A THESIS

entitled

STUDIES IN AROMATIC POLYACETYLENIC MACROCYCLES

Submitted in part fulfilment of the
requirements for admittance to the Degree of

DOCTOR of PHILOSOPHY

in the

UNIVERSITY of GLASGOW

by

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TO MY PARENTS

This work, probably the only concrete evidence I can give them of all that they have done for me.

SUMMARY

This work may be divided into three closely related sections. The initial problem was to elucidate the structure of an unstable, cyclic polyyne isolated in 1957 by Eglinton and Galbraith[1] in this department. The compound has now been shown to be the cyclic 'dimer' of o-diethynylbenzene, 1,2:7,8-dibenzocyclododeca-1,7-diene-3,5,9,11-tetrayne, and is the first known highly strained acetylene. This unusual structure has been confirmed independently by the X-ray work of Grant and Speakman[2]. It should be noted that the dimers, trimers, tetramers, etc. referred to in this work are not true polymers since two atoms of hydrogen are lost in the oxidative coupling of terminal acetylenes. However, the convenience of this terminology is so great that it has been used throughout the work reported. Transannular effects were found to occur during the reduction of the dimer and several interesting products have been isolated and identified.

Second, attempts to synthesise the trimer of o-diethynylbenzene, 1,2:7,8:13,14-tribenzocyclooctadeca-1,7,13-triene-3,5,9,11,15,17-hexayne, were not successful, though the course of the work has indicated a possible route to it. During these attempts an unexpected reaction of bromophenyl acetylenes with amines was observed, and some of the products obtained were identified.

Finally, a further strained acetylene, the cyclic tetramer of o-diethynylbenzene, 1,2:7,8:13,14:19,20-tetrabenzocyclotetracosa-1,7,13,19-tetraene-3,5,9,11,15,17,21,23-octayne, has been synthesised by an unequivocal route, and its structure verified.

Ultraviolet spectra for a hitherto unknown series of aromatic polyynes are presented.

The author wishes to express his gratitude to Professor R.A. Raphael for the opportunity to carry out this research and for his guidance and close interest in this work. He is sincerely grateful to Dr. G. Eglinton for his constant help, stimulation and encouragement.

He wishes to thank Dr. J.C.D. Brand, Dr. E. Clar, and Dr. M.C. Whiting for helpful discussions. He cordially thanks Mr. J.M.L. Cameron and his staff for the micro-analyses, and Mrs F. Lawrie and Mr. F.Gisbey for the infra red measurements.

Finally he is indebted to the British Petroleum Company for a grant covering part of the period of this research, and the University of Glasgow for the award of a Demonstratorship for the remaining period.

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Copper - Catalysed Oxydative Coupling of $R - C \equiv CH$

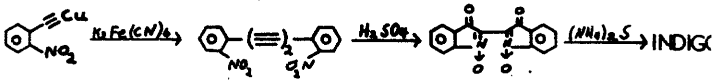
1869	Glaser	$PhC \equiv CH \longrightarrow PhC \equiv C.Cu \xrightarrow{O} Ph(C \equiv C)_2Ph$	
1882	Baeyer		
1897	Noyes and Tucker	$C_2Cu_2 \xrightarrow{CuCl_2} C_4Cu_2$	
1905	Straus	$PhC \equiv C.Cu \xrightarrow[\text{hot AcOH}]{O} PhC \equiv C.CH = CH.Ph$	
1926	Strauss and Kollek	$PhC \equiv C.Cu \xrightarrow[100^\circ]{CuCl_2} Ph(C \equiv C)_2Ph$	88%
1936/9	Zalkind *et al.*	$R.C \equiv CH \xrightarrow[O]{Cu_2Cl_2} R(C \equiv C)_2R$	
ca. 1940	Reppe	$HO.CH_2C \equiv CH \xrightarrow[O]{Cu_2Cl_2} HO.CH_2(C \equiv C)_2CH_2OH$	Industrial
1950	Sorensen *et al.*	$RC \equiv CH + HC \equiv CR' \xrightarrow[O]{Cu_2Cl_2} R(C \equiv C)_2R'$	Natural poly-ynes.
1952	Armitage, Jones, and Whiting	Improved Zalkind conditions; carbinols 80/100 %, poly-ynes.	
1953	Milas and Mageli	Cu_2Cl_2 / H_2O_2	
1955	Baxendale	Mechanism of the coupling reaction: $RC \equiv CH + 2Cu^{++} \longrightarrow 2RC \equiv C.Cu + R(C \equiv C)_2R + 4H^+$	
1956	Eglinton and Galbraith	$RC \equiv CH \xrightarrow{Cu(OAc)_2 / Py} R(C \equiv C)_2R$, cyclic diynes (high dilution).	

FIG: 1

HISTORICAL

Section 1. Oxidative Coupling.

The oxidative coupling of acetylenes to form a conjugated diyne system has been known since 1869[3]. Since that time several different methods have been developed. These have been reviewed by McCrae[4] in some detail, therefore they will only be considered in outline here, and attention will be concentrated on recent applications of these methods to the formation of cyclic polyacetylenes and some of the properties of these latter.

There are five important methods of oxidative coupling of terminal acetylenes.

a) Historically the first of these was the Glaser[3] coupling wherein the cuprous derivative of the acetylene was formed and then oxidised (usually aerially) to give the coupled product.

$$\mathrm{Ph.C{\equiv}CH} \xrightarrow{Cu^{+}} \mathrm{Ph.C{\equiv}C.Cu} \xrightarrow[\mathrm{pH\ 5\text{-}6}]{O_2} \mathrm{Ph.C{\equiv}C.C{\equiv}C.Ph.}$$

Using potassium ferricyanide as the oxidant, this method was employed by Baeyer[5] in his synthetic proof of the structure of indigo. Another variation was developed by Heilbron[6,7], Jones[8], Sorenson[9] and their coworkers, who made use of a reagent comprising an alcoholic solution of cuprous chloride, ammonium chloride, and a few drops of concentrated hydrochloric acid, to synthesise a large number of naturally occurring polyynes and polyeneynes.

b) The cupric ion oxidative coupling, based on earlier work, was developed in 1956 by Eglinton and Galbraith[10]

$$\mathrm{R.C{\equiv}CH} \xrightarrow[\mathrm{C_5H_5N/MeOH}]{\mathrm{Cu(OAc)_2}} \mathrm{R.C{\equiv}C.C{\equiv}C.R} + \mathrm{Cu.OAc} + \mathrm{H.OAc}$$

$$(\mathrm{OAc.} = \mathrm{CH_3.CO.O{-}})$$

It was found that the most favourable results were obtained by solvating the cupric ion as a complex of copper acetate with pyridine in methanol. The method has been used by its originators as well as by Bohlmann[11], Sondheimer[35], Nakagawa[13,14] and their coworkers to couple mono and diethynyl compounds. The solvent system used had several advantages in that it removed the acidic hydrogen liberated in the course of the reaction, and provided a homogeneous reaction medium not previously obtainable by other methods, the latter property making the method invaluable for the preparation of cyclic acetylenes. It is unfortunately not very suitable for the coupling of alkyl acetylenes (unless an activating group is present not too distant from the ethynyl grouping) since in this class the acetylenic hydrogen is only very slightly acidic, and the grouping reacts rather slowly; being more acidic, aryl acetylenes and conjugated alkadiynes react fairly rapidly.

The mechanism of the above oxidative coupling reactions is still not clear[15]. Klebanski[16] has postulated the following mechanism:-

$$\mathrm{R.C{\equiv}CH} \longrightarrow \mathrm{R.C{\equiv}C^-} + \mathrm{H^+}$$

$$\mathrm{R.C{\equiv}C^-} + 2\mathrm{Cu^{++}} \longrightarrow \mathrm{R.C{\equiv}C.} + \mathrm{Cu^+}$$

$$2\mathrm{R.C{\equiv}C.} \longrightarrow \mathrm{R.C{\equiv}C.C{\equiv}C.R}$$

Hay[17a] has used a cuprous complex (cuprous chloride/pyridine/oxygen) to effect the self coupling of phenylacetylene in good yield (86%). He has used this method to self couple m- and p-diethynylbenzene[17b]. The former gave a slightly soluble yellow polymer of molecular weight ca. 7000; this polymer was not cyclic as the infra red spectrum showed a band at 3290cm^{-1} (C≡CH stretch). It is an interesting measure of the intensity of this band, due to the stretching of only two bonds, that it is observable in a molecule of this size (ca. 600 carbon atoms). No cyclic compound was reported, but this was not remarkable as the high dilution procedure was not employed. When the compound was heated at 180° under vacuum, it decomposed to a black solid (probably carbon) and hydrogen and methane were evolved.

p-Diethynylbenzene was coupled by the same procedure and also gave a polymer which was completely insoluble in all solvents, and was less stable thermally than the meta- analogue.

c) Another very important advance was the Cadiot-Chodkiewicz coupling[18] which allowed the cross coupling of two different ethynyl compounds to give a single product,

$$\mathrm{R.C{\equiv}CH} + \mathrm{NaOBr} \longrightarrow \begin{array}{c} \mathrm{R.C{\equiv}CBr} \\ + \\ \mathrm{R'.C{\equiv}CH} \end{array} \xrightarrow[\mathrm{NH_2OH}]{\mathrm{CuCl,Base}} \mathrm{R.C{\equiv}C.C{\equiv}C.R'}$$

The self coupling of the bromoacetylene used was unfortunately a side reaction, but techniques have been developed to suppress it.

This coupling reaction probably takes place in two stages

$$R.C{\equiv}CH + Cu^{+} \longrightarrow R.C{\equiv}C.Cu + H^{+} \quad \ldots\ldots\ldots\ldots\ldots\ldots \text{ fast}$$

$$R.C{\equiv}CCu + Br.C{\equiv}C.R' \longrightarrow R.C{\equiv}C.C{\equiv}C.R' + CuBr \quad \ldots\ldots \text{ slow.}$$

If the temperature was too high (20°) and appreciably more than catalytic quantities (1-2%) of cuprous salt were used, then the self coupling of the bromoalkyne took place.

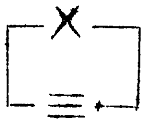
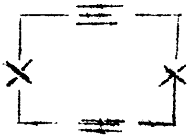
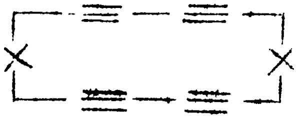
$$R'.C{\equiv}C.Br + 3Cu^{+} \longrightarrow R'.C{\equiv}C.Cu + Br^{-} + 2Cu^{++} \ldots\ldots \text{ slow}$$

$$\underline{R'.C{\equiv}C.Cu + Br.C{\equiv}C.R' \longrightarrow R'.(C{\equiv}C)_2.R' + CuBr} \quad \ldots\ldots \text{ fast}$$

$$2R'.C{\equiv}C.Br + 2Cu^{+} \longrightarrow R'.(C{\equiv}C)_2.R' + 2Br^{-} + 2Cu^{+}.$$

d) The oxidation of an acetylenic Grignard complex leads to self coupling in fair yield[19,20] (50-70%). However, this method is not satisfactory as a general preparative route as reactive substituent groups are often attacked by the Grignard reagent.

e) The coupling of acetylenic Grignards with 1-bromoalkynes using cobalt[20] ion catalyst appears to be of theoretical importance only.

1 Cyclo alkynes 	a) X = carbo-chain b) X = hetero-chain
2 Unconjugated[*] cyclo polyynes $(-X-\equiv-)_q$ i.e., q = 2 	a) X = carbo-chain b) X = hetero-chain
3 Conjugated cycloppolyynes $(-\equiv-X-\equiv-)_q$ i.e., q = 2 	a) X = carbo-chain b) X = hetero-chain

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[*] n.b. Unconjugated here is taken to mean that the acetylenic linkages are not present as conjugated polyynes.

Section 2. Cyclic Acetylenes.

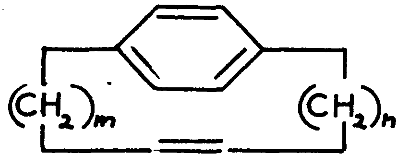
The interest which has been focussed on cyclic compounds containing one or more acetylenic linkages has from the beginning been founded on the ring strain involved, though more recent work has used them as synthetic intermediates in natural product syntheses[21,22] and in studies of aromaticity in large ring polyene systems[28-35].

Cyclic acetylenes fall into three main groups, the first two being fairly similar, i.e., those rings which contain a single isolated acetylenic link and those which contain more than one of such isolated links. The third group in which one or more αγ -diyne units are present has been the one to which most attention has been paid in the last four years, and the study of whose properties has been most rewarding.

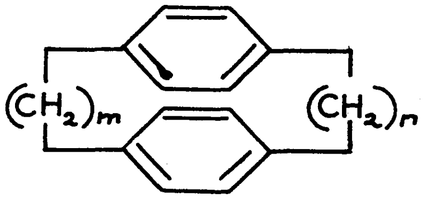
Most of the acetylenic ring systems so far have been of the carbocyclic type, in which the interacetylenic links may be alkyl, aryl, or alkaryl in nature. A small number of heterocyclic acetylenic compounds of this type have also been prepared.

The simple cycloalkynes are now very well known, and although in an earlier paper[36] in this field it was considered that it might not be possible to make a system smaller than cyclodecyne[37], cyclononyne[37] and cyclooctyne[38] have been prepared. It has been suggested that in 3,3,7,7-tetramethylcycloheptyne[39] the four methyl groups might serve in some way

A



1 a, m = n = 4
b, m = 4
n = 3



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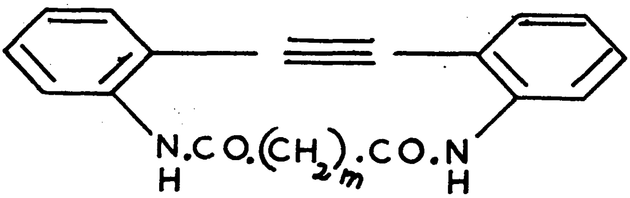
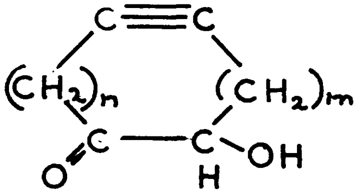
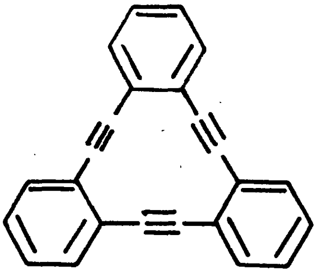


3 a → f
m = 2 → m = 7



4 a, m = 9, n = 5
b n = 9, m = 5



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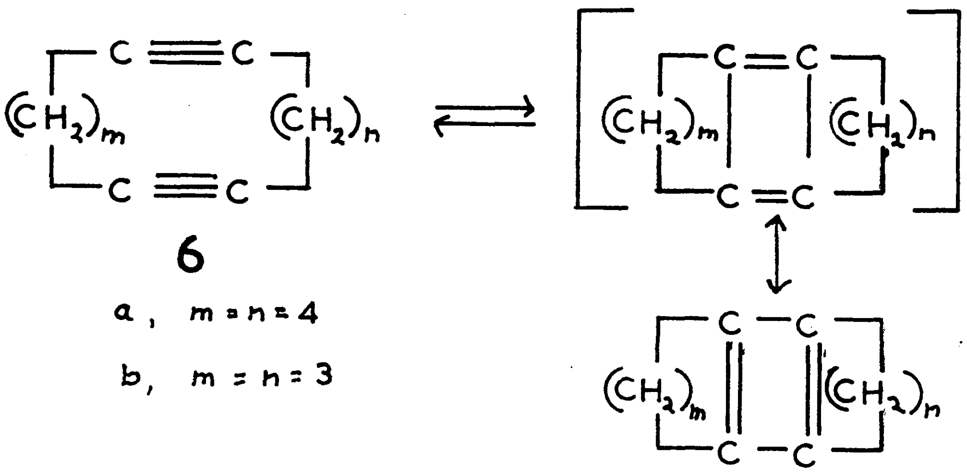


6
a, m = n = 4
b, m = n = 3

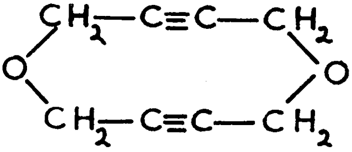
7

7′

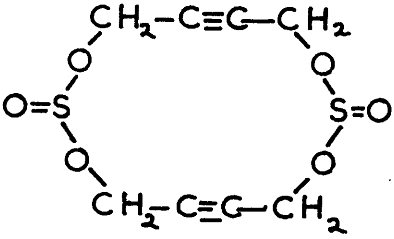
to take up the ring strain in the molecule, but neither this nor a simple cycloheptyne system has yet been prepared. Of the higher cycloalkynes, cycloundecyne[40], cyclododecyne[41], cyclopentadecyne[36], and cycloheptadecyne[36] have been formed. There are several methods of synthesis available for this general type of compound. The earliest was that due to Ruzicka[36] in which the cycloalkene was brominated in carbon disulphide solution and the product dehydrobrominated in two stages with potassium hydroxide. A variation on this theme was proposed by Domnin[42]. However, when this was applied to the synthesis of cyclodecyne by Blomquist et al.[43], they found that the desired product was contaminated by the corresponding allene. They therefore oxidised the requisite acyloin to the diketone, from which the dihydrazone was formed. Oxidation of this latter in the presence of mercuric oxide and potassium hydroxide yielded the acetylene in fair yield. A similar oxidation has more recently been carried out by Newman[109] who used silver trifluoracetate in triethylamine as the oxidant.

