethyl acetate (20 ml) was hydrogenated over 10% palladium charcoal (670 mg). After the absorption of 1.5 molar equivalents no more hydrogen was absorbed, (see note). Filtration of the catalyst and evaporation of the solvent left a semicrystalline oil which was recrystallised from benzene-light petroleum (b.p. 40-60°) at 0° to give the cis,cis-diene (128) as colourless cubes (49 mg; 73%), subliming between 130 and 170°. The cis,cis-diene was sublimed (120°/0.1 mm) for analysis. (Found: C, 56.1; H, 6.8. $C_8H_{12}S_2$ requires C, 55.8; H, 7.0%). ν max(Unicam)(KCl disc) 3023 (C=CH), 1424 s, (CH_2); (CS_2 solution) 769 s cm^{-1} (double bond). λ max (ethanol) end absorption, and 227 mμ (ε = 2,780). The n.m.r. spectrum ($CDCl_3$)(fig 7) showed the eight methylene protons as a doublet (τ = 6.89 and 6.78; J = 6.6 c.p.s.) and the four olefinic protons as a triplet (τ = 4.60, 4.52, and 4.42; J = 4.8 and 6.0 c.p.s.) and thus confirmed the proposed cis,cis-diene structure (128).

95

Repetition of this hydrogenation in a Clauson-Kaas hydrogenator consistently showed an absorption of 1.5 molar equivalents of hydrogen. T.l.c. examination of the crude product showed, with a ceric sulphate spray, only one spot corresponding to the diene (128); examination of the plate under ultra-violet light, however, showed five additional weak intensity spots.

Attempted hydrogenation of cis,cis-1,6-dithiacyclodeca-3,8-diene (128).

The following catalysts were used in attempts to hydrogenate the diene (128) further to the saturated heterocycle. The hydrogenations were carried out in a Clauson-Kaas hydrogenator[95] with prehydrogenation of the catalyst by flushing the system with hydrogen for 2 hours prior to the addition of the diene (128).

Wt. of diene (128) mg.	Catalyst	Wt. of catalyst. mg.	Solvent	Reaction Time hrs.
4.84	10%Pd/C.	44	EtOAc	5
3.42	PtO	25	EtOAc	5
6.28	$PtO/HClO_4$	15 2 drops $HClO_4$	HOAc	5

In the three attempts shown no absorption of hydrogen was observed and the diene (128) was recovered unchanged (i.r.; t.l.c.).

Sodium-liquid ammonia reduction of 1,6-dithiacyclodeca-3,8-diyne (124).

The diyne (124)(436 mg; 2.6 m.mol) in dry tetrahydrofuran (50 ml) was added over 10 minutes to a solution of sodium (1.0 g; 43.5 m.mol) in liquid ammonia (200 ml). After 3 hours' stirring, ammonium chloride was added in excess, followed by moist ether. The ammonia was then allowed to evaporate completely and dilute hydrochloric acid was added. Extraction with ether (X3), and washing of the combined extracts with water furnished, on removal of the solvent, a brown volatile malodorous oil (126 mg). ν_{max} (film) 2950 s, 2890 s (CH_2), 1460 s, 1380 m (CH_2), 750 w cm^{-1}. A sodium fusion test indicated the presence of sulphur in the product while the absence of olefinic unsaturation was confirmed by a tetranitromethane-carbon tetrachloride test. T.l.c. (silica; benzene) examination showed only one elongated spot; however g.l.c. examination (10% Apiezon L on Embacil; 125^{o}) of a sample of the product after preliminary purification by chromatography (Woelm alumina; grade 1 neutral; benzene) indicated the presence of a complex mixture containing eight minor and two major components with retention times ranging from 1.3 to 37.9 minutes. As detailed study would have required the application of time-consuming preparative g.l.c. techniques, the process was not further examined.

Attempted synthesis of 1,6-dithiacyclodeca-3,8-diene (128).

Cis-1,4-dichlorobut-2-ene[96] (6.0 g) was stirred with a solution of ammonium sulphide (16%; 150 ml) for 18 hours. Chloroform extraction (X2), washing of the extracts and removal of the solvent furnished a pale malodorous oil (3.5 g), whose infra-red spectrum was unlike the starting dichloride or the desired diene (128). Distillation (180°/1.0 mm) gave a red oil whose t.l.c. (silica; benzene) showed one long streak without discrete spots.

Mercuric chloride complex of cis,cis-1,6-dithiacyclodeca-3,8-diene (128).

A solution of the diene (128)(33 mg; 0.192 m.mol) in hot ethanol (15 ml) was treated with an ethanolic solution (5 ml) of mercuric chloride (52 mg; 0.192 m.mol). On cooling to room temperature the bis mercuric chloride complex was deposited as colourless plates (69 mg; quantitative yield based on the mercuric chloride) decomp p.213°, preceeded by sublimation. The product was purified by sublimation (100°/1.0 mm) (Found: C, 13.5; H, 1.55; Cl, 17.75. $C_8H_{12}S_2.Hg_2Cl_4$ requires C, 13.45; H, 1.7; Cl, 19.85). ν max (Unicam)(KCl disc) no 3023 (=CH), 1424 s (CH_2), 758 s cm^{-1} (double bond).

Attempted molybdenum hexacarbonyl complex of the diene (128).

The diene (128)(23 mg; 0.132 m.mol) and molybdenum hexacarbonyl (35 mg; 0.132 m.mol) were allowed to react in nitrogen-saturated n-hexane under the conditions described for the reaction

between the diyne (124) and iron pentacarbonyl. The diene was recovered unchanged in 75% yield by sublimation of the crude product. A t.l.c. examination of the crude product (silica; benzene) showed only one spot of the same R_f value as the starting diene (128).

Attempted photoisomerisation of the diene (128).

The experimental conditions for the solid state irradiation of the diyne (124) were applied to the diene (128), which, similarly, was recovered unchanged (i.r.; t.l.c.)

1,6-Dithiacyclodeca-3,8-diene-1,1,6,6-tetroxide (129).

The diene (128)(25 mg) in acetic acid (25 ml) was treated with hydrogen peroxide (30%; 0.5 ml) and set aside at room temperature for 4 days. The dienedisulphone (129) was deposited as colourless needles (31 mg; 90%) decomp. without melting 300-310°. (Found: C, 40.6; H, 5.35. $C_8H_{12}S_2O_4$ requires C, 40.65; 5.1%). ν max (Unicam)(KCl disc) 3025 w (=CH), 1422 s (CH_2), 1325 vs and 1120 vs (SO_2), 720 vs cm^{-1} (double bond ?). The dienedisulphone (129) was soluble in warm dimethylsulphoxide but was sparingly soluble in the more common solvents.

Attempted base catalysed rearrangement of 1,6-dithiacyclodeca-3,8-diene (128).

A solution of the diene (128)(35 mg; 0.204 m.mol) in t-butanol (15 ml) was refluxed under nitrogen with a solution of potassium t-butoxide (23 mg; 0.204 m.mol) in t-butanol (2 ml). An

aliquot, on acidification and ether extraction, furnished a white solid whose infra-red and ultra-violet spectra were identical to those of the starting diene (128).