Cram[49] postulated that in principle it might be possible to convert two molecules of acetylene into one of cyclobutadiene, since this did not appear to involve a large amount of molecular reorganisation. The synthesis of type (2a) compounds was therefore attempted in the hope that they might isomerise to give a substituted cyclobutadiene structure(A7a). The compound(A6a) where (m=n=4) was formed via the corresponding acetylenic acyloin and no evidence of

B



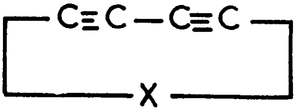
1



2

$HC\equiv C.X.C\equiv CH$

3



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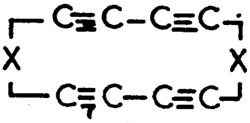

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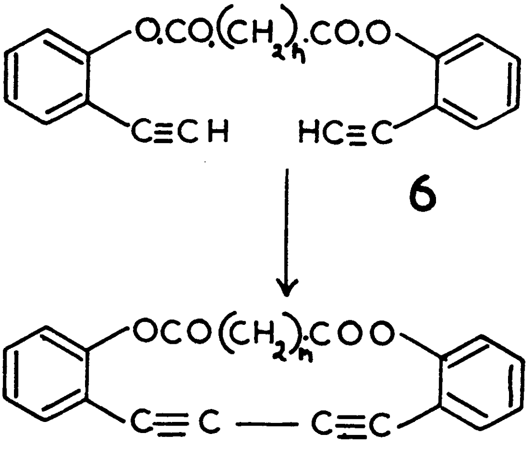
a, X = $(CH_2)_{10}$ b, X = $\{(CH_2)_2.O.CO.(CH_2)_4\}$ c, X = p-Ph.$CO_2(CH_2)_n$



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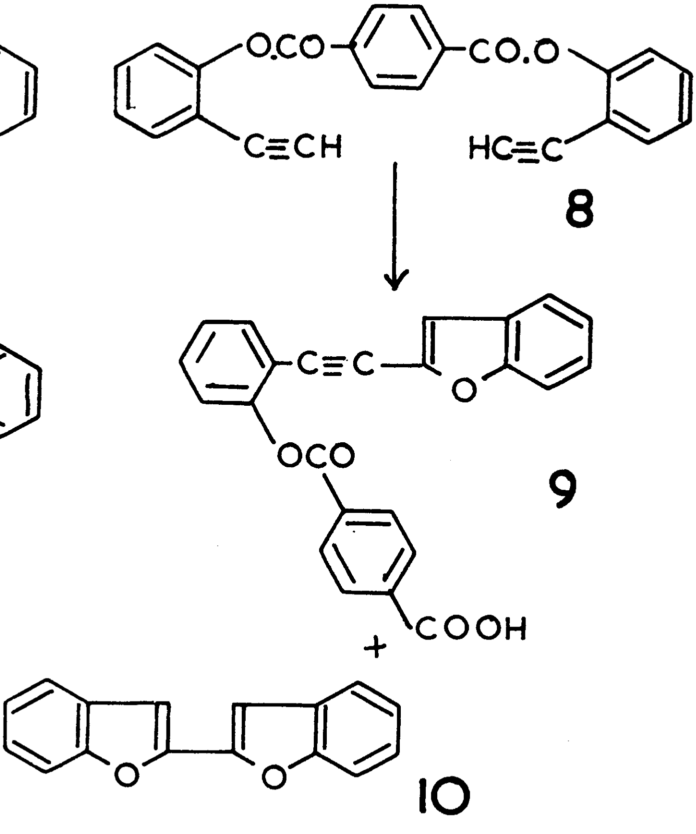
7



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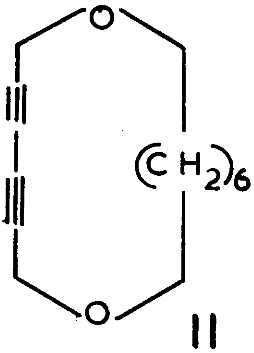
10



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rearrangement to a cyclobutadiene was found, though a by-product, 1,7,(6,4,0)-bicyclododecadiene, was isolated in which transannular reaction had taken place. An attempt to bring the acetylenic groups closer together by synthesising (A6b) where (m=n=3) was not successful since the precursor dimethyl dec-5-ynedioate did not undergo acyloin ring closure, although after partial reduction, ring closure of the ethylenic diester was achieved and the resulting acyloin converted to the corresponding enyne. Independently, Marsak[48] had prepared a cyclic acetylenic acyloin (A4), which could probably be readily converted to a diacetylene of the above type.

Cyclic αγ -diynes (3a,3b; q=1) were first described by Eglinton and Galbraith[52,53] who employed their cupric ion/pyridine complex under high dilution conditions to achieve the cyclisation of αω -diethynyl compounds. Among these were dibut-3-yn-1-yl sebacate (B3b) which gave rise to both the cyclic monomer (B4b) (3b; q=1) (63%) and the cyclic dimer (B5b)~~(3b;~~ q=2) (9%) and tetradeca-1,13-diyne (B3a) which gave the cyclic monomer (B6a) (3a; q=1) (17%), and the cyclic dimer (B5a)(3a; q=2) (30%): they were, however, unable to cyclise the ω -dipropynyl, dibutynyl, or dihexynyl terephthalates (B3c).

In the course of his studies of the transannular π-electronic effects in the paracyclophane series, Cram prepared two (1a) compounds, 5,(10)-paracyclophyne[44] and 4,(9)-paracyclophyne[45] (A1a and A1b), whose ultra violet absorption spectrum did not appear to exhibit the intensity enhancement due to transannular interaction which was found in compounds of the type (A2), where m and n are small.

Cyclic aryl compounds containing monoyne units (2a) have not yet been reported, although numerous schemes are extant in this department for the synthesis of the tribenzocyclododecatriyne (A5).

An aromatic cyclic compound containing $\alpha\gamma$ -diyne units (3a) was first reported by Eglinton and Galbraith[1] who, on the evidence then available, provisionally assigned the structure as the triangular trimer of o-diethynylbenzene (S6). The present work has shown that, in fact, it is the strained dimer (S5) in which the acetylenic bonds are bowed outwards; the tetramer (S19) in which the acetylenic bonds are probably bowed inwards is also described in this thesis. The originally postulated trimer has not yet been prepared, but two possible routes to it are discussed in a later section in this thesis. Galbraith[54] attempted unsuccessfully to synthesise 1,8-diethynylnaphthalene in order to dimerise it. The anthracene analogue, 1,8-diethynyl anthracene has recently been prepared and cyclically dimerised by Nakagawa and Akiyama[14]. It appeared to be fairly stable and decomposed to a black solid at 370° without apparent change of shape. The ultra violet absorption spectrum of this dimer is rather complex and has not yet been interpreted.

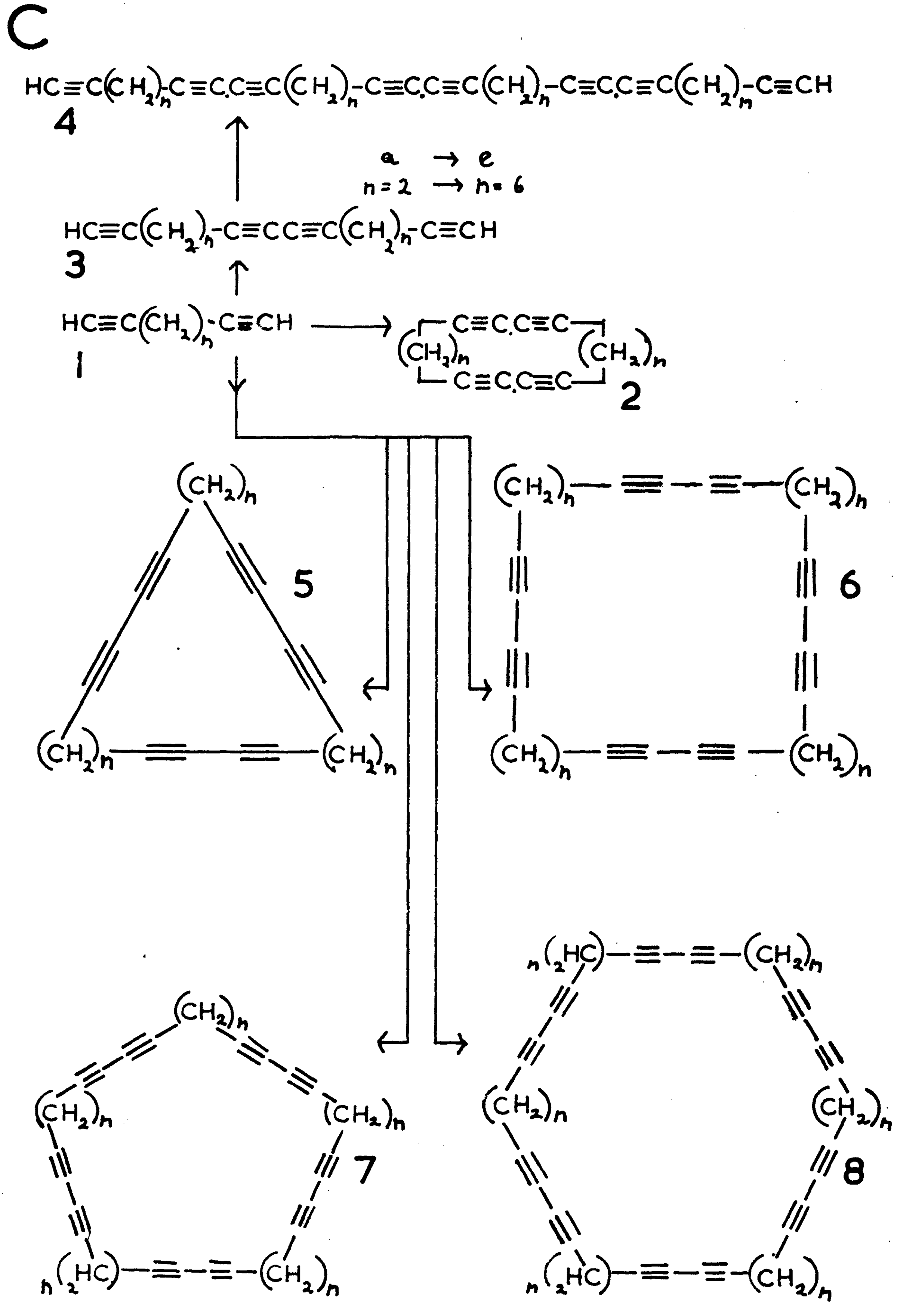
The first heterocyclic acetylene was the cyclosuccinoyldiamidotolan[46] (A3a)(lb) reported by Ruggli, who also claimed the synthesis of the glutaroyl, adipoyl, pimeloyl, suberoyl and azelaoyl (A3b-A3f) analogues[47]. Although Ruzicka[36] has not entirely accepted this claim, it has not yet been disproved. Non-conjugated heterocyclic diynes also appear to have been synthesised by Lespieau[50](B1) and Reppe[51](B2), in neither case deliberately, and the former was not well characterised.

A series of heterocyclic αγ-diynes formed by the cyclisation of di(o-diethynylphenyl)polymethylenedioates (B6)(3b;q=1;n=3,4,5,7) have recently been prepared by Nakagawa and Toda[13] using the cupric ion reaction. It is of interest to note that the strain involved was too great for the formation of a stable system where (n=2, and n=8), but in these cases compounds containing the benzofuran system were isolated. This shows some resemblance to our own work (see p.) on the cyclic dimer of o-diethynyl benzene (S5-S10) in which fluorene derivatives were isolated. Nakagawa's cyclic compound (B7)(n=3) was strained, and was highly photosensitive, becoming coated with highly coloured insoluble polymers on exposure to light (no mention was made of its thermal stability), but unlike (S5) the ultra violet absorption spectrum was not at all abnormal. In the course of the preparation of this compound, a by-product containing the benzofuran system was also formed simultaneously, 2,2'-di-benzofuran (B10). This latter compound as well as 2,(2'-dibenzofuranethynyl) phenylhydrogen terephthalate (B9) was also isolated in the attempted cyclisation of diethynylphenylterephthalate (B8); the cyclic acetylene, however, was not formed in this case. It is not clear what the actual mechanism of formation of these benzofurans is, but Nakagawa has produced evidence that it does not involve ring fission of the expected cyclic diacetylene.

Treibs and Poster[40] have synthesised a member of the unknown but-2-yn-1,4-diolpolymethyleneether series. They obtained but-2-yn-1,4-diolhexamethylene ether (B11) by a high dilution 'head to tail' cyclisation of but-2-yn-1,4-diolmono(ω-bromohexyl) ether with potassium hydroxide in dioxan. They found that the corresponding ω-bromobutyl ether could not be cyclised.

The most significant contribution, since 1956, to the field of cyclic acetylenes has been that of Sondheimer and his group who have practised acetylenic architecture on a rather impressive scale[23-35]. The work may be arbitrarily divided into three parts: the synthesis of cycloalkatetraynes (3a; q=3), the synthesis of cycloalkpolyynes (3a; q=2), and the study of poly-π electron systems obtainable therefrom.

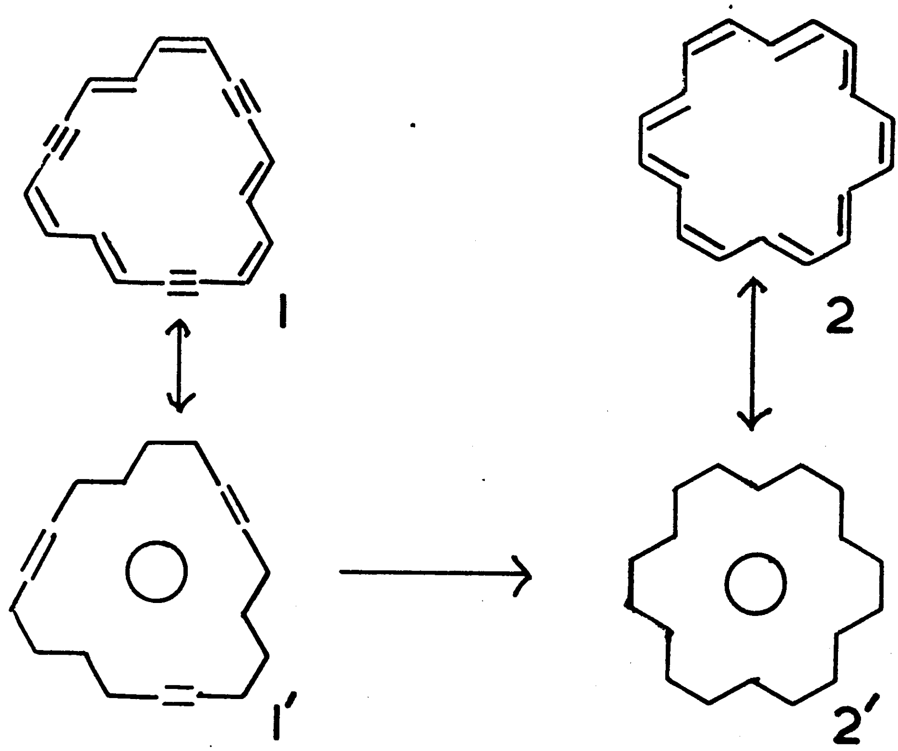
The first part was being carried out using the heterogeneous cuprous chloride/ammonium chloride/water/oxygen coupling procedure[25,26] at about the same time as the cupric acetate/pyridine method was being developed in this department.

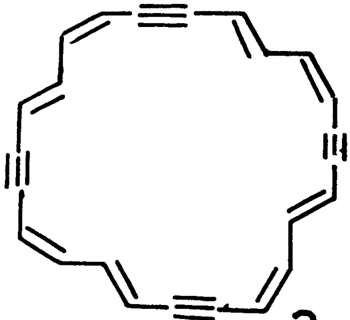

C
HC≡C(CH2)n-C≡C.C≡C(CH2)n-C≡C.C≡C(CH2)n-C≡C.C≡C(CH2)n-C≡CH
4
a → e
n=2 → n=6
HC≡C(CH2)n-C≡CC≡C(CH2)n-C≡CH
3
HC≡C(CH2)n-C≡CH
1
C≡C.C≡C
(CH2)n
(CH2)n
C≡C.C≡C
2
(CH2)n
5
6
7
8
n(2HC)

Terminal diynes (C1)(a,n=2;b,n=3;c,n=4;d,n=5;e,n=6) were coupled though (C1a and c) did not give cyclic products. (C2b) was of particular interest as it might be considered to exist in either the boat or the chair conformations. X-ray methods have shown that it existed in the latter form. As expected in this system, the intensity of the ultra violet absorption increased as the number of carbon atoms in the interacetylenic bridge decreased. This was thought to be due to interaction between the π electrons in the two diacetylenic groupings. The same phenomenon was observed by Cram[110] in those paracyclophanes which have a second paradisubstituted phenyl group in the ring lying parallel to the first.

It appeared from the study of the cyclisation of 1,7-octadiyne[25] that the cyclic dimer (C2c) was formed by more or less simultaneous coupling at both ends of the monomer rather than the internal cyclisation of the linear dimer (C3c), since the latter, on coupling yields only the linear tetramer (C4c). This was in contrast to the finding of the present work, where the linear dimer of o-diethynylbenzene (S12) formed the cyclic dimer (S5) in better yield than in the cyclisation of the monomer. We cannot, however, place too much significance on this apparent difference between the aliphatic and aromatic series, as high dilution was used in the latter case but not in the former, though the reagents were similar.

D

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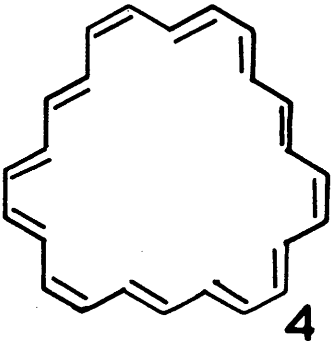
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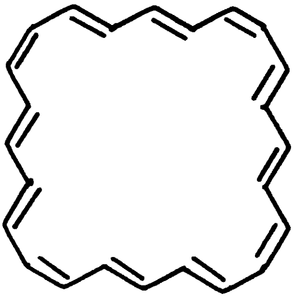
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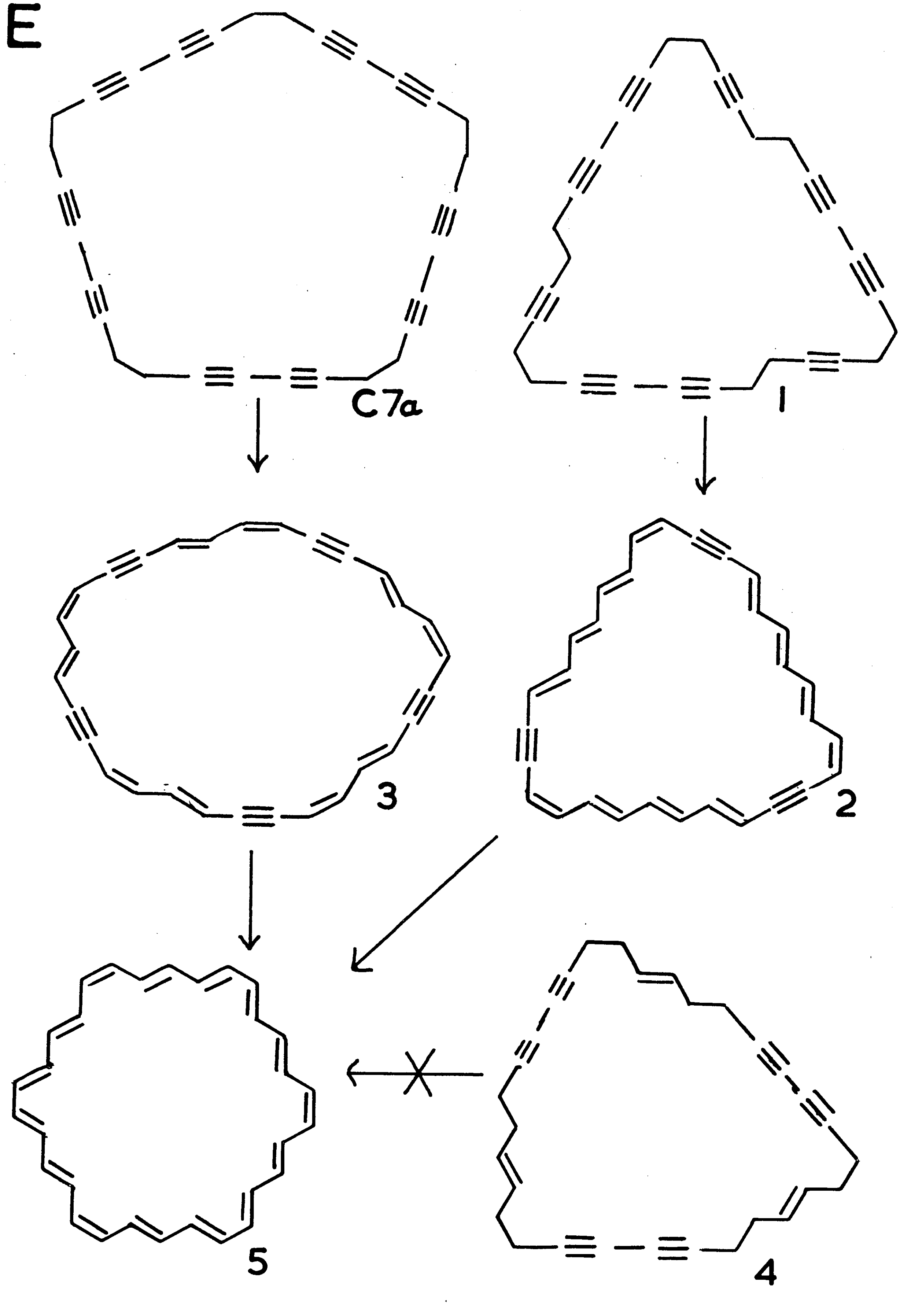
The synthesis of the cycloalkapolyynes (3a,$q>2$) was carried out in the cupric ion/pyridine/methanol medium[27,30], but not at high dilution. Terminal diynes (C5)(a,n=3;b,n=4; c,n=5;d,n=6) were merely heated under reflux in the coupling medium for periods up to three hours and the resultant mixture extracted therefrom very carefully chromatographed on alumina to give the variety of compounds shown (C2,C5 → 8). The compounds were characterised by analysis, hydrogenation and analysis and determination of the molecular weight of the hydrogenate. An argon gas/liquid chromatograph would have enabled Sondheimer's group to assess very accurately the relative proportions of the products obtained in the coupling by analysing the hydrogenate of the crude reaction product.

According to Hueckel's[55] rule for aromatic stability in cyclic molecular orbitals (4n + 2) conjugated π electrons are required. That is to say, in a fully conjugated carbocyclic system there must be 6, 10, 14, 18, 22, 26 or 30 carbon atoms. Two of such rings were available from the aforementioned synthesis, i.e., C_{18} and C_{30}. Cyclooctadecahexayne (C5a) was readily obtained from the coupling of 1,5-hexadiyne (C1a) (6%). When this was heated under reflux with potassium t-butoxide in t-butanol[28] for about half an hour, it rearranged to the hexaenetriyne (D1). It therefore followed that a prototropic shift had occurred in which each 1,5-diyne unit became a 1,3-diene-5-yne. Full hydrogenation to cyclooctadecane showed that no transannular reaction had occurred. The polyeneyne (D1) having a melting point (with decomp.) near 200°, is a reasonably stable compound, as judged by its mode of formation[29] in good yield (ca. 50%) and by the fact that it could be kept in the solid state at room temperature for several days without noticeable deterioration.

Partial hydrogenation over Lindlar catalyst yielded the polyene (D2) whose ultra violet absorption spectrum indicated a single, continuous, and therefore comparatively planar chromophoric system, and this view was supported by the X-ray evidence. Thus trans addition of hydrogen must have occurred, which was contrary to the experience that hydrogenations over Lindlar catalyst result in cis addition.

The cyclotetracosaoctayne (C6a) was synthesised, similarly treated and rearranged[33] to give the octaenetetrayne (D3); this was partially hydrogenated over Lindlar catalyst to give a cyclic dodecaene (probably the more stable isomer (D4), since it could not be rearranged by boiling in benzene with iodine; this postulate was supported by the nature of the ultraviolet absorption spectrum). This compound (D4) is a 24 π electron system and does not conform to Hueckel's rule. It was much less stable than the nonaene (D2) both in the solid state (99% destroyed at room temperature in 24 hours) and in solution, while the latter compound (D2) was almost unchanged under these conditions, thus


E
C7a
1
3
2
5
4

lending prima facie support to Hueckel's rule. However, very recent molecular orbital calculations on the ultra violet spectral data of (D2) have shown that the double bonds exist as separate entities rather than in a resonating system. The similarity of the spectrum of (D2) to the linear analogue [111] prepared by Bohlmann appears to indicate that in such an extensive cyclic conjugated system, the individual double bonds do not seem to "know" whether they are in a cyclic or linear system.

Experiments[34,35] in the C_{30} ring system, which were intended to show support for Hueckel's rule do not, in fact, do so unequivocally. The C_{30} decayne (C7a) was the pentamer obtained in the coupling of 1,5-hexadiyne, and the nonayne (E1) was similarly obtained as the trimer of 1,5,9-decatriyne; these on alkaline rearrangement gave the fully conjugated systems (E3) and (E2). Both of these are Hueckel systems and were found to be fairly stable, both in the solid state and in solution. According to precedent in this series, partial hydrogenation over Lindlar catalyst of both (E3) and (E2) should have given the same fully conjugated pentadecaene (E5), which has been described[56] as the smallest possible fully conjugated polyene with aromatic properties, as the degree of proximity which exists between every 'internal' hydrogen atom in cyclooctadecanonaene (D2) exists only between every alternate 'internal' hydrogen in (E5).

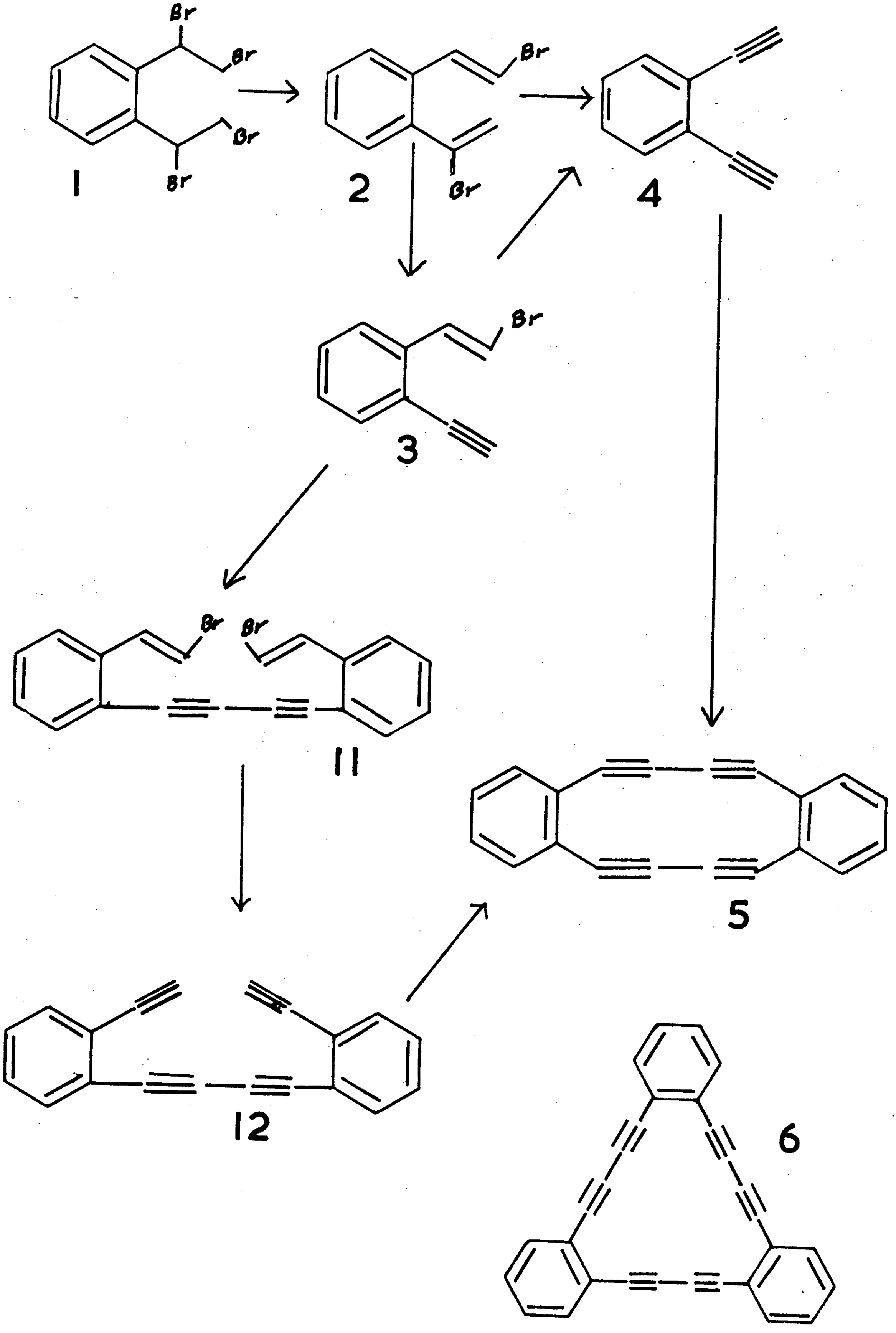
Such reduction did in fact give apparently the same compound, which was extremely unstable both in the solid state and in solution.

Attempts to form (E5) by alkaline rearrangement of the cyclotriacontatrienehexayne (E4) were quite unsuccessful even though, under similar conditions, the corresponding open chain polyeneyne rearranged readily.

Although the possibility does exist that the compound formed was not (E5) but a non planar stereoisomer, the evidence tends to suggest that it was not an aromatic system and thus does not fit in with Hueckel's rule.

Sondheimer has thus shown that polyacetylenic macrocycles can be synthesised which can be rearranged and reduced to give fully conjugated cyclic systems. It was found, however, that Hueckel's predictions do not hold in most of these cases. The route also provides a convenient method of synthesising large saturated aliphatic rings.

S



DISCUSSION.

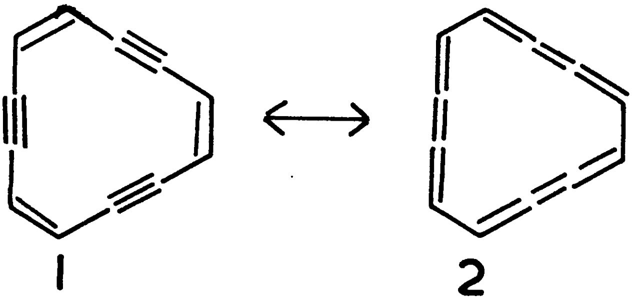
PART A : The synthesis and structure of the 'dimer' 1,2:7,8-dibenzocyclododeca-1,7-diene-3,5,9,11-tetrayne.

The development of the high-dilution oxidative coupling technique by Eglinton and Galbraith[10] made feasible the synthesis of novel conjugated polyacetylenic systems. Long before this Sworski[52] had suggested that a trienetriyne system (F1) might be capable of existence in a resonance stabilised cumulene form (F2). A similar argument would presumably apply to a compound containing an $\alpha\gamma$ -diyne unit in each arm. The system might be further stabilised both sterically and electronically by the presence of a benzo group at each apex. Such a compound (S6) should be rigid, planar, and stable, and a study of its bond lengths and spectroscopic properties would be of considerable interest. Eglinton and Galbraith therefore attempted its synthesis by the "trimerisation" of o-diethynylbenzene by oxidative coupling using the high dilution method, it being postulated that the monomer would impose its own rigidity on any polymer it formed, and the most favoured of such cyclic units would be the trimer.

Section 1. The preparation of o-diethynylbenzene and the problems relating thereto.

o-Diethynylbenzene had been made by Deluchat[12] from the tetrabromide (S1) of o-divinylbenzene by treatment with

F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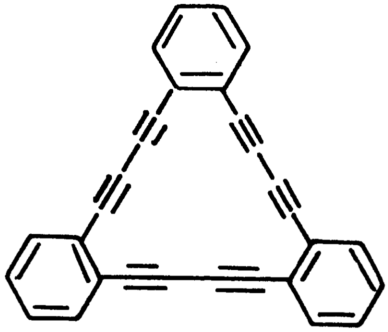
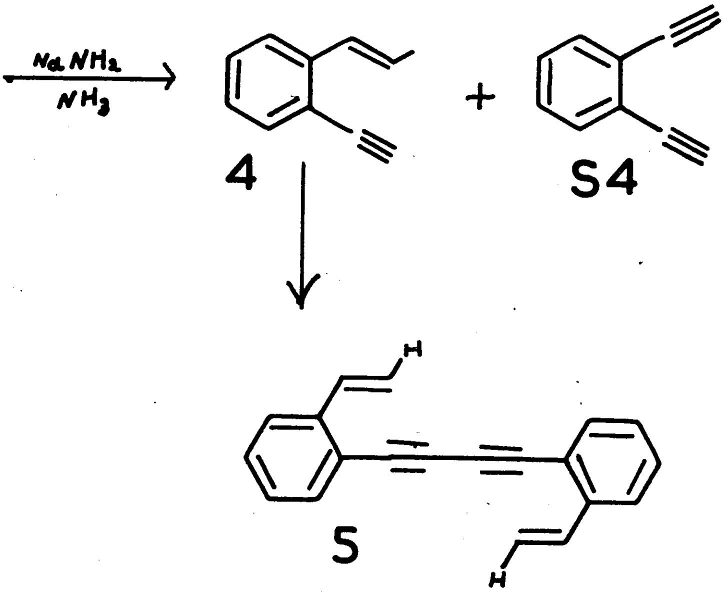
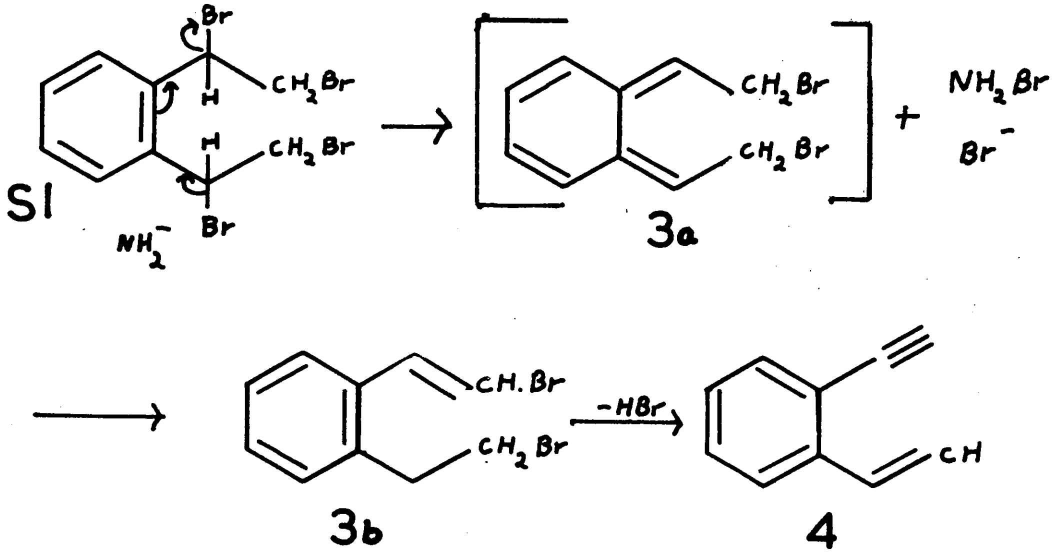
2



S6


NaNH2
NH3
4
+
S4
H
5
H


Br
H
CH2Br
H
CH2Br
Br
S1
NH2−
CH2Br
CH2Br
3a
+
NH2Br
Br−
CH.Br
CH2Br
−HBr
CH
3b
4

sodium ethoxide, which gave a mixture containing the desired product as well as the dienedibromide (S2) and the enebromyne (S3) together with polymeric material, while potassium ethoxide gave mainly naphthalene. This was considered to be rather unsatisfactory as a preparative route, particularly as the yields obtained were only of the order of 10%.