Further additions of large amounts of base and prolonged reflux periods did not induce rearrangement.

4,9-Dithiabicyclo-$[5,3,0]^{(10)}$-deca-1,2,7-triene (130).

General:

Solutions of the diyne (124) and potassium t-butoxide in t-butanol were mixed at the temperatures stated and left for a variety of reaction times. The reaction was worked up by acidification (H_2SO_4; 6N) and ether extraction and washing of the extracts with water. The crude product was then chromatographed (Woelm alumina, grade 1; benzene) and further purified, if necessary, by recrystallisation from aqueous ethanol to give the pure thiophene (130).

Expt. No.	Wt. of diyne mg.	Wt. of KO^tBu g.	T°C	Time (hrs.)	Vol. of ^tBuOH. ml.	Wt. of Crude Product mg.	Wt. of product after Al_2O_3 mg.	Wt. of product from aq. ethanol mg.	Yield %
1	23	0.5	20	6	30	27	9	1	4
2	70	1.0	25	2	20	54	29	10	14
3	70	1.0	40	1	20	57	(27)	14	20
4	22	0.25	45	0.17	10	16	—	5	25
5	192	2.04	50	0.25	225	196	117	92	47
6	228	1.18	60	0.25	145	—	122	94	41
7	322	1.67	60	0.25	200	286	207	—	64.

Notes:

(1) Only in experiment 4 was there a trace of the diyne (124)(t.l.c. evidence) in the product.

(2) Purification by chromatography was omitted in experiments 3 and 4 and in the former the crude product was sublimed (50°/0.02 mm)

(3) In experiments 2 and 3 the diyne (124) was ground in a mortar and used as a solution-suspension in t-butanol.

(4) Only in experiment 7 was freshly prepared potassium t-butoxide used; in all the others resublimed potassium t-butoxide from M.S.A. Research Corporation, Callery, P.A. was used.

4,9-Dithiabycyclo-[5,3,0]$^{(10)}$-deca-1,2,7-triene (130)

recrystallised from aqueous ethanol as short colourless needles m.p.56-57° with a strong naphthalenic odour. (Found: C, 57.0; H, 4.75. $C_8H_8S_2$ requires C, 57.1; H, 4.8%). ν max (Unicam) (CS_2 solution) 3096 w (thiophene C=CH), 3010 w (cis HC=CH), 1398 m (CH_2 lowered in frequency by the adjacent sulphur atom[92]), 797 vs and 788 vs (thiophene α-proton), 745 s cm^{-1} (HC=CH cis). λ max (ethanol) end absorption and 290 mμ (ε = 15,800).

The n.m.r. spectrum (fig 7) showed four methylenic protons (τ = 7.17 and 6.98; J = 11.4 c.p.s.(CH_2 adjacent to S) and τ = 6.81 and 6.67; J = 8.4 c.p.s. (CH_2 adjacent to the thiophene ring)), two cis vinyl protons as an AB quartet (τ = 4.30 and 4.14; J = 9.6 c.p.s. (adjacent to S) and τ = 3.63 and 3.44; J = 11.4 c.p.s. (adjacent to the thiophene ring)), and the two α-protons

of the thiophene ring as two doublets (τ = 3.31, and 3.25; J = 3.6 c.p.s. and τ = 3.12 and 3.07; J = 3.0 c.p.s.) The mass spectral break-down pattern showed strong intensity peaks at the following mass numbers:- 168 (parent molecular ion), 167, 153, 140 (loss of $-CH_2CH_2-$), 136, 135 (loss of HS), 134 (loss of H_2S), 123, 121, 97, 91, 77, 69, 65, 63, 51, 45, 39.

A test for the presence of a thiophene nucleus [63(b)] with isatin and concentrated sulphuric acid gave a positive violet colouration. The thiophene (130) did not form a mercuric chloride complex.

Attempted preparation of 4,9-Dithiabicyclo-[5,3,0]-deca-1[10],2,7-triene (130) using a variety of basic catalysts.

Ethanolic potassium hydroxide.

A solution of the diyne (124)(26 mg) and potassium hydroxide (1 g) in ethanol (20 ml) was refluxed for 2 hours. The reaction was worked up as described in the potassium t-butoxide in t-butanol experiment. An 8% yield of the thiophene (130) was achieved.

4 hours reflux of the diyne (124) in triethylamine did not produce any of the thiophene (130). No change was observed on heating a light petroleum solution of the diyne (124) for 10 minutes at 100° in the presence of potassium hydroxide pellets. The diyne (124) was refluxed in benzene with grade H alumina without change. 2 Hours' reflux of the diyne (124) with potassium t-butoxide in benzene or sodium methoxide in methanol produced no trace of the thiophene (130)

(t.l.c. examination).

Attempted Raney nickel desulphurisation of 4,9-dithiabycyclo-[5,3,0]-deca-1(10),2,7-triene (130)

(a) Attempted isolation of gaseous products.

The reaction was carried out as described for the desulphurisation of the parent diyne (124). More stringent conditions (refluxing diglyme for 0.75 hours) were employed and the gas collected was shown by g.l.c. analysis (25% Apiezon 'L' on celite; 20°) to contain no high molecular weight organic components as no peaks were observed in the trace.

(b) Attempted isolation of products by ether extraction.

The desulphurisation was carried out with Raney nickel in ethylene glycol in a sealed Carius tube for 0.5 hours at 100°, followed by 18 hours at room temperature. The tube was cooled to -80°, unsealed and the open end resealed with a serum cap. Once again no gaseous product was detected by g.l.c. Ether extraction of the reaction mixture afforded no product. Decomposition of the Raney nickel with acid (HCl; 6N) followed by ether extraction was still ineffective in securing any product.

(c) Attempted 'cold-trap' isolation of products.

The desulphurisation of the thiophene (130) with Raney nickel was carried out in triethylene glycol at 55° for three hours. At the same temperature the reaction was flushed with nitrogen for

1,5 hours and the volatile products collected in a cold trap at -80°. The infra-red spectrum of the oil product showed no resemblance to that of 3,4-dimethyhexane (A.P.I. Research Project 44 No. 664). The g.l.c. of the oil showed one peak (R.T. = 132 secs; cf n-butane with R.T. = 83 secs.). No further attempt at identification was made.

Attempted oxidation of 4,9-dithiabicyclo-[5,3,0]-deca-1(10),2,7-triene (130).

(a) Alkaline potassium permanganate.

The thiophene (130) (36 mg; 0.214 m.mol) was refluxed for 1 hour with a solution of potassium permanganate (157 mg; 1 m.mol) and sodium hydroxide (1 g) in water (7 ml). The solution was then acidified (H_2SO_4; 6N), treated with sulphur dioxide and extracted with ether (x2). The ether extracts were washed with brine (x 2) and extracted with sodium bicarbonate, and after drying and removal of the solvent furnished the unchanged thiophene (130)(26 mg). The bicarbonate extracts were neutralised and extracted with ether to provide the acidic fraction as a brown oil (14 mg) whose infra-red spectrum was characteristic of an acid. The oil could not be induced to solidify.

(b) Potassium permanganate in acetone

A solution of the thiophene (130)(26 mg) in acetone (2 ml; distilled from potassium permanganate) was refluxed for 4 hours with a solution of potassium permanganate (140 mg) in the same solvent

(3 ml). Constant ether extraction of the reaction mixture, after acidification (H_2SO_4; 6N) and treatment with sulphur dioxide, afforded a brown oil (11 mg) whose infra-red spectrum was not acidic in character and whose t.l.c. showed it to be a complex mixture.

(c) Performic acid.

A solution of the thiophene (130)(26 mg) in formic acid (4 ml) and hydrogen peroxide (30%; 5 ml) was maintained at 70-75° for 3 hours. Evaporation of the reaction mixture gave no organic product (no infra-red absorption between 1500-1300 cm^{-1}; no spots on t.l.c. examination); only inorganic peroxide stabiliser was isolated. It is conceivable that the thiophene (130) was completely oxidised to sulphur dioxide and volatile acids.

Attempted sulphur extrusion and aromatisation of 4,9-dithiabicyclo-$[5,3,0]^{(10)}$-deca-1,2,7-triene (130).

The thiophene (130)(17 mg) and N-bromosuccinimide (18 mg) were refluxed in carbon tetrachloride (10 ml) for 72 hours, using a 100 watt lamp as the heat source. Examination of the reaction mixture with t.l.c. (ceric spray and ultra-violet light) showed only the presence of the starting material.

Attempted dehydrogenation of 4,9-dithiabicyclo-[5,3,0]$^{(10)}$-deca-1,-2,7-triene (130).

The thiophene (130) was recovered unchanged after 16 hours' reflux under nitrogen with 10% palladium-charcoal in either toluene or p-cymene. Similarly no reaction occurred on heating the thiophene (130) with 10% palladium-charcoal in the absence of solvent for 1 hour at 180°. After 4 hours at 300° under the same conditions, a strong odour of hydrogen sulphide was noted on opening the Carius reaction tube. However no product could be isolated by chloroform extraction.

4,9-Dithiabicyclo-[5,3,0]$^{(10)}$-deca-1,7-diene (133)

The thiophene (130)(60 mg) in methanol (30 ml) was hydrogenated over 10% palladium-charcoal (320 mg). The theoretical volume of hydrogen (8 ml) for the saturation of one double bond was taken up in less than one minute. Filtration through celite and removal of the solvent furnished the saturated thiophene (133) (58 mg; 97%) m.p. 47-49° which recrystallised from aqueous ethanol as colourless needles m.p. 50-52°. (Found: C, 56.35; H, 5.8. $C_8H_{10}S_2$ requires C, 56.45; H, 5.9%). λ max(ethanol) end absorption, 244 mμ (ε = 5,330), and a shoulder at 250 mμ (ε = 4,060). (cf. 3,4-dimethylthiophene[63 (d)] λ max (isooctane) end absorption, 243 mμ (ε = 5,600) and a shoulder at 250 mμ (ε = 3,200).). ν max(Unicam)(crystalline film) 3085 w (thiophene =CH), 805 s and 793 s cm^{-1} (thiophene α-H). The n.m.r.

spectrum (fig 7) showed two quartets corresponding to four methylene protons adjacent to S (τ = 7.58, 7.43, 7.27, 7.21) and four methylene protons adjacent to the thiophene ring (τ = 6.90, 6.86, 6.79, 6.70) and two thiophene α-protons as a singlet (τ = 3.17).

Attempted partial desulphurisation of 4,9-dithiabycyclo-[5,3,0]-(10)deca-1,7-diene (133).[70]

(a) Raney nickel-acetone.[94]

Raney nickel (2.5 ml of suspension) was refluxed with acetone (20 ml) for 2.5 hours to render it less active. The saturated thiophene (133)(20 mg) was then added and the solution was refluxed for 10 minutes. The product obtained by filtration and evaporation was unchanged starting material. When the reaction was repeated with 1 hour's deactivation of the Raney nickel and a reaction period of 1 hour, again the saturated thiophene (133) was the only product.[71]

(b) Hydrazine hydrate-triethylene glycol.

A solution of the saturated thiophene (133)(20 mg), triethylene glycol (1 ml), hydrazine hydrate (100%; 2 drops) and potassium hydroxide (40 mg) was heated at 160° for 5 hours. Ether extraction furnished the starting compound (133)(15 mg) unchanged. (i.r.; mixed m.p.).

Attempted synthesis of 1,6-dioxacyclodeca-3,8-diyne (125).

(a) Equimolar quantities of 1,4-dichlorobut-2-yne and 1,4-dihydroxybut-2-yne in tetrahydrofuran (or water) were refluxed

in the presence of excess sodium carbonate for 2 hours. The reaction mixture was extracted with ether and the extracts washed with water and dried. Removal of the solvent furnished a brown malodorous oil whose infra-red spectrum corresponded to a mixture of the two starting materials. T.l.c. (silica; benzene) examination of the product showed the absence of any new compound.

(b) 1,4-Dihydroxybut-2-yne (1.13 g; 13.2 m.mol) was dissolved in dry pyridine (20 ml) and p-toluenesulphonyl chloride (3.25 g; 17 m.mol) added. After 1 hour at reflux temperature, the reaction mixture was acidified (HCl ; 6N) and constant chloroform extraction overnight followed by washing of the extracts with water and sodium carbonate solution gave a brown oil from which no solid could be extracted. The oil was shown by t.l.c. to contain at least six components and it was not further investigated.

Attempted synthesis of 1,8-dithiacyclotetradeca-3,5,10,12-tetrayne(134)

Glaser coupling of propargyl alcohol by the method of Cameron and Bennet[97] furnished hexa-2,4-diyne-1,6-diol which was converted, using thionyl chloride in pyridine and the conditions of Armitage and Jones,[98] to 1,6-dichlorohexa-2,4-diyne (n_D^{20} = 1.5748) in 66% yield (Armitage and Jones[98] found n_D^{20} = 1.5750, 80%).

1,6-Dichlorohexa-2,4-diyne (14 g) was added dropwise over 3 minutes to a stirred solution of ammonium sulphide (400 ml)(for preparation see diyne (124) synthesis). After 18 hours stirring at room temperature the reaction mixture was extracted with chloroform

(x 3, total 750 ml) to furnish a brown oil (1.9 g; 14%) whose infra-red spectrum was almost identical to that of the starting dichloride Filtration of the aqueous layer furnished a dark brown amorphous solid (15.3 g) which was found highly insoluble in solvents such as hot acetonitrile, hot trifluoracetic acid and hot dimethylsulphoxide. It did not melt below 320° and would not sublime (120°/10^{-7} mm). Constant chloroform extraction for 2 days gave only a low yield of the original.

Attempted coupling of dipropargyl sulphide.