The first approaches to improve the yield were made by Galbraith. Firstly a better route to the tetrabromide (S1) due to Halford and Weissmann[57] was used, and secondly attempts were made to improve the dehydrobromination procedure.

Dehydrobromination of the tetrabromide (S1) with sodamide in liquid ammonia gave[54] a mixture of hydrocarbons (S4) and (F4): on coupling only the dienediyne (F5) could be isolated. Attempts to separate the eneyne (F4) from the diethynylbenzene by various methods were unsuccessful. Anomalous reactions of sodamide in liquid ammonia of this type are known[58]. Bourguel[59] showed that the treatment of αα-dibromoethylbenzene with sodamide in toluene-petrol gave styrene as well as phenyl acetylene. The formation of the eneyne may be rationalised by the postulate that two α-bromines on the tetrabromide were removed by 1:4 elimination followed by rearomatisation and simple 1:2 elimination (F3a) - (F4).

Yields of o-diethynylbenzene of the order of 50%

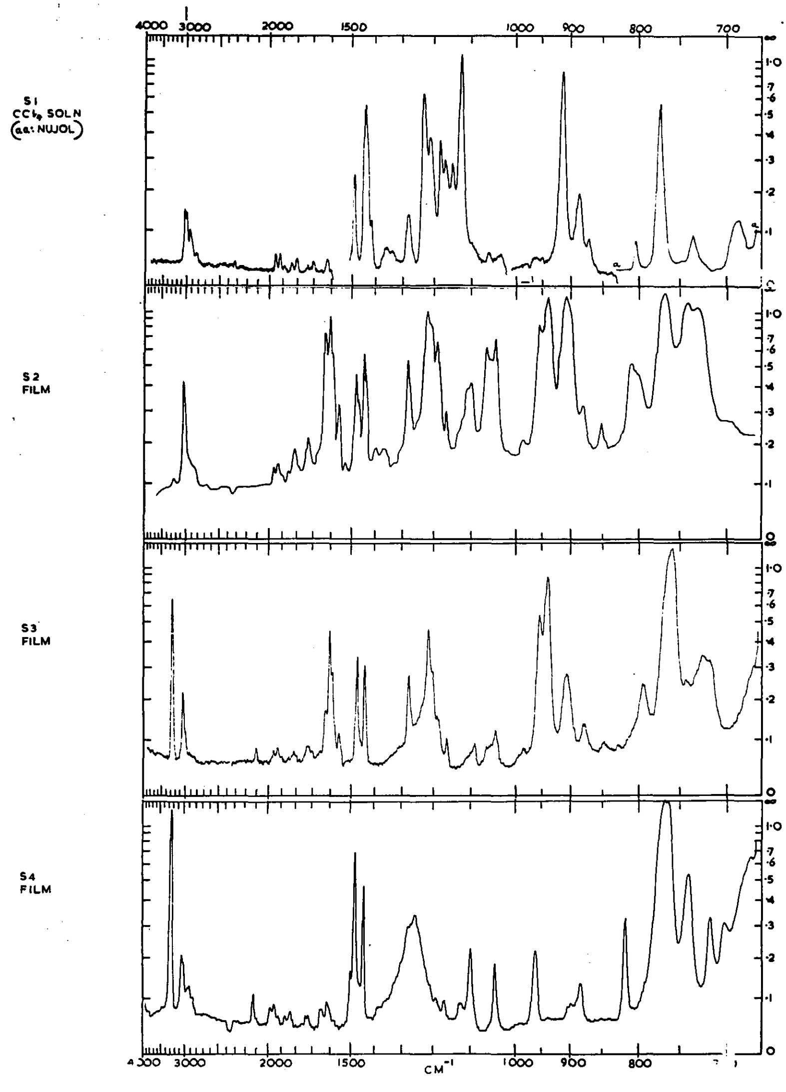

S1
CCl4 SOLN
(a.a: NUJOL)
S2
FILM
S3
FILM
S4
FILM
4000
3000
2000
1500
1000
900
800
700
CM⁻¹
1·0
·7
·6
·5
·4
·3
·2
·1
0
∞

FIG. 2

were obtained by carrying out the dehydrobromination using excess potassium t-butoxide in t-butanol, and heating under reflux for several hours.

Some of the infra red absorption spectra obtained by Galbraith during preliminary experiments with this reagent warranted a closer investigation of the course of the dehydrobromination and at least a qualitative survey of the rates of reaction of the various stages.

It was found that the reaction proceeded in three stages which could be carried out as discrete reactions. The first stage was the elimination of two moles of hydrogen bromide from the tetrabromide (S1). A stoichiometric amount (2 moles) of potassium t-butoxide in t-butanol was added to tetrabromide (S1) in dioxan. The reaction was exothermic and was apparently fast as a white precipitate of potassium bromide was deposited almost immediately; the optimum temperature was found to be ca. 7°. The product was examined by infra red and by gas liquid chromatography. The latter showed that the product was the diene dibromide (S2) of more than 90% purity, the contaminants being unchanged tetrabromide (S1), together with bromoeneyne (S3) and diyne (S4). The last two were identified in later experiments, and tended to constitute a larger proportion of the product as the reaction temperature rose. There were a number of significant features to be observed in the infra red absorption spectrum.

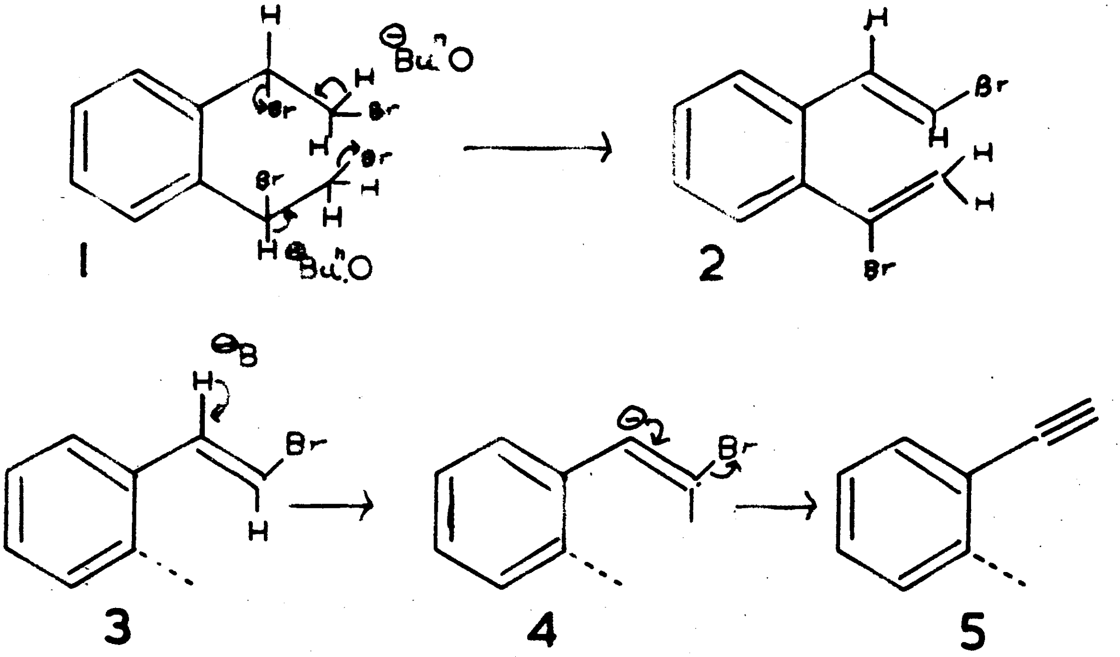
There was a total absence of bands due to ethynyl absorption (3300 cm^{-1}), the peak at 1620 cm^{-1} indicated a <u>trans</u> double bond and the two strong peaks at 935 and 901 cm^{-1} were readily assigned to trans C=CHBr[60,61], and $C=CH_2$ respectively. The product was thus the asymmetrically substituted dienedibromide (S2).

When first observed the 935 and 901 cm^{-1} bands were thought to be due to two separate compounds; however, the single major peak found in gas liquid chromatography showed that this was not the case.

In (S1) the α-hydrogens are more acidic than the β-hydrogens due to their position vicinal to the benzene ring, and for similar reasons the α-bromines are more labile than those in the β-position. Hence it was not possible to predict which way the first two moles of hydrogen bromide would undergo elimination, since <u>trans</u> elimination is possible in either case. The asymmetric elimination which did take place was probably due to steric factors which permitted attack on one α-hydrogen by only one of the bulky t-butoxide groups, thus forcing attack on the β-hydrogen of the other side chain (C1) - (C2).

The removal of the third mole of hydrogen bromide was effected by heating (S2) under reflux with a stoichiometric amount (1 mole) of potassium t-butoxide in t-butanol. (In a preliminary experiment the dienedibromide (S2) had been

G



shaken with the basic solution for half an hour at room temperature. The reaction was assayed titrimetrically and found to be only 15% complete. This reaction is therefore rather slow at room temperature but rapid at ca. 90°). Gas liquid chromatography showed the product to be the bromoeneyne (S3) of 90% purity, the contaminants being diethynylbenzene and unchanged starting material. Infra red absorption showed the expected ethynyl band at 3260 cm^{-1} and the *trans* C=CHBr band at 934 cm^{-1} (with only a trace at 901 cm^{-1}). Thus the elimination in this case had gone as was predicted, since only the remaining α-bromine can be removed by the ready *trans* elimination which is a one stage process and requires less energy than the two stage *cis* elimination which would be needed to remove the β-bromine (G3 ⟶ G5).

In order to remove this remaining hydrogen bromide it was found necessary to heat under reflux for two to four hours with potassium t-butoxide in benzene with particularly vigorous stirring. This reaction can only proceed by *cis* elimination (G3 - G5). In the actual large scale synthesis of o-diethynyl benzene, this procedure was used to remove two moles of hydrogen bromide from the dienedibromide (S2).

Section 2. The synthesis of (S5) and X-ray proof of structure.

The o-diethynylbenzene was coupled under high dilution according to Eglinton and Galbraith's[10] method, and a product identical to that previously obtained was isolated. When this compound was first obtained it was expected that it would have the trimeric structure (S6). Since it was rather unstable, it was thought that chemical structural determination would prove lengthy and difficult; in the eventuality a correct assumption. At that time (Summer 1957) no direct method of molecular weight determination was available, as the compound decomposed under ebullioscopic conditions, exploded on being ground for Rast determination, and was too insoluble to give rise to significant temperature changes in cryoscopic methods. Three possible structures were considered, a noncyclic polymer, the cyclic dimer (S5), and the cyclic trimer (S6).

The first was immediately rejected because of the total absence of ethynyl absorption near 3300 cm^{-1}. The possibility that an eneyne rather than a diyne linkage was formed by the coupling was improbable in view of the conditions employed[62]; furthermore, the infra red absorption spectrum gave no indication of such a structural feature.

The infra red spectrum (Fig. 3) of the hydrocarbon clearly demonstrates the presence of the o-disubstituted

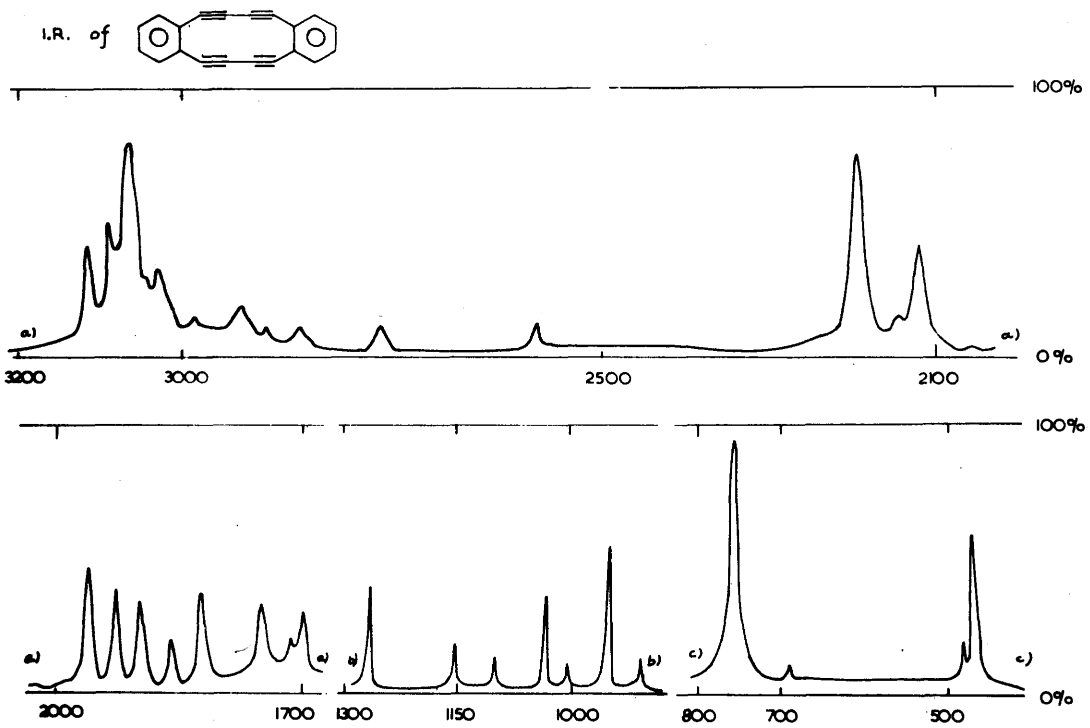


FIG: 3

a) 8.15 x 10^{-3} M. Soln. in CCl_4 , 20 mm. path (NaCl/ grating)
b) 2.14 x 10^{-2} M. Soln. in CS_2 , 2 mm. path ('')
c) 3.80 x 10^{-3} M. Soln. in CS_2 , 2 mm. path (KBr).

benzene rings, there being only a single intense peak (753 cm^{-1}, $\Delta^{a}_{\nu\frac{1}{2}}$ = 3.5 cm^{-1}, ε = 1530) in the 750 cm^{-1} region. Under similar conditions, 1,2-diethynylbenzene (S4) o-xylene and tetralin had absorption maxima at 756 (Δ^{a}_{ν} = 5 cm^{-1}, ε = 564), 741 ($\Delta^{a}_{\nu\frac{1}{2}}$ = 4 cm^{-1}, ε = 495) and 742 ($\Delta^{a}_{\nu\frac{1}{2}}$ = 5 cm^{-1}, ε = 356) cm^{-1} respectively. There are four relatively weak (ε = 10-50) bands at 1270, 1163, 1109 and 1035 cm^{-1} which probably correspond to the in-plane C-H bending modes[63], the triply bonded carbon atoms being classified as weak acceptors. The pattern in the 1700-2000 cm^{-1} region, like the rest of the spectrum, is unusually simple and probably reflects the symmetry of the molecule; most of the peaks are readily accountable as summation bands of the out of plane C-H deformations at 1005, 947, 910 and 753 cm^{-1} [64]. The main C-H stretching band at 3063 cm^{-1} is accompanied by several weaker peaks, which are probably combination bands (reference 65, page 65). The twin peaks at 2187 cm^{-1} ($\Delta^{a}_{\nu\frac{1}{2}}$ = 11 cm^{-1}, ε = 36) and at 2116 cm^{-1} ($\Delta^{a}_{\nu\frac{1}{2}}$ = 14 cm^{-1}, ε = 14) must originate from the diyne systems. Their intensities are unusual, the peak at 2187 cm^{-1} having almost the same ε as the ν_{C-H} at 3063 cm^{-1}, whereas diphenyldiacetylene absorbs only weakly at 2216 ($\Delta^{a}_{\nu\frac{1}{2}}\sim$ 25 cm^{-1}, $\varepsilon\sim$ 3) and 2147 cm^{-1} ($\Delta^{a}_{\nu\frac{1}{2}}$ $\sim$ 20, $\varepsilon\sim$ 4). This left only a cyclic structure of which (S5) and (S6) were the first members. At a later date the cyclic nature

X-Ray Data

Original cell dimensions (Å) a = 28.3, b = 3.84, c= 11.45, β = 90°

volume = 1244 Å^3

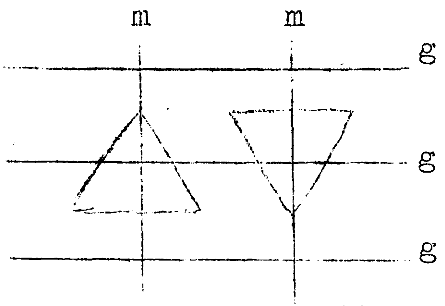
Final " " (Å) a = 28.3, b = 3.87, c = 11.5, β = 90°

volume = 1260 Å^3

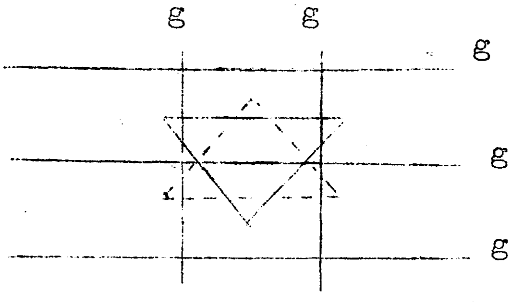
from / Observer	Observed Density			Theoretical Density
	Benzene	Dioxan	Ether	
Calbraith	1.076	0.995	0.988	a) 0.994 b) 1.098 c) 1.324
Grant	1.306	--	--	a') 0.983 b') 1.083 c') 1.308
Behr	1.297	1.283		

Orig.cell vol.used	Final cell vol.used	Content of unit cell
a)	a')	 + C_6H_6
b)	b')	
c)	c')	

Originally postulated packings:



(1)



(2)

of the structure was confirmed by the nuclear magnetic resonance spectrum, which showed only a single asymmetric peak corresponding to the absorption of benzene hydrogens.

Crystals of analytical purity were produced by Galbraith which analysed correctly for one trimer unit containing half a mole of benzene of crystallisation. This benzene of crystallisation was determined by freeze drying from dioxan crystals obtained from benzene solution, condensing out the dioxan/benzene mixture and estimating the benzene present spectroscopically. Catalytic hydrogenation over platinum oxide yielded intractable oils and a small amount of gummy crystalline material, m.p. 137-8°, which analysed fairly well for $C_{30}H_{36}$. (Found: C, 90.6; H, 8.9, $C_{30}H_{36}$ requires C, 90.85; H, 9.15%).

At this stage it was felt that X-ray determination of the structure might be the best and most rapid means of solving the problem. This work was therefore initially undertaken by Dr. J.C. Speakman in this department (and later continued by Mr. K. Grant in collaboration with him) who obtained a number of photographs on a particularly fine lath-like crystal ; the cell dimensions were determined and two possible space groups postulated (H1 and H2). The density of crystals obtained from benzene, dioxan and ether as solvent was determined by Galbraith. The figure obtained for the crystals from benzene was higher than that from the other two solvents, thus lending further weight to the postulate of benzene of crystallisation. On the basis of these measurements and the cell dimensions, six monomer units per unit cell were indicated; that is, either two trimer units or three dimer units. Since the latter packing would be very awkward, though not impossible, in an orthorhombic cell, the initial postulate of trimeric structure was made[1]. This was especially attractive as it fitted in with the concept that the rigidity of the o-diethynylbenzene unit would be maintained throughout the coupling reaction.

A Patterson projection subsequently drawn for the intensity data did not show the features to be expected from a compound with the trimeric structure (S6), and all attempts to base a trial structure on this formula have failed. The trimeric structure could not be completely ruled out on this evidence, as there were several, though rather unlikely, modes of disordered packing which could have accounted for the difficulties. At this point (December 1957) it was decided to reopen the chemical investigations. These were completed in April 1959 as described in the next section of this thesis, and the compound in question shown to have the dimeric structure (S5). The X-ray investigation was then recommenced.

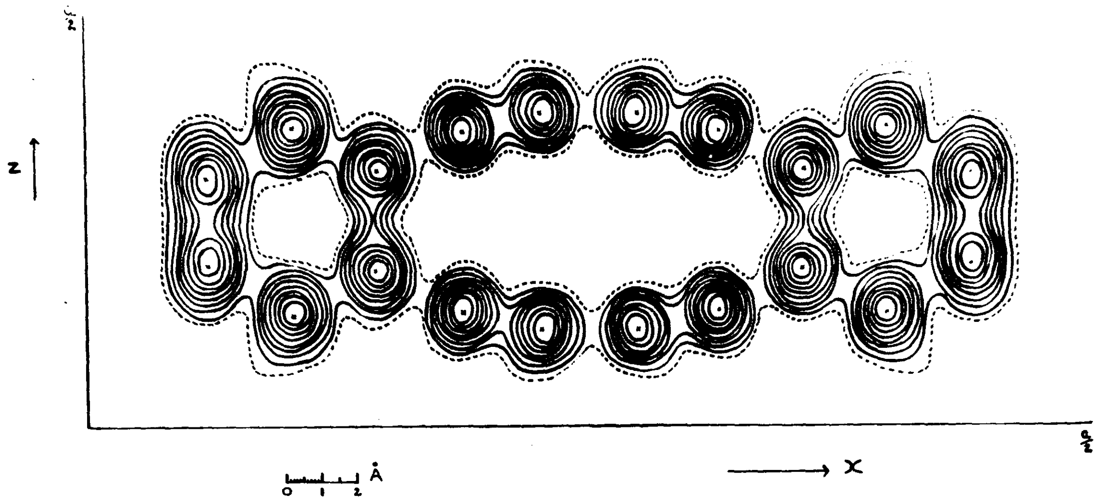
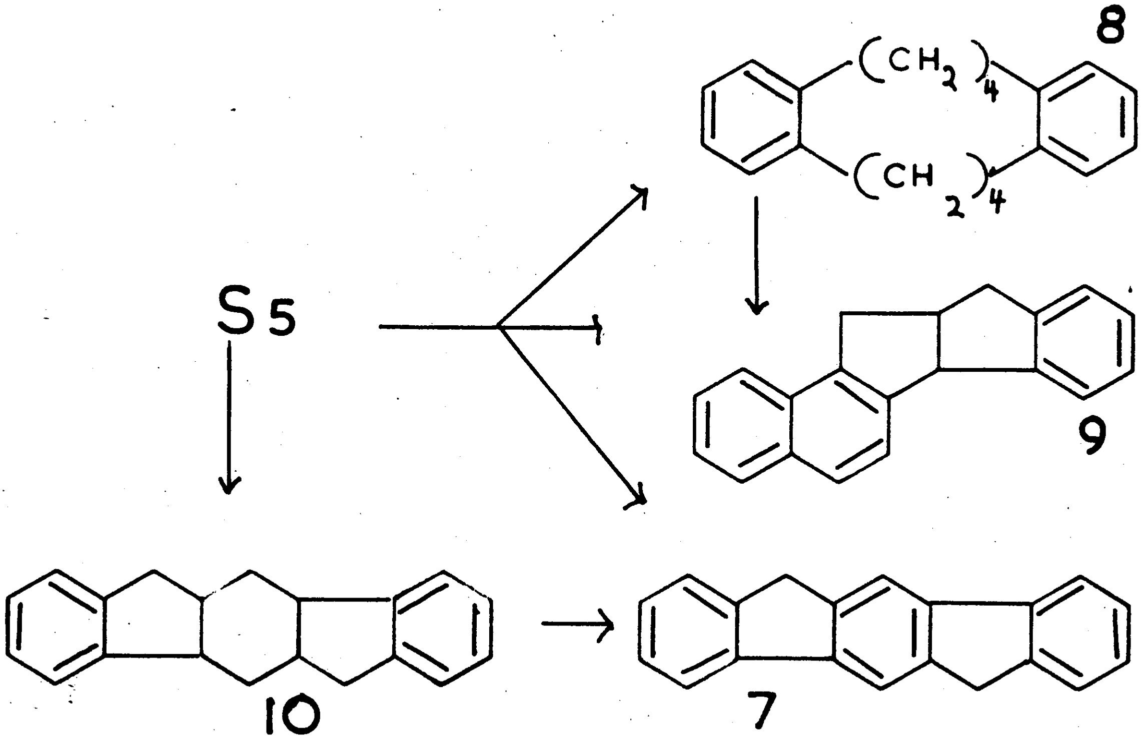


FIG. 4

The author and Grant, together and independently, redetermined the density of a number of different crystals obtained from different solvents. It was found important that the crystals were 'large' (at least 5 mm by 0.2 mm) otherwise consistent results could not be obtained because of convection currents in the flotation bath. It was also found vital to remove absorbed air from the crystals when they were immersed in the flotation bath by pumping under water pump vacuum. These precautions had presumably not been taken sufficiently rigorously by Galbraith and account for his figures being 30% less than the correct values. The densities obtained for the crystals from different solvents differed by not more than 2%, a figure well within the experimental limits for the method, and the best figure was within 1% of the theoretical value which would allow the packing of four monomer units per unit cell. A fresh microanalysis on a very carefully purified specimen showed that the empirical formula was $(C_{10}H_4)_x$ exactly; these results taken together destroyed the postulate of benzene of crystallisation.

Using their original data, Grant and Speakman now very quickly confirmed the dimeric structure (June 1959) with the results shown (Fig. 4), and found that the analysis showed no crystallographic anomalies, thus justifying the original idea that the problem could be readily solved by

S



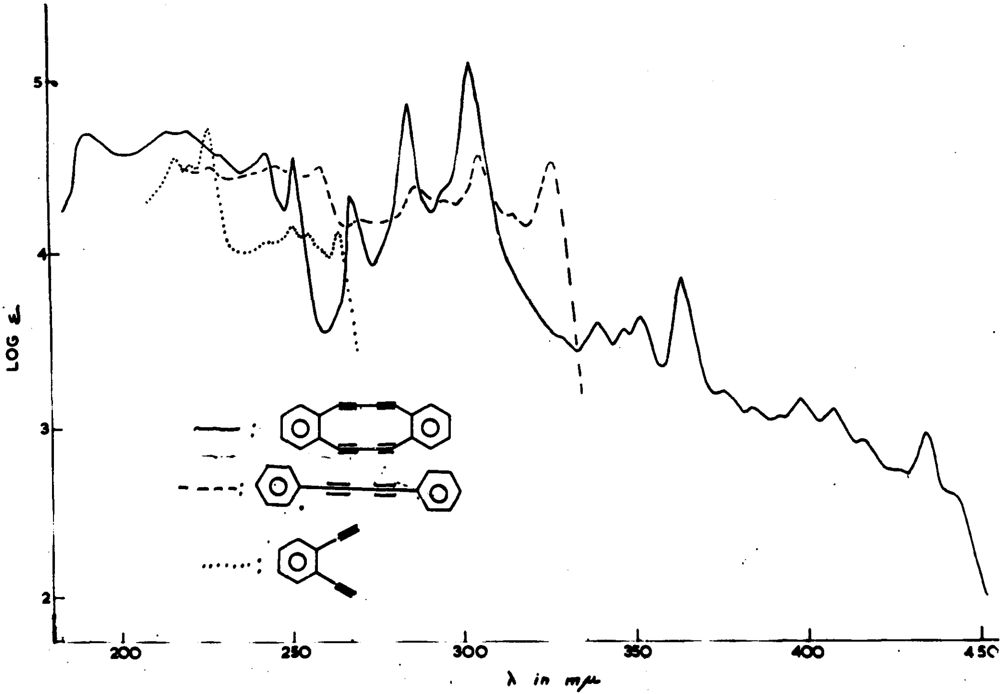


FIG: 5

U.V. Spectra

X-ray methods. Furthermore, their two dimensional projection showed very clearly the previously postulated bowed nature of the acetylenic links.

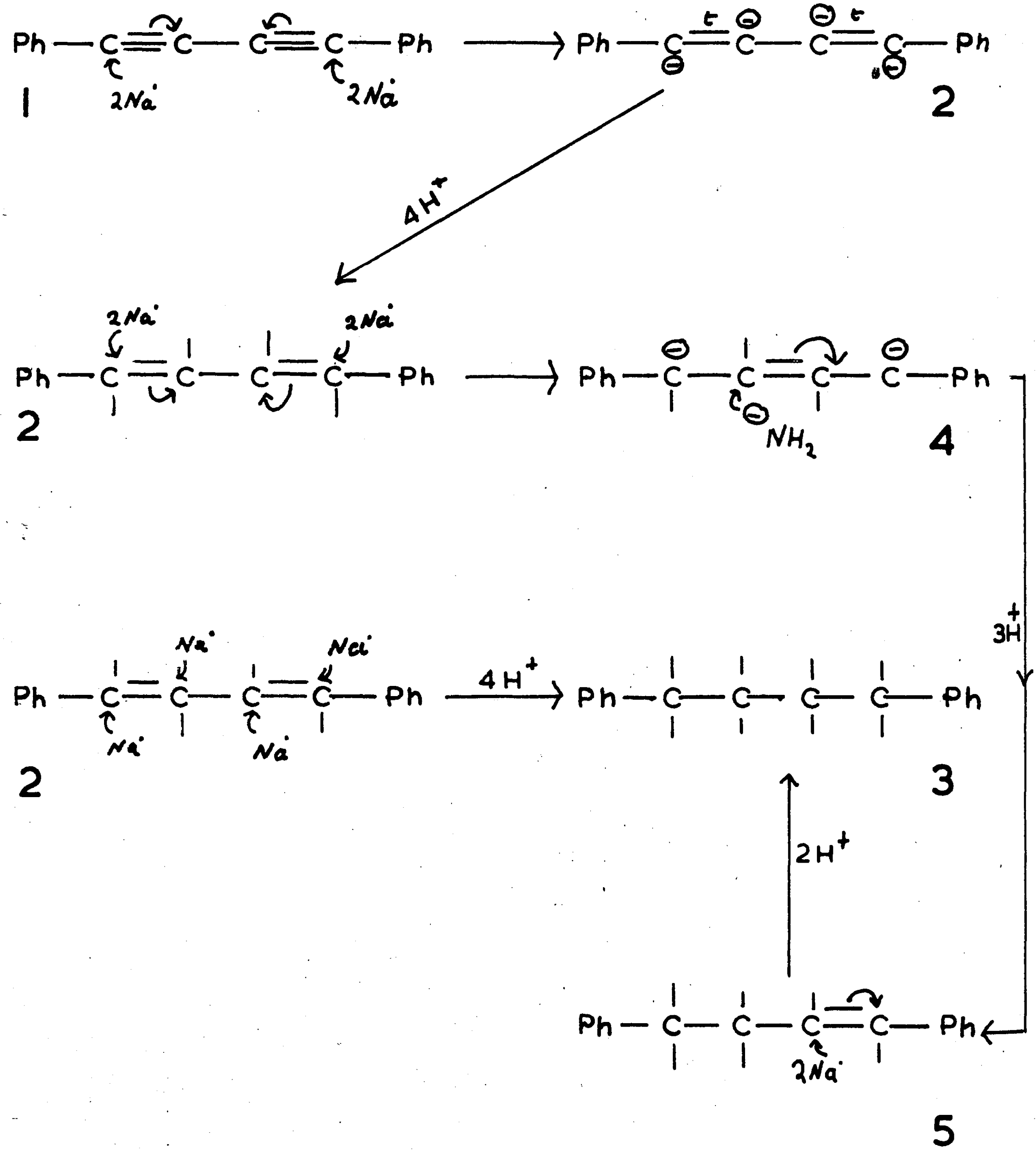
It is interesting to note that had the correct density been measured by Galbraith, the postulate of the triangular structure for the compound would have been eliminated immediately and unambiguously since only four dimers or two tetramers could be fitted into a unit cell of the dimensions and density given.

Section 3. The chemical proof of structure of (S5).

When both Galbraith's hydrogenation studies and the first part of the X-ray work failed to give conclusive results, the phase of the work reported in this thesis was begun.

It was still felt that hydrogenation of the unknown hydrocarbon would be the best approach since even the mildest hydration procedures involved conditions which would decompose the compound[66]. As a preliminary pilot step, Purdie in this department attempted the reduction of diphenylbut-1,3-diyne with sodium in liquid ammonia. He obtained a mixture of compounds which were not identified at the time. Further investigations showed that diphenylbutane and trans diphenylbut-2-ene (strong band in the infra red spectrum at 966 cm^{-1}) were formed in about equal proportions. The

J



amount of fully saturated hydrocarbon ranged from 40% on immediate work up to ca. 60% if the reaction was worked up after about six hours. This was shown by measuring the uptake of hydrogen on catalytic hydrogenation of the crude product. Since the intensity of absorption in the ultra violet corresponded to that due to two benzene rings per mole, the double bond was obviously not in conjugation with either. The reduction probably proceeded in the following manner. The diyne (J1) first underwent reduction to the conjugated diene (J2), 1:4 reduction of which produced the but-2-ene (J4). The fully reduced butane (J3) could be derived either by two 1:2-additions to the diene or by isomerisation of the but-2-ene to the conjugated but-1-ene (J5), followed by reduction of the latter. There is good precedent[67] for this postulate in the work of Strauss[68] who reduced this butadiene with sodium in ether to give a similar product and proved the nature of his product by successive brominations and dehydrobrominations to known compounds.

Klages[69] showed that the but-2-ene (J2) can be rearranged to the but-1-ene (J4) by heating with alcoholic potassium hydroxide. Under our reaction conditions it is possible that a little sodamide was formed, thus enabling the fourth stage of the reduction to occur in which the base shifts the double bond into conjugation where it can then be

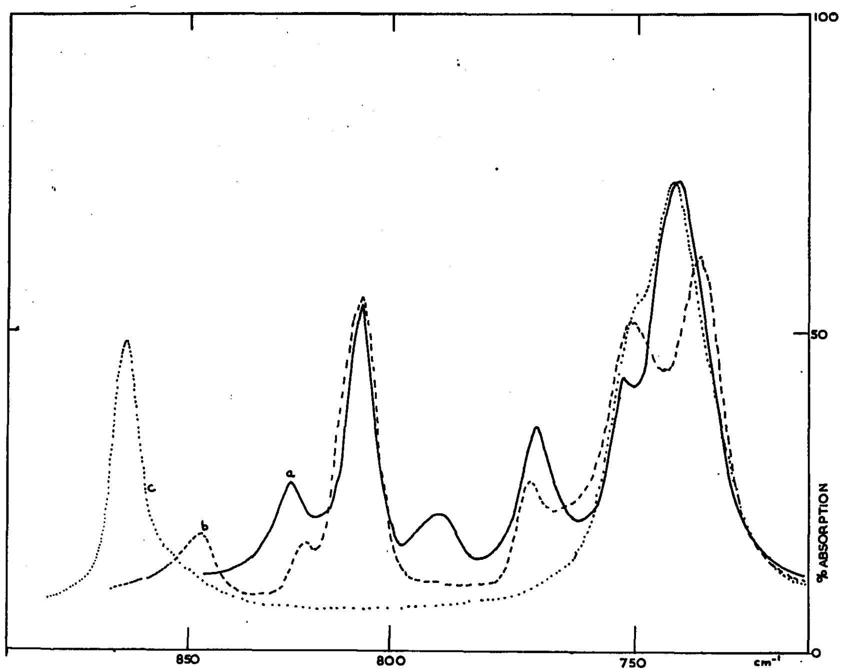


FIG: 6

Infra Red Spectra of Solns. in CS_2 (0.5 mm. path) of

a) S 9, 0.056 M.

b) 1,2-dimethylnaphthalene, 0.028 M., and indane, 0.028 M.

c) 2,3-dimethylnaphthalene, 0.028 M., and indane, 0.028 M.