Propargyl bromide (n_D^{19} = 1.4944) was prepared in 56% yield from the alcohol by treatment of the latter with phosphorus tribromide in pyridine using Kirrmann's[99] procedure. (Kirrmann n_D^{19} = 1.4942). Conversion of the bromide to dipropargyl sulphide was achieved in 60% yield by the method of Sato[100] (sodium sulphide in aqueous methanol).

Dipropargyl sulphide (635 mg) was added dropwise over 1.5 hours to a refluxing solution of cupric acetate (3.5 g) in pyridine:methanol (1:1; 160 ml). The solution was refluxed for a further 2 hours and left overnight at room temperature. Acidification (H_2SO_4; 6N) and ether extraction (x2) furnished a dark brown oil (156 mg) whose infra-red spectrum showed it to contain mainly the starting sulphide; t.l.c. examination (silica; benzene) confirmed this. The low yield of starting material was attributed to the complexing effect of the copper salt with the sulphide.

Dipropargyl sulphone (135)

Dipropargyl sulphide (1.41 g) was dissolved in acetic acid (50 ml) and hydrogen peroxide (30%; 20 ml) added. After 3 days at room temperature the solvent was removed by evaporation to leave an oil which solidified on trituration to give the diynesulphone (135) as colourless prisms (1.6 g; 88%) which recrystallised from ethanol (or water) as rods (1.43 g; 80%) m.p. 98-99° (preceeded by sublimation). (Found: C, 50.8; H, 4.4. $C_6H_6O_2S$ requires C, 50.65; H, 4.25%). λ max end absorption only. ν max(Unicam)(KCl disc) 3270 s ($\equiv$CH), 2130 m (C$\equiv$C), 1325 s and 1133 s cm^{-1} (SO_2). The n.m.r. spectrum ($CDCl_3$) showed the four methylene protons as a doublet (τ = 5.88, 5.92; J = 2.4 c.p.s.) and the acetylenic proton as a triplet (τ = 7.37, 7.41, 7.45; J = 2.4 c.p.s.).

Attempted coupling of dipropargyl sulphone (135)

(a) Glaser coupling (pH < 3)

Dipropargyl sulphone (135)(190 mg; 1.34 m.mol) in ethanol (20 ml) was added dropwise over 1.5 hours to a stirred, oxygenated, solution of cuprous chloride (670 mg; 6.7 m.mol) and ammonium chloride (1.1 g) in water (50 ml) and hydrochloric acid (6N; 1 ml). After 20 hours at room temperature the reaction mixture was neutralised with ammonium hydroxide (0.880) and extracted with ether to provide a pale yellow limpid oil (120 mg). ν max ca. 3300 w ($\equiv$CH), 1960 s and 1930 s (twin)(conjugated allene)[106], 1325 s and 1135 s cm^{-1} (SO_2). λ max end absorption and an inflexion at

250 mμ (ε = 1,750). Sublimation (50°/0.02 mm) of the crude product gave a colourless oil with the same spectral properties. T.l.c. (silica; methanol:benzene (1:4)) examination of the sublimate showed one long spot, whose 'tail' corresponded in R_f value to that of the starting diynesulphone (135).

(b) Glaser coupling (pH = 7).

Cuprous chloride (670 mg) and ammonium chloride (1.1 g) were dissolved in water and the pH of the resulting solution raised from 3 [75] to 7 by the addition of concentrated ammonium hydroxide solution. Dipropargyl sulphone (135)(190 mg) in ethanol (20 ml) and hydrogen peroxide (30%; 8 ml) was added dropwise over 1 hour with waterbath cooling of the reaction mixture. Addition of concentrated ammonium hydroxide and ether extraction gave a limpid colourless oil with spectral and t.l.c. properties similar to those found for the product from (a) above.

(c) Glaser coupling (pH = 8-9).

Cuprous chloride (670 mg) was dissolved in concentrated ammonium carbonate solution [101] (50 ml). A blue solution of pH 8-9 resulted.

Dipropargyl sulphone (135)(190 mg) in ethanol (15 ml) and hydrogen peroxide (30%; 8 ml) was added over 0.75 hours to the stirred solution which gradually darkened in colour. An aliquot, removed after the addition of the diynesulphone (135), was extracted with ether to provide an oil whose infra-red spectrum showed allenic absorption but

no acetylenic absorption. After 24 hours at room temperature the whole reaction was extracted with ether to furnish an oil (130 mg) whose infra-red spectrum showed no allenic or acetylenic absorption; it absorbed at ca. 1670 cm^{-1} and had λ max end absorption and an inflexion at 225 mμ (ε = 1,680). This oil probably contained the oxathin (137) (see later).

(c) Hay coupling[102].

Oxygen was passed through a stirred solution of N,N,N',N',-tetramethylethylenediamine (6 mg) and cuprous chloride (7 mg) in acetone (20 ml). Dipropargyl sulphone (133 mg; 0.94 m.mol) in acetone (20 ml) was added dropwise at room temperature over 2 hours. Removal of the solvent after a further 3 hours and recrystallisation of the product from ethanol furnished the unchanged diynesulphone (135) (101 mg) m.p. 98-99°(identical i.r.).

(d) Coupling of the preformed cuprous acetylide.

The cuprous salt of dipropargyl sulphone (135) was obtained as a yellow powder by the treatment of the diynesulphone (135) (221 mg) in ethanol (10 ml) with an excess of cuprous chloride in water. The cuprous acetylide was then refluxed for 18 hours with cupric chloride dihydrate (1g) in water (20 ml) and chloroform (20 ml). Chloroform extraction furnished an oil (62 mg) which showed allenic but no acetylenic absorption in the infra-red. T.l.c. (silica; methanol:benzene (1:4)) examination of the oil showed five indistinct spots.

Complex formation between dipropargyl sulphone (135) and tertiary bases.

(a) Pyridine complex.

Dipropargyl sulphone (135)(35 mg) in benzene (2 ml) was treated with pyridine (1 ml). The reaction mixture developed a red-brown colouration and after 2 hours a red amorphous precipitate had been deposited (decomp. without melting above 300°). The complex was highly insoluble in the more common solvents; it was soluble in dimethylsulphoxide at room temperature. It could not be recrystallised for analysis which, on the crude product, did not favour a 1:1, 1:2 or 2:1 complex. ν max(nujol) no ethynyl absorption, 1610 m, 1560 m, 1310 m (SO_2) and 1120 s cm^{-1} (SO_2). λ max (ethanol) end absorption and a broad shoulder from 230 to 260 mμ.

(b) Triethylamine complex.

Similarly the diynesulphone formed a yellow ochre, insoluble, amorphous complex with triethylamine. Again the infra-red spectrum showed sulphone but no acetylene absorptions and the analysis of the crude complex was not informative.

No complex formed between dipropargyl sulphide and either pyridine or triethylamine.

Potassium t-butoxide in t-butanol rearrangement of dipropargyl sulphone (135).