G.L.C. OF Na / NH_3 REDUCTION PRODUCT.

TEMP. : 224°

FLOW. : 20 ml / min

S. PHASE : 5 % Ap. 'L'.

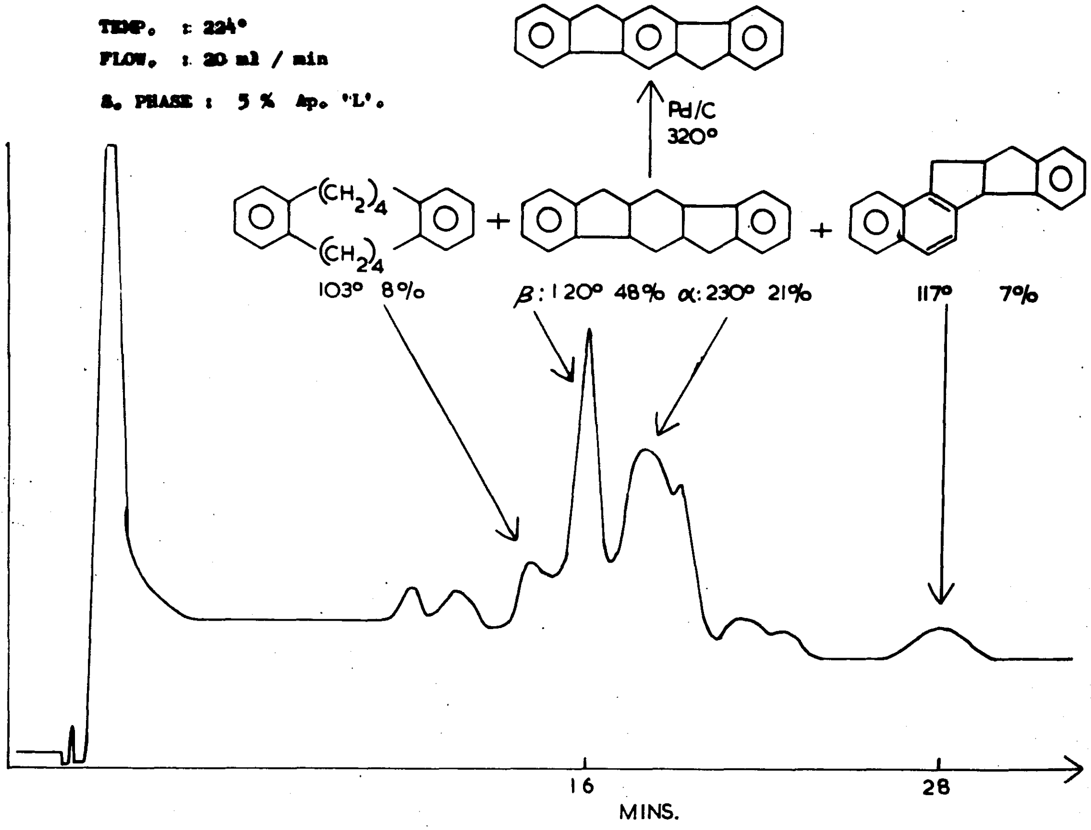


FIG: 7

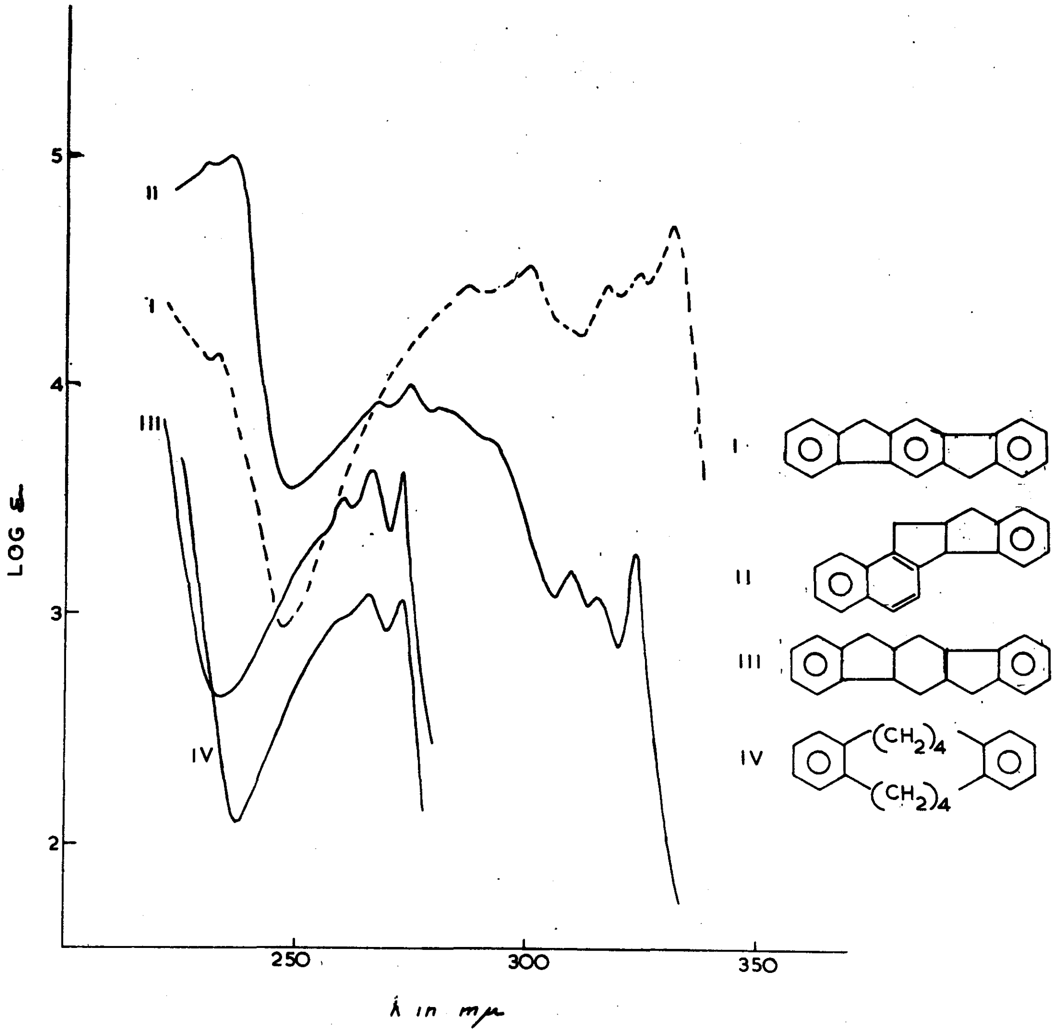


FIG: 8

reduced by the excess sodium present in the reaction mixture.

The hydrocarbon (S5) was therefore reduced using excess sodium in liquid ammonia. The crude reaction product was found to contain a negligible amount of ethylenic material which was removed by catalytic hydrogenation. Gas liquid chromatography (Fig. 7) showed the presence of two major components (ca. 20 and 50%) which were isolated after careful chromatography on alumina, and two minor components (ca. 10% each) which could not be so isolated, but were later shown to be (S8) and (S9) (the major products of catalytic hydrogenation of (S5), see later).

These two major components were isolated and proved to be isomeric hydrocarbons, $C_{20}H_{20}$, m.ps. 230-231° and 120-122°. The fact that both underwent smooth dehydrogenation to give the same fluorenacene (S7) suggested that they were two stereoisomers of the structure (S10). Their almost identical ultraviolet spectra (Fig.8) resembled closely in their maxima those of 1,2-dimethylindane[70] with double the relevant intensities. Further, the infra red spectra showed no C-methyl groups but did clearly indicate 1,2-disubstituted benzene rings (Fig. 6). Evidently additional factors, presumably of a steric nature, other than strain in an attached ring, are capable of seriously perturbing the "umbrella" C-H out of plane deformation mode[64b] (cf. A.P.I. project 44, spectra numbers 678, 1419, 1511, 1585, 1599, 1709). The

N.M.R. spectrum of the 120° isomer conclusively showed the absence of olefinic or methyl hydrogens; diffuse absorption, typical of rigid alicyclic systems, occurred between $\tau = 2$ and 4 (maximum at 2.7 corresponded to benzylic CH_2). A further indication of the close relationship of these two hydrocarbons was provided by the finding that the 120° compound appeared to undergo partial conversion to the 230° hydrocarbon during gas-liquid chromatography, the degree of isomerisation being dependent on the contact time. However, we have been unable to effect this conversion under other circumstances. It appears that in view of this finding the isomerisation probably only occurs at high temperatures, in the vapour state, and is dependent on surface effects.

The molecular weight of several samples of the 120° hydrocarbon was measured by the thermistor drop method[71] (October to December 1958) and gave values consistently in the range 220-240. The highest value obtained was 259 (May 1959), a sample of the parent hydrocarbon (S5) on the same occasion giving a value of 245. These findings were in direct conflict with those obtained from the mass spectrometer which gave 392.8 for 120° isomer and 388.2 for the 230° isomer. Since $C_{30}H_{32}$ requires 392.6, $C_{30}H_{30}$ requires 390.5, and $C_{20}H_{20}$ requires 260, these differences were most confusing. We can only surmise that in view of the excellent results given by the mass spectrometer to us and to other workers in this department at later dates, the errors may have been due either to the machine being in a state of reconstruction or to impurities contaminating the sample. The correspondence of the results with the wrong answer was however quite remarkable.

At this stage a detailed examination of the catalytic hydrogenation products of (S5) was begun.

A new brand of extremely active palladium charcoal catalyst came into our hands, and (S5) was hydrogenated under conditions which quantitatively converted 1,4-diphenylbutadiyne into 1,4-diphenylbutane. Hydrogen absorption was extremely rapid but ceased completely when only 68% of the theoretical volume for 4 triple bonds had been taken up. From the product a sparingly soluble, crystalline hydrocarbon, $C_{20}H_{14}$, m.p. 300-302° (3%), was isolated very easily in spite of its low concentration. The ultraviolet absorption strongly resembled that of fluorene and the compound was speedily identified as the known "trans-fluorenacene" (S7) by direct comparison with a genuine sample[72]. This correlation with a known compound first clinched the molecular size of the hydrocarbon (S5) at a time when the above conclusive physical measurements were not yet available.

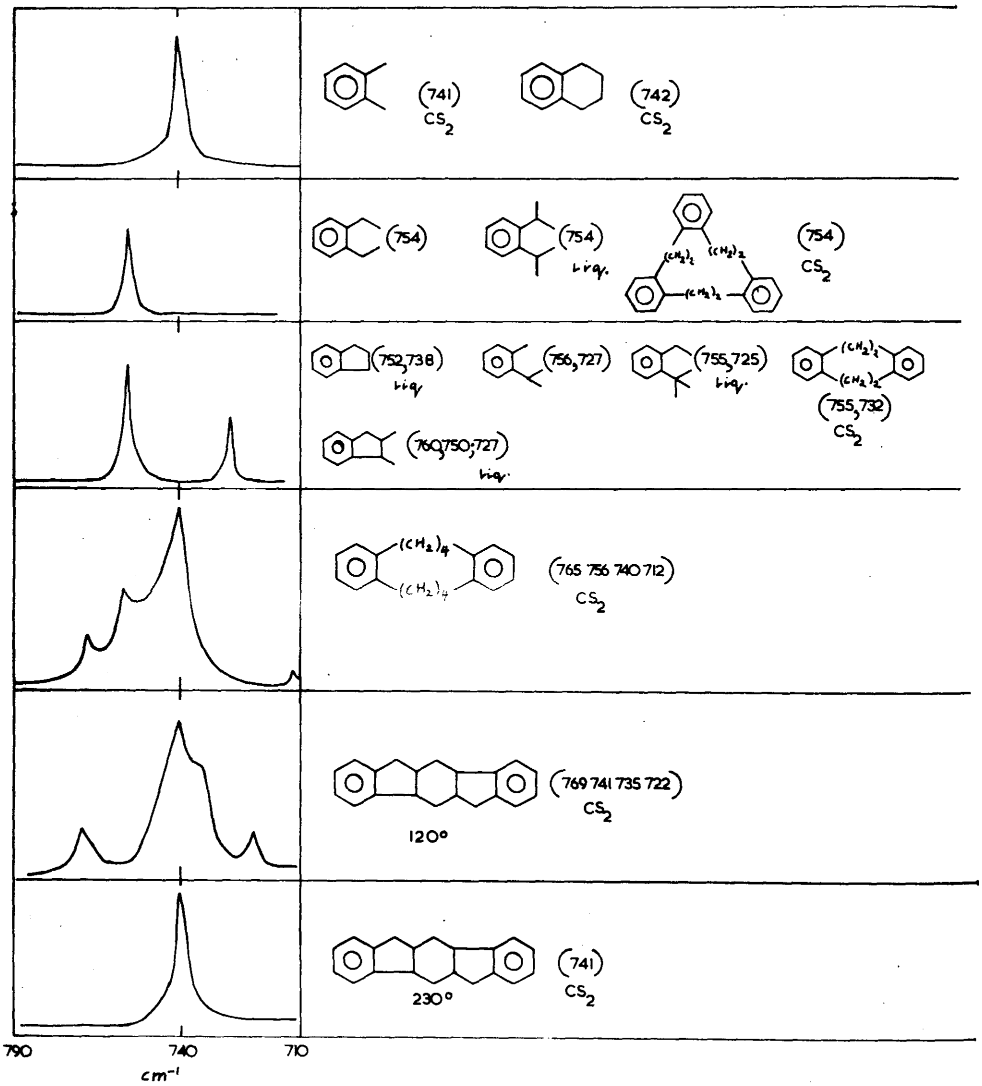
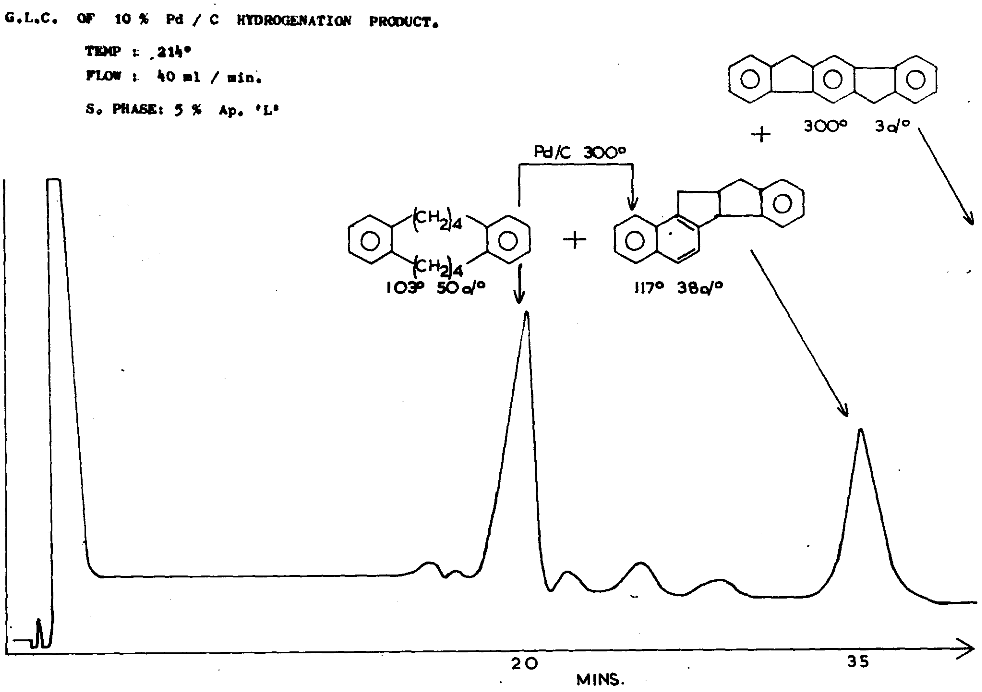


FIG: 9

Infra Red Spectra

The main products of the catalytic hydrogenation were isolated by careful chromatography and crystallisation. The major hydrocarbon component, $C_{20}H_{24}$, m.p. 103-105° (50%), showed spectral characteristics [U.V. (Fig. 8) I.R. (Fig. 9) and N.M.R.] closely resembling those of tetralin and diethyl benzene and was undoubtedly the expected hydrogenation product (S8). The second substantial constituent, a hydrocarbon $C_{20}H_{16}$, m.p. 117-119° (38%) was provisionally allotted the structure (S9) on the following grounds: the ultraviolet absorption (Fig. 8) was strongly suggestive of an α; -disubstituted naphthalene, a contention further substantiated by the infra red[65] evidence (Fig. 9). The mass-spectrogram of its breakdown fragments was fully consistent with a structure containing benzindane, methyl naphthalene and toluene residues (we are indebted to Dr. R.I. Reed of this department for this information). It was found, very remarkably, that this naphthalene was the sole detectable product of the palladium-induced catalytic dehydrogenation at 320° of the hydrocarbon (S8). The fact that (S9) is formed under these circumstances suggests the thermally more stable cis-fusion of the two five-membered rings[73].

The proportions of the above compounds in the product of hydrogenation of (S5) were conveniently assessed by gas-liquid chromatography[22] which also indicated trace



G.L.C. OF 10 % Pd / C HYDROGENATION PRODUCT.

TEMP : 214°

FLOW : 40 ml / min.

S. PHASE: 5 % Ap. 'L'

FIG: 10

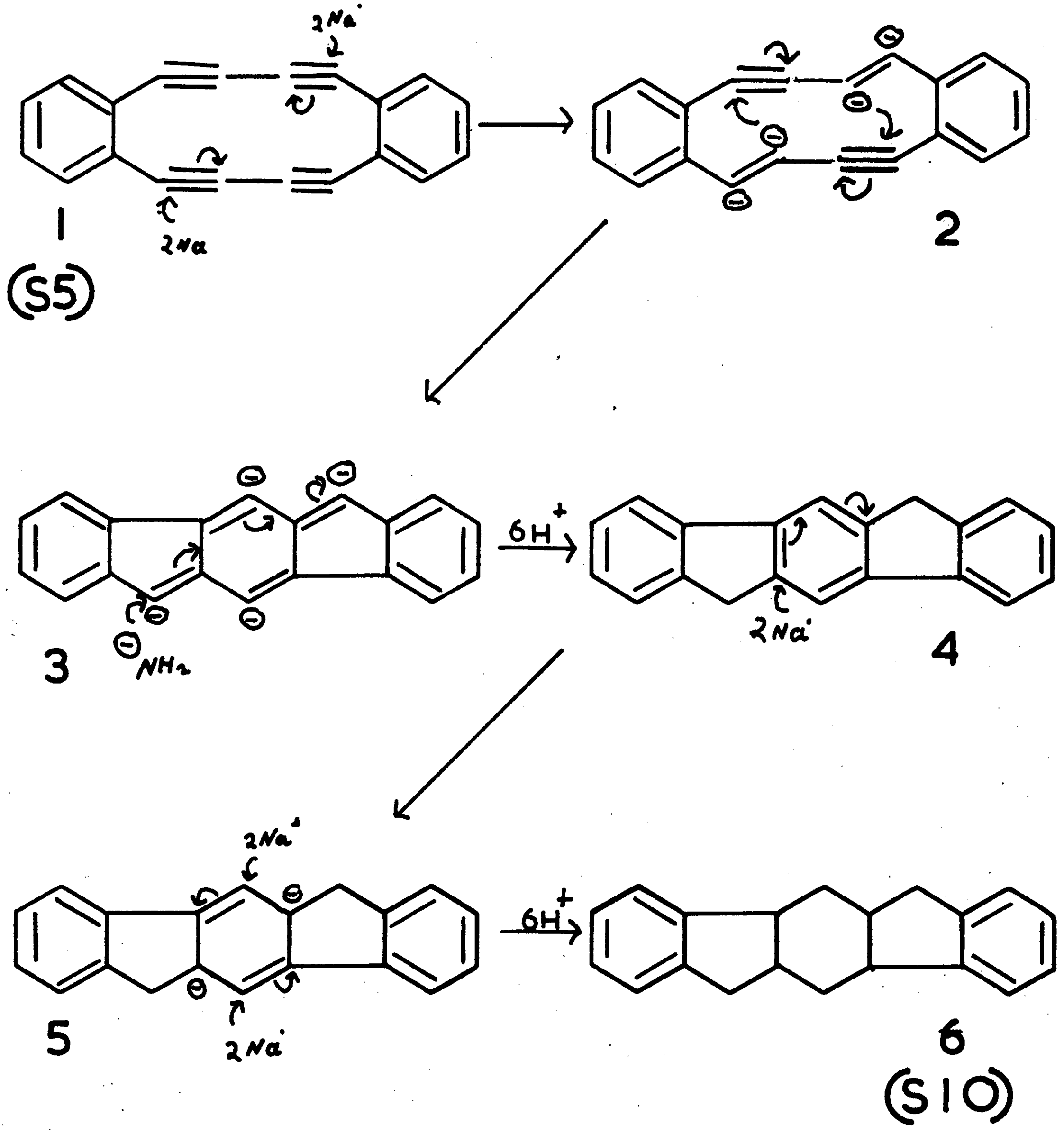
amounts of other substances not further investigated. Calculation of the hydrogen uptake derived from these found proportions of the hydrogenation product amounted to ca. 70%, an excellent, if surprising, correlation with the 68% actually observed.

A beautiful correlation between the products of the two reduction procedures was the finding that the fluorenacene obtained on dehydrogenation of the 120° and 230° isomers from the chemical reduction was identical with that isolated from the catalytic hydrogenation. We therefore considered that, on the available evidence, the dimeric structure (S5) could be assigned to the parent cyclic acetylene.

Two interesting points arose from the findings discussed above. Firstly, why was the dimer and not the theoretically more likely trimer formed in the oxidative coupling of o-diethynylbenzene, and secondly, what was the course of the transannular reactions? We can provide some indication of the reason for the first, but merely conjecture as to the answer to the second.

A normal cupric ion self coupling of o-bromovinylethynyl benzene (S3) was effected, and the resultant dimer (S11) dehydrobrominated using potassium t-butoxide in butanol. Considering that a cis elimination of hydrogen bromide was involved, the reaction went surprisingly readily.

K



The tetrayne (S12) thus obtained was in effect the open chain dimer of o-diethynylbenzene. Coupling of this product under high dilution conditions most surprisingly gave the highly strained cyclic dimer (S5) in good yield. This result is in contrast to Sondheimer's[25] findings in the aliphatic series as mentioned in the Historical Section of this thesis. It is therefore permissible to postulate that in the high dilution process, o-diethynyl benzene first dimerises linearly. Since the statistical possibility of the linear dimer unit meeting and then coupling with another dimer or monomer unit is very small, it will undergo intramolecular 'head to tail' ring closure preferentially despite the high energy barrier which must be involved.

Section 4. The Transannular Effect.

The transannular effect as observed in this work falls into two categories, that due to chemical and that due to catalytic agents.

In the chemical reduction of the cyclic tetrayne (S5) we assumed that the first acetylenic bonds to be reduced took on a <u>trans</u>[74] ene configuration. While this initial assumption is probably quite justified in view of the many precedents, the mechanism given (K1 ⟶ 6) for the later stages of the reduction is purely one postulate of several that might be written. From a consideration of 'Catalin' models of (K2) it was noted that the β carbons of one branch come into close proximity with the α carbons of the other. Transannular reaction might then take place, either by the mechanism shown or by a type of Diels-Alder condensation between a double bond and a conjugated acetylene[65b].

Ziegler[75] found that sodium in liquid ammonia will cause linear dimerisation of 1,1-diphenyl ethylene.

$$Ph_2.C{=}CH_2 \rightarrow Ph_2.\overset{-}{C} - \overset{-}{C}H_2 + (Ph_2.CH.CH_2) \longrightarrow$$

$$Ph_2.\overset{-}{C}H.CH_2.CH_2.\overset{-}{C}H.Ph_2.$$

which is a fair parallel to the situation under consideration. However, in the presence of an 'acid', i.e., indene, a different course was taken due to the ready availability of protons.

$$Ph_2.\overset{-}{C} - \overset{-}{C}H_2 + (2H^{+}) \longrightarrow Ph_2.CH.CH_3.$$

The protons which neutralise the negative charges on the hydrocarbon when there is no 'acid' present must come from the dissociation of the solvent. Ammonia being a good polarising medium, is not highly dissociated. The addition of protons was probably not simultaneous. According to Wooster's[76] 'benzhydryl rule' where there is a successive addition, the unstabilised charge corresponding to the weakest 'acid' is the first to abstract a proton from the solvent.

$$(H^{+}) + Ph_2.\bar{C} - \bar{C}H.Ph \rightleftharpoons Ph_2.\bar{C} - CH_2.Ph.$$

Although the 'rule' itself was only meant to apply to compounds with the benzhydryl group, it appears to have general application[77].

The conjugated tetraene (K3) may have rearranged to the fluorenacene (K4) which was further reduced to the hexahydrofluorenacene. Hueckel[78] has recently investigated the chemical reduction of fluorene and found that a dihydrofluorene was formed first which disproportionates (on isolation) to fluorene and a tetrahydrofluorene. However, if excess sodium was used, an isomeric tetrahydrofluorene was formed.

In our system, although rearrangement to a non conjugated di- or tetrahydrofluorene is possible, it appears not to be a major factor as catalytic hydrogenation of the crude reaction product showed the presence of only a negligible amount of ethylenic material. Further light would be thrown on this particular aspect of the problem if the reduction of trans-fluorenacene (S7) itself was attempted using varying proportions of sodium. Unfortunately, insufficient material was available for this experiment.

Transannular reactions on catalyst surfaces are now well known, e.g., the internal dehydrocyclisation of medium sized ring hydrocarbons to benzenoid derivatives[79-83].

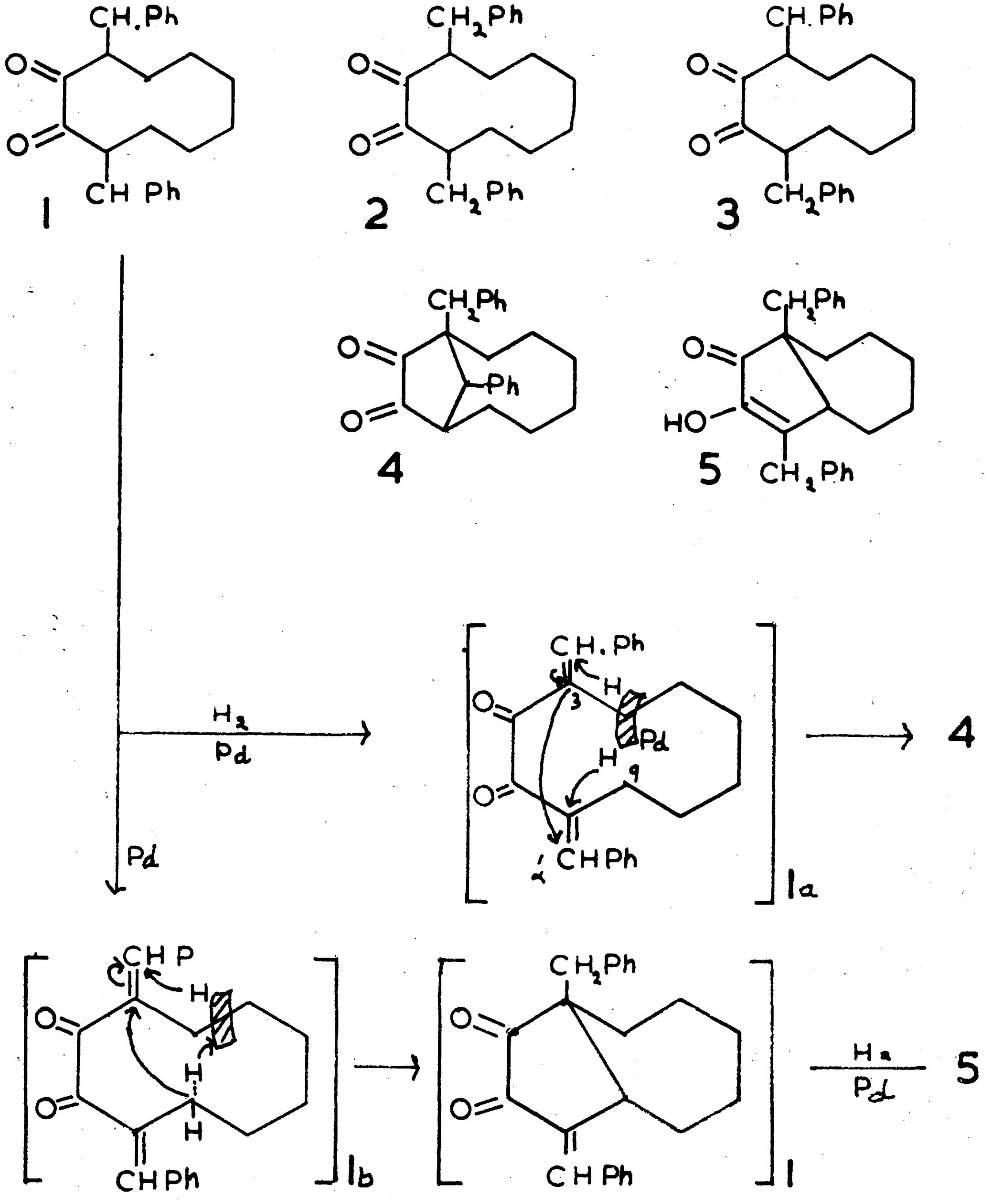
Thus Prelog found that the dehydrogenation of cis-cyclotetradecaene[83] with palladium charcoal at 300° gave mainly phenanthrene together with a trace of anthracene. He postulated two possible routes:-

a) Chemisorption of the hydrocarbon on the catalyst, followed by 1,6-hydrogen elimination, and consequent cyclisation to a cyclohexane derivative which is then dehydrogenated, or

b) after chemisorption a series of 1,2-eliminations followed by an internal Diels Alder reaction.

In order to facilitate the identification of the products of the reaction ^{14}C labelled carbon atoms were placed at positions 1- and 2- in the ring (i.e., at the carbons involved in the double bond). If reaction mechanism (b) were responsible, the degradation of the reaction products should show that the radioactivity was unevenly distributed between the carbon atoms. It was found that each carbon atom carried an equivalent amount of radioactivity, thus lending support to mechanism (a). These indications are by no means conclusive, since it is quite possible that under the fairly vigorous conditions employed, hydride shifts could have occurred, even though merely heating the parent hydrocarbon to the reaction temperatures did not induce such shifts.

L


CH.Ph
CH Ph
1
CH2Ph
CH2Ph
2
CH. Ph
CH2Ph
3
CH2Ph
Ph
4
CH2Ph
HO
CH2Ph
5
H2
Pd
Pd
CH.Ph
H
3
Pd
H
9
α
CHPh
1a
4
CH P
H
H
H
CHPh
1b
CH2Ph
CHPh
1
H2
Pd
5

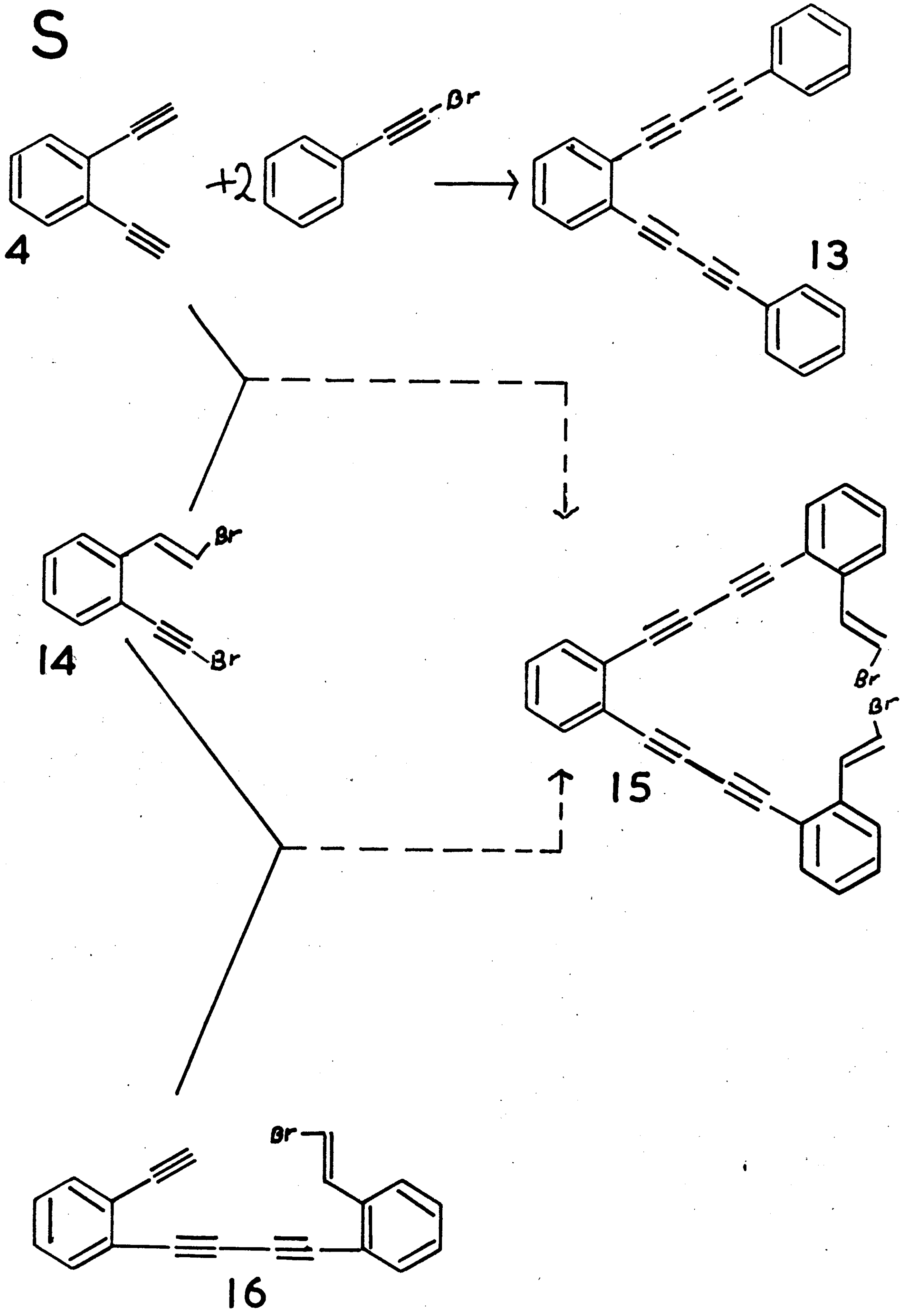
Leonard[85] observed transannular effects in the treatment of 3,10-dibenzilidene-1,2-cyclodecanedione with palladium charcoal at 280° Apart from the experimental results quoted, this paper constitutes a valuable source of references to recent work on the effect. It is very important to point out that their catalyst had been prepared by a method[86] which left a considerable amount of hydrogen adsorbed on it. This factor would account for the finding that 90% of the products obtained contained more hydrogen than the starting material.