The diynesulphone (135) (121 mg) in dry t-butanol (5 ml) was added to a solution of potassium t-butoxide (6 mg) in the same

solvent (5 ml). A small amount of brown flocculant precipitate was immediately precipitated. Aliquots were removed at time intervals ranging from 1 minute to 1 week after the mixing of the solutions. Acidification dissolved and decolourised the brown precipitate and ether extraction furnished in all cases, an oil whose infra-red spectrum indicated the presence of allenic (1970 m and 1930 m cm^{-1}) and acetylenic (3270 m cm^{-1}) absorptions of equal intensity. After 1 week the remainder of the reaction was similarly worked up and the crude product (50%) sublimed (50°/0.05 mm) to give a mixture of the diynesulphone (135) and the diallenesulphone (136) as a colourless oil with an infra-red spectrum as quoted for the aliquots. (Found: C, 50.65; H, 4.55. $C_6H_6O_2S$ requires C, 50.65; H, 4.25%). The n.m.r. spectrum of the product indicated the presence of the isomers (135) and (136) in the ratio of about 1 to 5. The allene group was represented by a triplet corresponding to the methine proton (τ = 5.07, 5.20, 5.34; J = 6.6 c.p.s.) and an ill-defined quartet corresponding to the two methylene protons (τ = 5.98, 6.06; J = 3.0 c.p.s. and τ = 6.14, 6.21; J = 3.0 c.p.s.). The propargyl group showed as a doublet for the methylene protons (τ = 6.20, 6.25; J = 3.0 c.p.s.) and as a triplet for the acetylenic proton (τ = 7.55, 7.60, 7.65; J = 3.0 c.p.s.). (cf. the n.m.r. spectrum of pure dipropargyl sulphone (135).).

Notes.

1. Similar treatment of dipropargyl sulphide with potassium t-butoxide furnished an oil with neither ethynyl not allenyl absorption in the infra-red. The structure of this oil was not investigated.

2. Treatment of an aqueous solution of dipropargyl sulphone (135) with a saturated sodium carbonate solution at 100° for 10 minutes furnished the same allene-acetylene product mixture. However this rearrangement could be achieved only once; in all other attempts the product was the oxathiin (137)(described later).

Attempted characterisation of the crude diallenyl sulphone (136)

(a) Cyclopentadiene addition.

The impure diallenyl sulphone (136)(8 mg; 0.055 m.mol) (contaminated by dipropargyl sulphone (135)) in benzene (2 ml) was treated with cyclopentadiene (0.25 ml) and the reaction followed by measuring the intensity of the allene absorption in the infra-red. After 20 hours at room temperature or 18 hours at reflux temperature no decrease in the intensity of the allene absorption was observed.

(b) Dibromocarbene addition.[103]

The impure diallenyl sulphone (136)(221 mg) in t-butanol (5 ml) was added to a solution of potassium t-butoxide (340 mg) in t-butanol (10 ml). A dark brown suspension developed immediately. Bromoform (850 mg) was added dropwise to the ice-cold stirred solution.

After 2 hours at room temperature the reaction mixture was acidified, extracted with pentane (x 2) and the extracts washed with water (x 2) to provide an oil (60 mg) whose infra-red showed an absorption at 1750 s (C=O) and no SO_2 absorption. T.l.c. (silica; methanol: benzene (1:4)) examination of the oil showed it to be a complex mixture. Filtration of the aqueous layer, which contained an emulsion, provided a pale brown amorphous powder (134 mg) decomp. (without melting) 300-320°. ν max (nujol) 1310 s and 1120 s cm^{-1} (SO_2). The powder was found highly insoluble in the more common solvents and it was not investigated.

(c) Silver nitrate complex.

Treatment of the impure diallenyl sulphone (136) with 0.5 molar equivalents of ethanolic silver nitrate precipitated a colourless complex. The filtrate, on removal of the solvent, provided an oil whose infra-red spectrum showed acetylene (3300 cm^{-1}) and allene (1960 and 1930 cm^{-1}) absorption which was present in the initial mixture.

2,6-Dimethyl-1,4-oxathiin dioxide (137).

Dipropargyl sulphone (135)(350 mg) was dissolved in warm water (10 ml) and saturated sodium carbonate solution (15 ml) added. The solution turned yellow immediately and after 10 minutes at 100° was red. Chloroform extraction (x 5; 100 ml total) furnished the oxathiin (137) as colourless prisms (341 mg; 86%) m.p. 160-166° which recrystallised from ethanol as colourless needles (236 mg; 60%) m.p. 167-168° . (Found: C, 45.14; H, 5.4. M.W. (osmometer) 167.

$C_6H_8SO_3$ requires C, 45.0; H, 5.05% M.W. 160.). ν max(Unicam) (CCl_4) 3078 m (= CH), 1673 s (ε = 800) (C=C), 1295 s (SO_2), 1194 m (=C-O-C), 1112 s cm^{-1} (SO_2), λ max(ethanol) end absorption and inflexion at 226 mμ (ε = 1,750). T.l.c. examination (silica; methanol:benzene (1:4)) showed one pale brown spot with the same R_f value as dipropargyl sulphone (grey spot). The n.m.r. spectrum showed the two olefinic protons as a doublet (τ = 3.95, 3.96; J = 1 c.p.s.) approximately one third the total intensity of the methyl group singlet (τ = 7.81).

2,6-Dimethyl-1,4-oxathiane dioxide (138).

The oxathiin (137)(57 mg) in ethyl acetate (10 ml) was hydrogenated over 10% palladium-charcoal (50 mg). After 1 hour the absorption of hydrogen ceased. Filtration of the solution through celite and removal of the solvent furnished a mixture of colourless needles and oil (55 mg) m.p. 70-85°. T.l.c. examination of this crude product (silica; methanol: benzene (1:25)) showed two well separated spots. Recrystallisation (x3) from light petroleum gave the oxathiane (138) as colourless needles (24 mg; 40%) m.p. 104-105°. (Found: C, 44.0; H, 7.05. $C_6H_{12}SO_3$ requires C, 43.9; H, 7.35%). ν max (Unicam) (CCl_4) 1320 s (SO_2), 1256 m (=C-O-C), 1135 s cm^{-1} (SO_2). Transparent in the ultra-violet region. The n.m.r. spectrum showed a broad band (a multiplet of seven peaks) from τ = 5.78 to 6.07 centred on τ = 5.93 (methine proton adjacent to an ethereal oxygen atom), a broad singlet at τ = 7.11 (flanked by low intensity peaks at τ = 6.78, 6.92, 7.27, 7.34, and 7.50)

corresponding to the methylene protons, and a methyl group doublet (τ = 8.61, 8.72; J=6.6 c.p.s.).

Evaporation of the mother liquors of the recrystallisation of the oxathiane (138) furnished an oil with a small proportion of needles (the oxathiane (138)) still present. ν max(Unicam) (CCl_4) 1719 s (C=O), 1320 s (SO_2), 1256 m (=C-O-C), 1134 s cm^{-1} (SO_2). The structure of this oil was not investigated.

Note.

Hydrogenation of the oxathiin (137) in a Clauson-Kaas[95] hydrogenator showed the uptake of 1.6 molar equivalents of hydrogen in 2 hours, and after this time no more hydrogen was absorbed.

Diacetonyl sulphone (139).

Mercuric oxide (1.5 g; 7m.mol)) was dissolved in hot acetic acid (5 ml) and allowed to cool. Some mercuric acetate crystallised out of solution (cf. 104, 105). Dipropargyl sulphone (135)(200 mg; 1.41 m.mol) in acetic acid (5 ml) was added portionwise with water-bath cooling. After 4.5 hours reflux concentrated HCl (5 ml) was added and the solution was extracted with chloroform (x6) to furnish a brown oil (157 mg). ν max (film) 1730 s (C=O), 1325 s and 1125 s cm^{-1} (SO_2), and no ethynyl absorption. T.l.c. examination (silica; methanol:benzene(3:50)) showed predominantly one spot. The product gave a yellow 2,4-dinitrophenylhydrazone m.p. 177-182°(from ethyl acetate) which was not purified.

3-Methyl-5-thiacyclohex-2-en-1-one dioxide (140).

(a) A mixture of diacetonyl sulphone (252 mg) and p-toluenesulphonic acid (250 mg) was refluxed in benzene (20 ml) for 2 hours and left at room temperature overnight. Addition of excess sodium carbonate solution and chloroform extraction (x3) provided brown needles (94 mg) which were recrystallised from ethanol: light petroleum (1:4) to give the conjugated ketone (140) as off-white needles (60 mg; 26%) m.p. 118-119°. This product was decolourised by treatment with charcoal (in ethanol) and purified by sublimation (110°/0.1 mm) to provide colourless needles m.p. 118-119° (from ethanol:light petroleum). (Found: C, 45.55; H, 5.6. $C_6H_8SO_3$ requires C, 45.0; H, 5.05 %). ν max (Unicam)(CCl_4) 1692 s (C=O), 1636 w (C=C), and (KCl disc) 3015 m (=CH), 1322 s and 1145, 1137 s (twin) (SO_2), 848 m (trisubstituted double bond ?). cm^{-1}. λ max (ethanol) 236 mμ (ε = 10,900). The n.m.r. spectrum ($CDCl_3$) showed the vinyl proton as a broad singlet (τ = 3.75), the methylene protons as a doublet (τ = 6.05, 6.11 with fine structure at τ = 6.08) and the methyl protons as a singlet (τ = 7.71 with fine structure at τ = 7.70, 7.72). The conjugated ketone (140) gave an orange 2,4-dinitrophenylhydrazone m.p. 215-219° which was not purified.

(b) Diacetonyl sulphone (139)(40 mg) in ethanol (2 ml) was heated for 10 minutes at 100° with saturated sodium carbonate solution (2 ml). The reaction mixture was extracted with chloroform (x3)

to furnish a semi-solid which was recrystallised from ethanol: light petroleum (1:4) to give the conjugated ketone (140) as colourless needles (1.0 mg) m.p. 116-118° identical to the product from (a) (i.r.; mixed m.p. undepressed).

Attempted preparation of 1,6-ditosylaminocyclodeca-3,8-diyne.

1,4-Dichlorobut-2-yne (3.05 g; 0.025 mol) and p-toluenesulphonamide (4.27 g; 0.025 mol) in acetone (100 ml) were added dropwise over 1 hour to a stirred refluxing solution of dry potassium carbonate (34.6 g; 0.25 mol) in acetone (300 ml) under an atmosphere of nitrogen. Refluxing was continued for 3 hours and the reaction was stirred at room temperature for 3 days. The inorganic salts were removed by filtration and the filtrate evaporated to furnish a semi-solid with a strong odour of 1,4-dichlorobut-2-yne. The crude product was dissolved in hot benzene (25 ml) and unchanged (m.p.; mixed m.p.; i.r.; and t.l.c. silica; benzene-methanol (88:12)) p-toluenesulphonamide recovered by precipitation with light petroleum (b.p. 40-60°). Removal of the solvent from the filtrate furnished a malodorous yellow oil whose infra-red spectrum was similar to that of 1,4-dichlorobut-2-yne.

The same result was achieved when a reaction time of 30 hours' reflux in methylethylketone was employed.

Attempted preparation of 1,4-ditosylaminobut-2-yne (142).

(a) 1,4-Diphthalimidobut-2-yne[107] (3.81 g) was refluxed in concentrated hydrochloric acid (100 ml) and acetic acid (100 ml). After 24 hours, more of the acid mixture (1:1; 60 ml) was added and the refluxing was continued for a further 24 hours. The acetic acid was removed by evaporation and the remaining solution cooled. Phthalic acid (3.05 g; 83%) was deposited and removed by filtration. The filtrate was concentrated further to 10 ml by rotary evaporation and brought to neutrality with sodium hydroxide solution (4N). A solution of sodium hydroxide (2.0 g) in water (20 ml) and p-toluenesulphonyl chloride (4.20 g) were added and the mixture shaken at room temperature for 28 hours. Acidification (HCl; 6N) and overnight refrigeration deposited a sticky brown gum which was dried on a porous plate. The crude product was dissolved in acetone (10 ml) and the addition of light petroleum (b.p. 40-60°; 30 ml) deposited a brown oil which was not further investigated. The supernatant liquid was decanted and treated with more light petroleum (100 ml); trituration and refrigeration furnished colourless prisms (365 mg; 8%) m.p. 114-117° which were recrystallised (x3) from light petroleum-acetone to m.p. 116-117°. It was not possible, on repetition of the experiment, to obtain this crystalline material. (Found: C, 50.7; H, 4.85; N,7.05. $C_{18}H_{20}N_2S_2O_4$ requires C,55.05; H, 5.15; N, 7.14%). ν max (nujol) 3300 m (NH), 1605 w (aromatic), 1330 m and 1160 s (SO_2), 815 m cm^{-1} (aromatic). λ max (ethanol)

end absorption and 230 mμ (ε = 20,300).

A repeated analysis gave the same result and it was concluded that the product was not the desired (142).

(b) Hydrolysis of 1,4-diphthalimidobut-2-yne (5.0 g) with hydrazine hydrate (3.0 g) in N-methylpyrrolidone (200 ml) at 100° for 3.5 hours furnished a high yield of phthalhydrazide on treatment of the reaction mixture with acid (HCl; 6N). However on subsequent tosylation with tosyl chloride in 10% sodium hydroxide solution, acidification deposited ditosylhydrazine as colourless needles m.p. 229-230° and not the desired (142). (Found: C, 50.2; H, 4.85; N, 7.93. $C_{14}H_{16}S_2N_2O_4$ requires C, 49.4; H, 4.75; N, 8.25%)(Jennings[84] m.p. 219-220°.)

Attempted hydrolysis with hydrazine hydrate in either water or dimethylformamide gave unchanged starting material after a reflux period of 20 hours.

Attempted synthesis of 1,6-ditosylaminocyclodeca-3,8-diyne.

The so-called '1,4-ditosylaminobut-2-yne' (from (a) above) (232 mg; 0.59 m.mol) and 1,4-dichlorobut-2-yne (72.5 mg; 0.59 m.mol) in dimethylformamide (15 ml) were added over 1 hour to a refluxing suspension of potassium carbonate (700 mg; 5.0 m.mol) in the same solvent (15 ml). After 5 hours stirring at room temperature water was added and the resulting solution was extracted with ether (x3). The ether extracts were then washed with sodium hydroxide solution (6N) and water, dried and evaporated to give a brown semi-solid which

recrystallised from acetone (x4) as colourless rods (5 mg) m.p. 207-210°. (Found: C, 55.8; H, 5.3. $C_{22}H_{22}S_2O_4N_2$ requires C, 59.6; H, 5.0%). ν max (nujol) 1603 w (aromatic), 1325 m and 1160 s (SO_2), 815 m cm^{-1} (aromatic). λ max (ethanol) end absorption and 233 mμ (ε = 23,400).

The analytical figures of this product preclude it's possessing the desired structure.

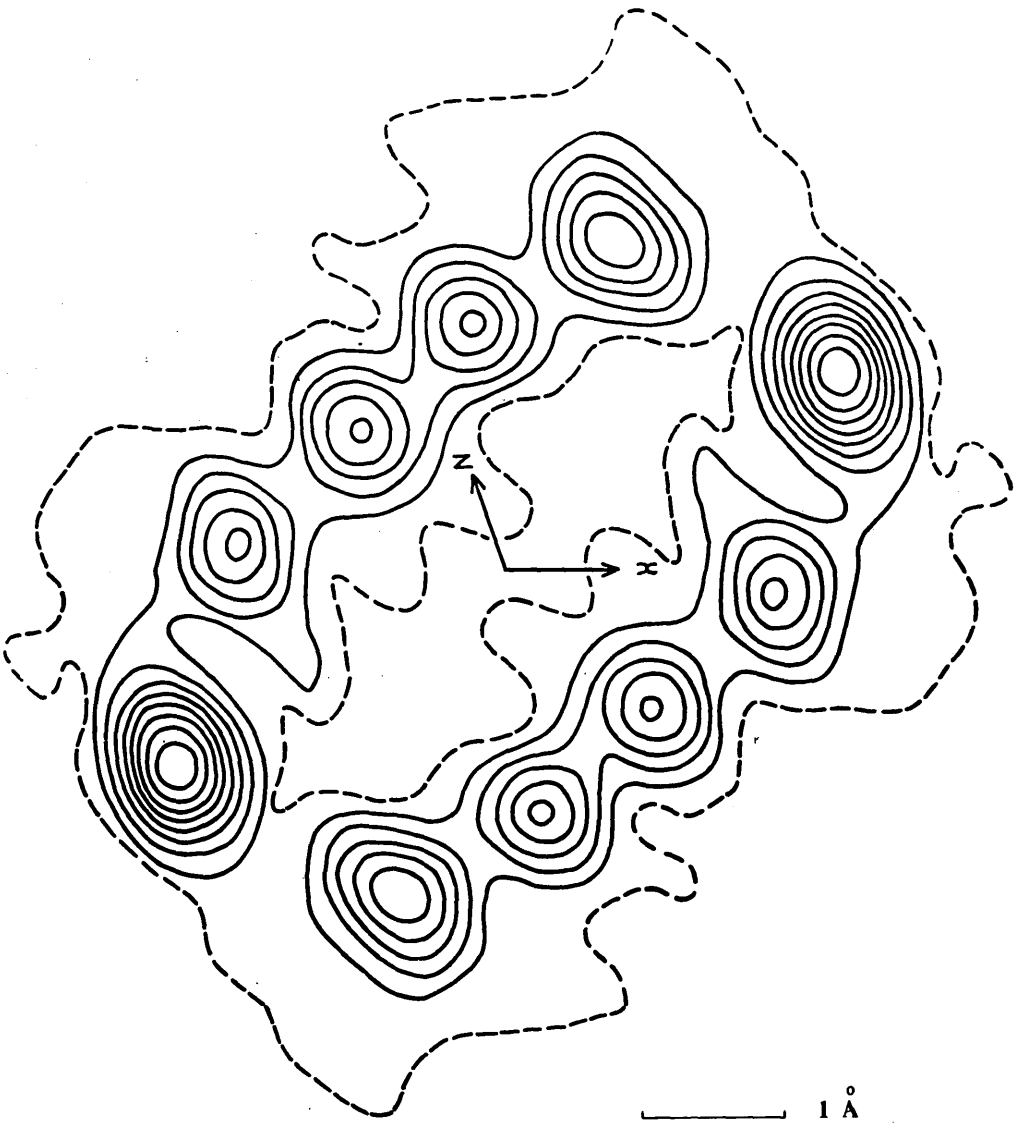
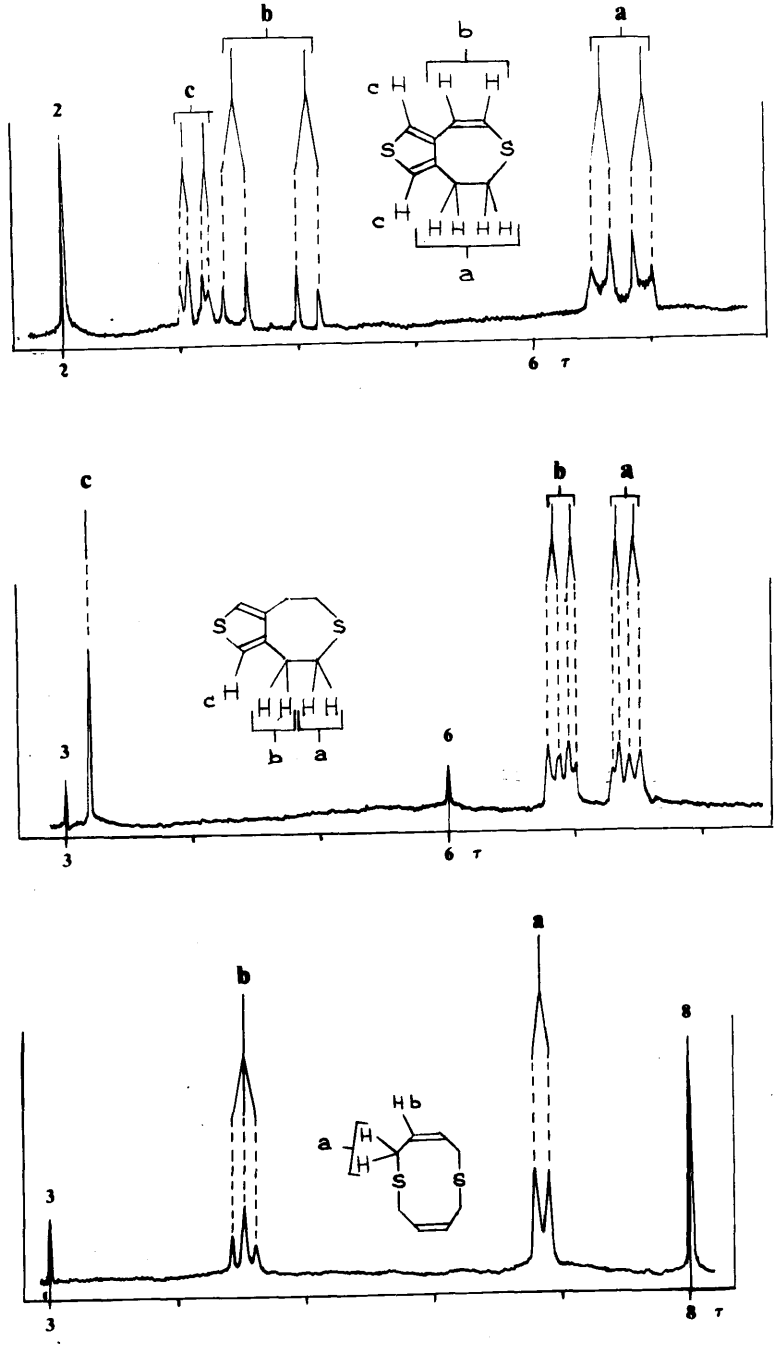


FIG. 6. Electron density projection of 1,6-dithiacyclodeca-3,8-diyne along the b-axis. Contour integral $1eA^{-2}$ except around the sulphur atoms where it is $2eA^{-2}$ above the 2-electron line. The one electron contour is broken.


b
a
c
2
b
c H
H H
S
S
c H
H H H H
a
2
6 τ
c
b a
S
S
c H
H H H H
b a
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a
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H
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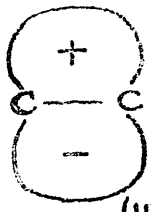
S
3
3
8
τ

FIG. 7



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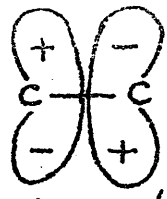
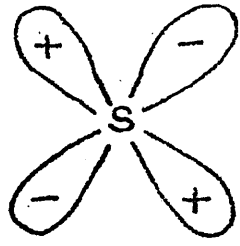


(117a)

(118)



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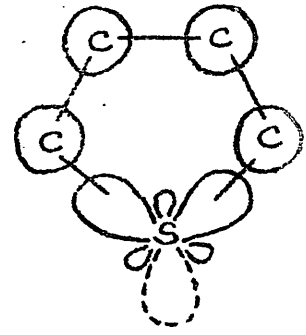

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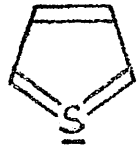

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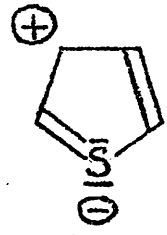

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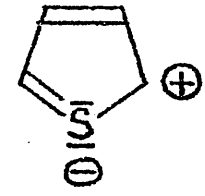

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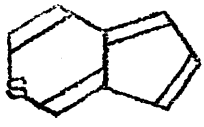

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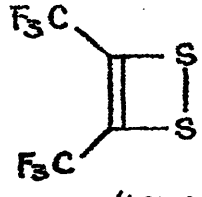

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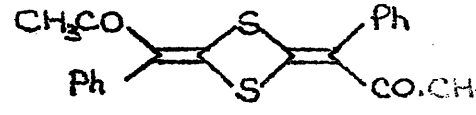

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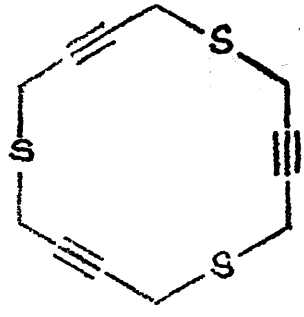

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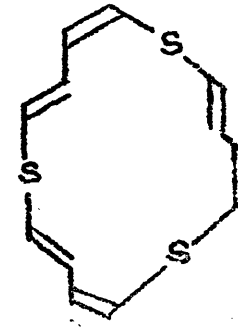

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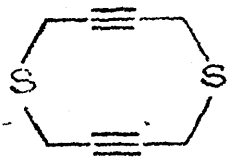

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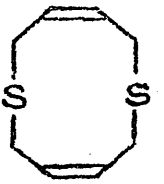

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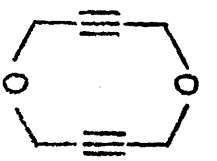

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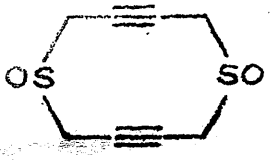

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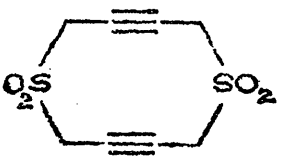

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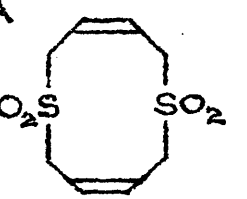

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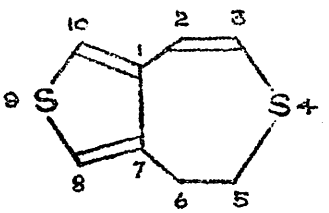

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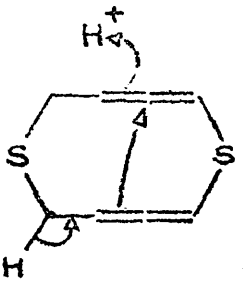

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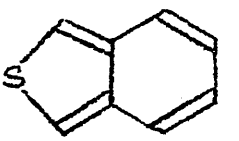

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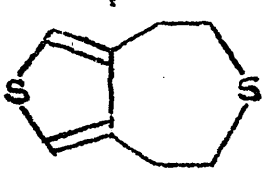

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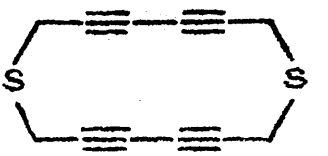
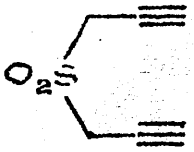
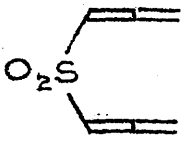


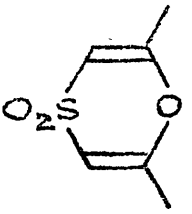
(134)



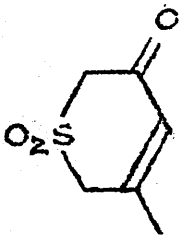
(135)



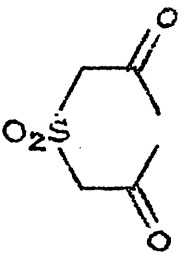
(136)



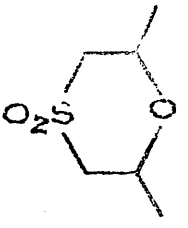
(137)



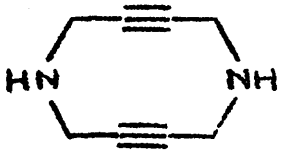
(140)



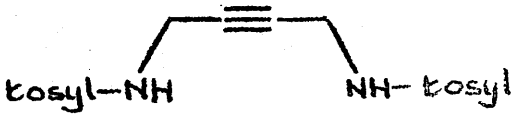
(139)



(138)



(141)



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