Four products were isolated from the reaction (L2, 27%), (L4, 9%), (L5, 61%), and an as yet unidentified hydrocarbon (3%). On treatment of (L1) with palladium charcoal under milder conditions (L3) was isolated. It is therefore not quite clear if (L2) arose as the hydrogenation product of (L1) or from the disproportionation of (L3) to (L1) and (L2). As details of the proof of structure of the isolated products are given in the paper, we will merely consider the proposed mechanism.

The identified products (L2, 4, 5) were conveniently accounted for by assuming that C = C reduction occurred in contact with the catalyst, and that hydrogen transfer and hydrogenation occurred within the molecule; evidence was presented for this postulate. Scale models show that the 3- and 9- carbons and the 3- and α'-carbons are in close proximity, and thus transannular bond formation is a logical consequence (L1 → L1a → L4, L1 → L1b → L1c → L5).

Although it is conceivable that a similar mechanism applies in the catalytic hydrogenation of (S5), it is astonishing that the _trans_ annular effect is found under such extraordinarily mild conditions. There is the difficulty that palladium charcoal usually gives rise to _cis_ hydrogenation of acetylenes, which would tend to separate the two bridges in the ring rather than bring them into closer proximity. However, ring strain might force an isomerisation to the _trans_ position, as in the case of some of Sondheimer's macrocyclic polyenes. Therefore we do not propose to postulate a specific mechanism for the catalytic transannular effect on (S5), but merely comment that a hydrogenation-dehydrogenation process on the surface of the catalyst is probable.

S



PART B : Synthetic approaches to the 'trimer' 1,2:7,8:13,14:-tribenzocyclooctadeca-1,7,13-triene-3,5,9,11,15,17-hexayne. (S6).

Section 1. The attempted synthesis.

Concurrently with the completion of the problem of the structure of (S5), a series of experiments was begun to synthesise the trimer (S6) by an unequivocal route. This goal has still not been reached, but some interesting results have been obtained in the course of the attempt.

The proposed route involved the coupling of o-diethynylbenzene (S4) with 1-bromovinyl-2-bromoethynylbenzene (S14) by means of the Cadiot-Chodkiewicz[18] method to give the dibromovinyl precursor of (S4), i.e., (S15), which could then be dehydrobrominated and ring closed. As a preliminary experiment the coupling of o-diethynylbenzene with bromophenylacetylene was attempted under standard Chodkiewicz conditions. Under these conditions, however, it was found that the diyne gave an insoluble canary yellow precipitate (probably a polymeric copper salt) which appeared to be quite unreactive to the bromoacetylene. When a mixture of n-butylamine/ethanol (4:1) was used as the solvent-base mixture, the copper salt was sufficiently solvated to allow reaction to take place, and the required tetrayne (S13) was formed in <u>ca</u>. 60% yield.

This tetrayne was reduced catalytically as well as

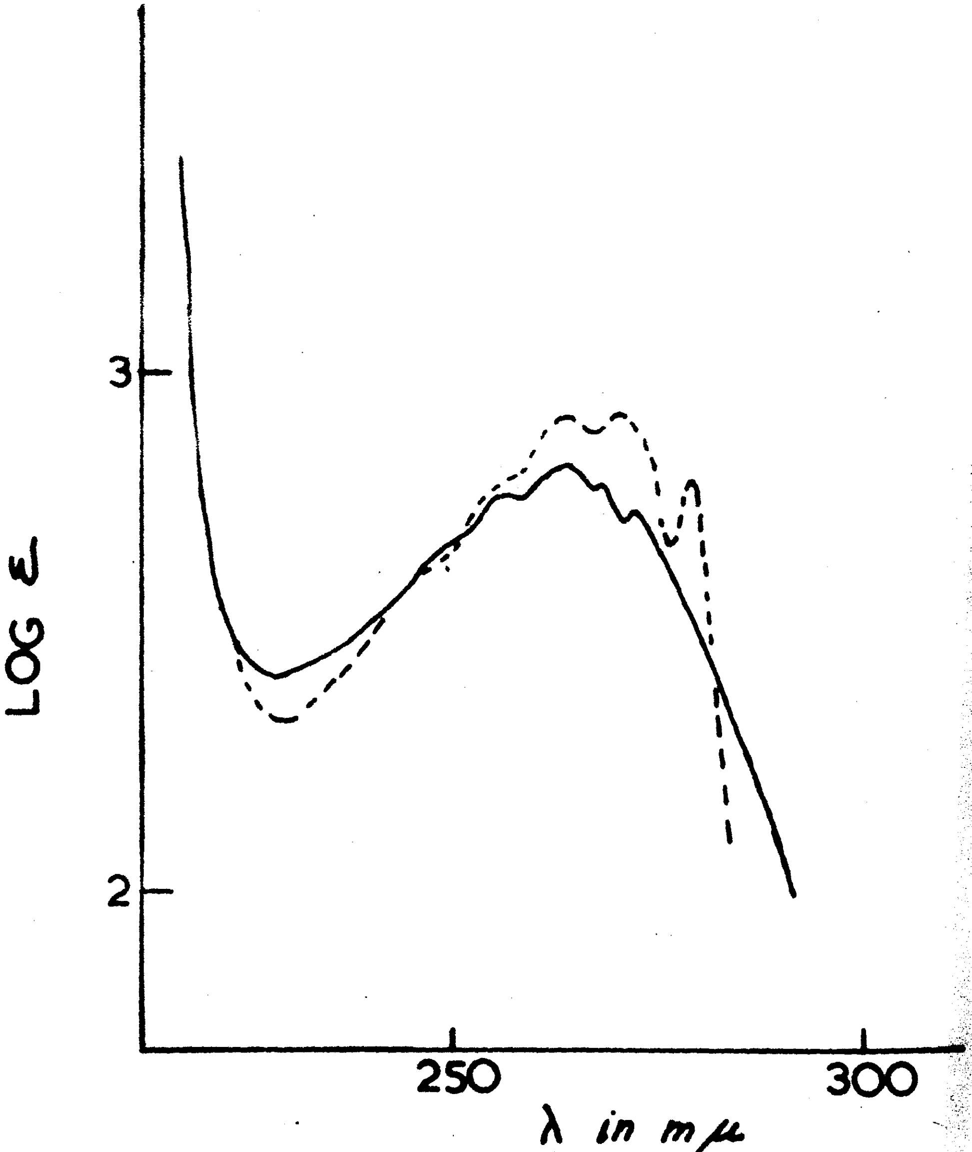


FIG 11

U.V. Spectra of the two main constituents of the Na/NH_3 hydrogenate of (S13)

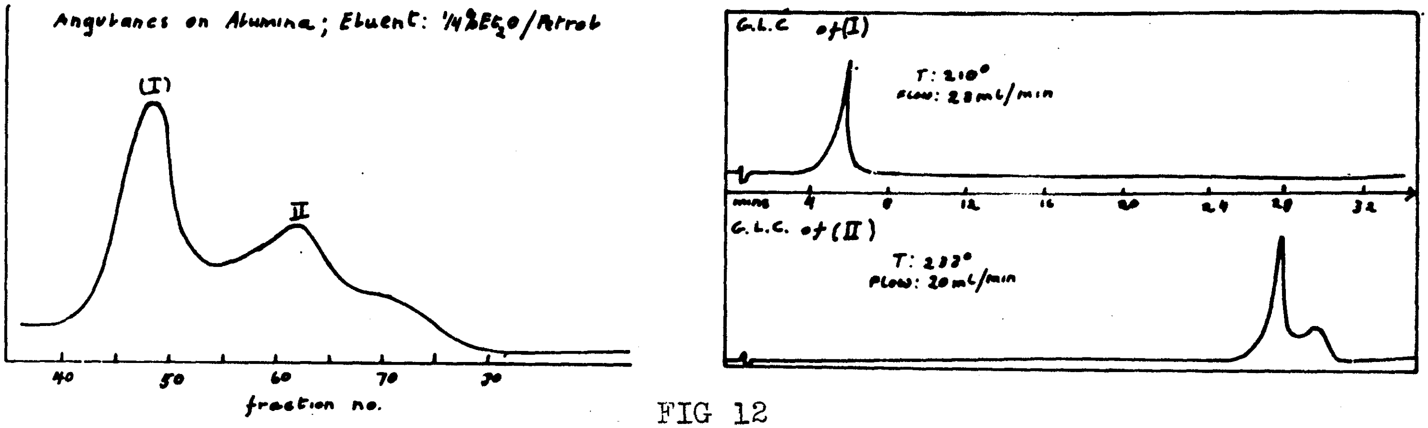


FIG 12

Chromatograms of Na/NH_3 hydrogenate of (S13) chemically. The empirical observation had been made that many aromatic compounds[87] in which the o-positions of the isolated benzene ring are connected by a short aliphatic chain (i.e., tetralin), have a sharp absorption band at 273 mµ separated from the normal benzenoid absorption region at 260-266 mµ by a well defined minimum. Hence it was assumed that if a compound had this side band in its ultra violet absorption spectrum, then it would also contain an aliphatic ring attached to the benzene nucleus. On this basis we found that the catalytic hydrogenation of (S13) gave the normal linear product.

The product from the sodium/liquid ammonia reduction did show the side band. By careful chromatography we were able to separate fractions in which the side band could be observed (Fig. 12). At a later date gas liquid chromatography showed that the catalytic hydrogenation product was in fact a single substance, while the fractions in which the 273 mµ band was observed consisted of a pair of substances with very similar retention times, which were considerably longer than that for the product from the catalytic hydrogenation which was found to appear in some of the 'side band' fractions as a slight contaminant. Thus though it has not been possible as yet to isolate, purify and identify these substances which showed the side band, we are probably justified in assuming that transannular reaction had taken place.

The bromoene bromoyne (S14) was synthesised (with W. McCrea) and attempts were made to effect its coupling with o-diethynylbenzene in the manner indicated above: despite variations in reaction temperatures, these were uniformly unsuccessful. On one occasion the product was dehydrobrominated and some linear dimer (S12) isolated, but it was not possible to repeat this. The infra red spectrum of the crude reaction products always showed bands due to free ethynyl and bromoethynyl groups, though the latter were relatively weak; the free ethynyl appeared to be present even when a considerable excess of (S12) was present. Although the synthesis of the tetrayne (S13) was repeated twice under identical reaction conditions, this particular coupling could not be effected.

There are nine possible reasons for the malfunction of this reaction:-

a) The insolubility of the cuprous salt of diethynylbenzene.
b) Self coupling of the acetylene.
c) Self coupling of the bromoacetylene.
d) Dehydrobromination of the bromovinyl group and subsequent reaction.
e) Reaction of the amine with the bromoacetylene.
f) Reaction of the reducing agent with the bromoacetylene.
g) Hydration reactions.
h) Unwanted oxidation reactions.
i) Addition of ethanol.

The first four could be rapidly eliminated.

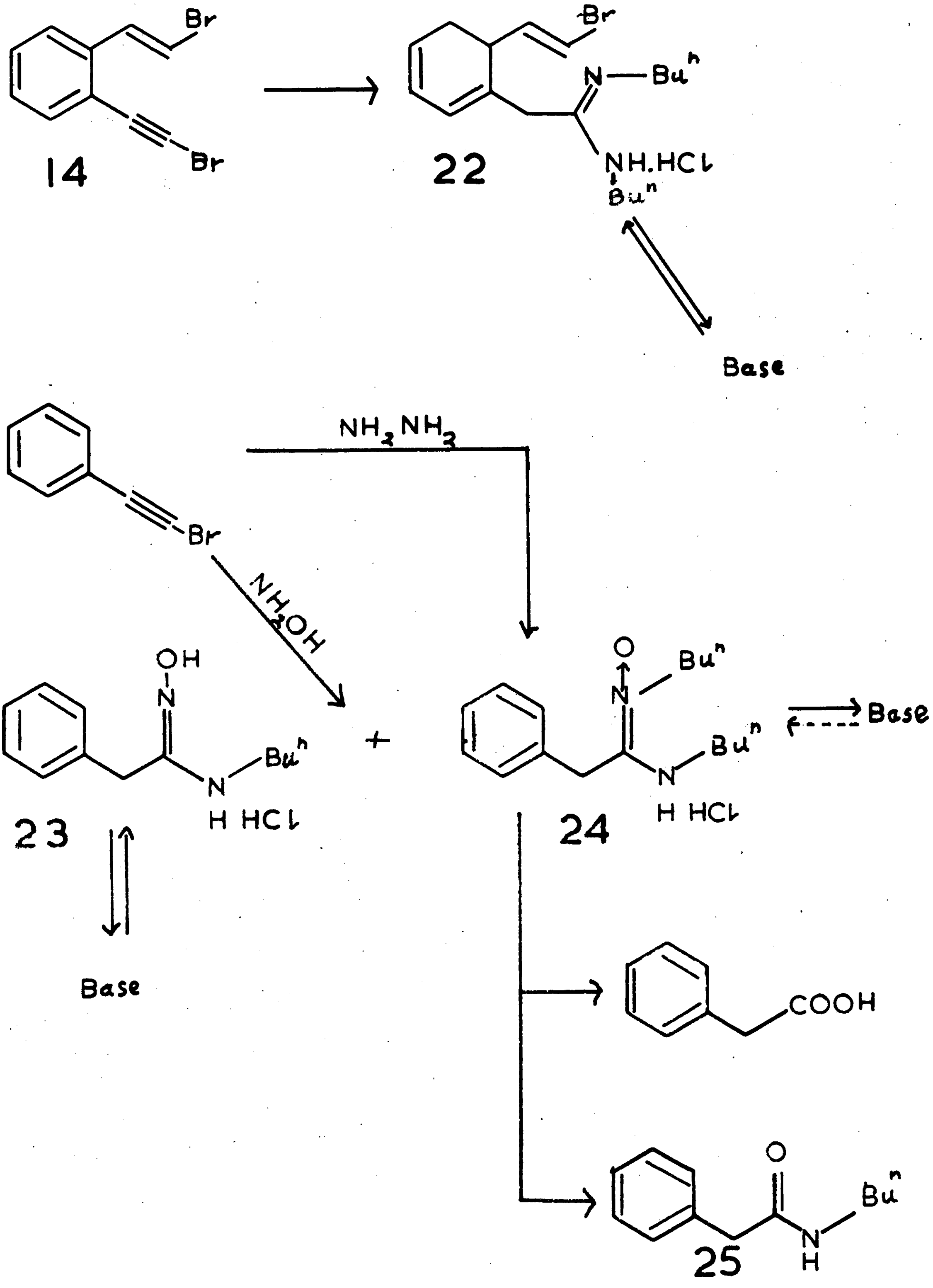
Factor (a) does not hold since (S13) can be formed under similar conditions. Since the free ethynyl band in the infra red spectrum of the crude product was very strong, (b) could not be a serious factor. Reaction (c) is favoured by high temperature and high cuprous concentration: even at reaction temperatures near -10°, and 1% Cu^+/per mole, we still observed the disappearance of the bromoethynyl compound. It was shown in a test experiment without the presence of cuprous ion that after five hours at room temperature the ethanol/butylamine mixture caused no detectable dehydrobromination; since later experiments showed that the cuprous ion is of little significance in this matter, factor (d) can also be ignored.

Section 2. The anomalous bromoacetylene/butylamine reaction.

We were thus compelled to examine the reaction when o-diethynylbenzene was not present (since it appeared to be substantially unaffected anyway). It was found in the course of the ensuing work that factors (e) and (f) were mainly responsible for the malfunction of the reaction, and that (g) and (h) might have a secondary influence.

A crystalline hydrochloride (S22) was isolated as the major product when (S14) was added to the standard coupling reagent consisting of 1% cuprous chloride in n-butylamine/ethanol (4:1), to which hydroxylamine

S


Br
Br
14
Br
N—Buⁿ
22
NH.HCl
Buⁿ
Base
NH₂NH₂
Br
NH₂OH
OH
N
Buⁿ
N
H HCl
23
Base
+
O
N
Buⁿ
Buⁿ
N
H HCl
24
Base
COOH
O
Buⁿ
N
H
25

hydrochloride was added as a reducing agent. It was possible to isolate the base (and regenerate the hydrochloride), whose solution infra red spectrum showed the presence of unbonded NH as well as bands due to C=N and <u>trans</u> C=CBr. The compound analysed for $C_{18}H_{27}N_2Br.HCl$ and on this evidence and that obtained from later experiments described below, the amidine structure (S22) was assigned, although the infra red spectrum does not correlate well with the spectra of amidines quoted by Prevorsek[58].

The bromovinylbromoyne (S14) was not very readily available, and thus degenerative experiments could not be carried out on a reasonable scale on (S22). It was therefore presumed that an analogous reaction would take place if bromophenylacetylene was used in place of (S14), as the former is readily available. Bromophenylacetylene did, in fact, react with the coupling reagent, and in this case two products were isolated.

The first was readily distinguished as insoluble white crystals floating at the water/ether interface during work up. This product analysed for a hydrochloride, $C_{12}H_{18}N_2O.HCl$, which by treatment with sodium carbonate solution yielded the base, which regenerated the crystalline hydrochloride on addition of hydrochloric acid. Infra red solution spectra of the base showed the presence of strongly interbonded OH which became 'free' on dilution, as well as

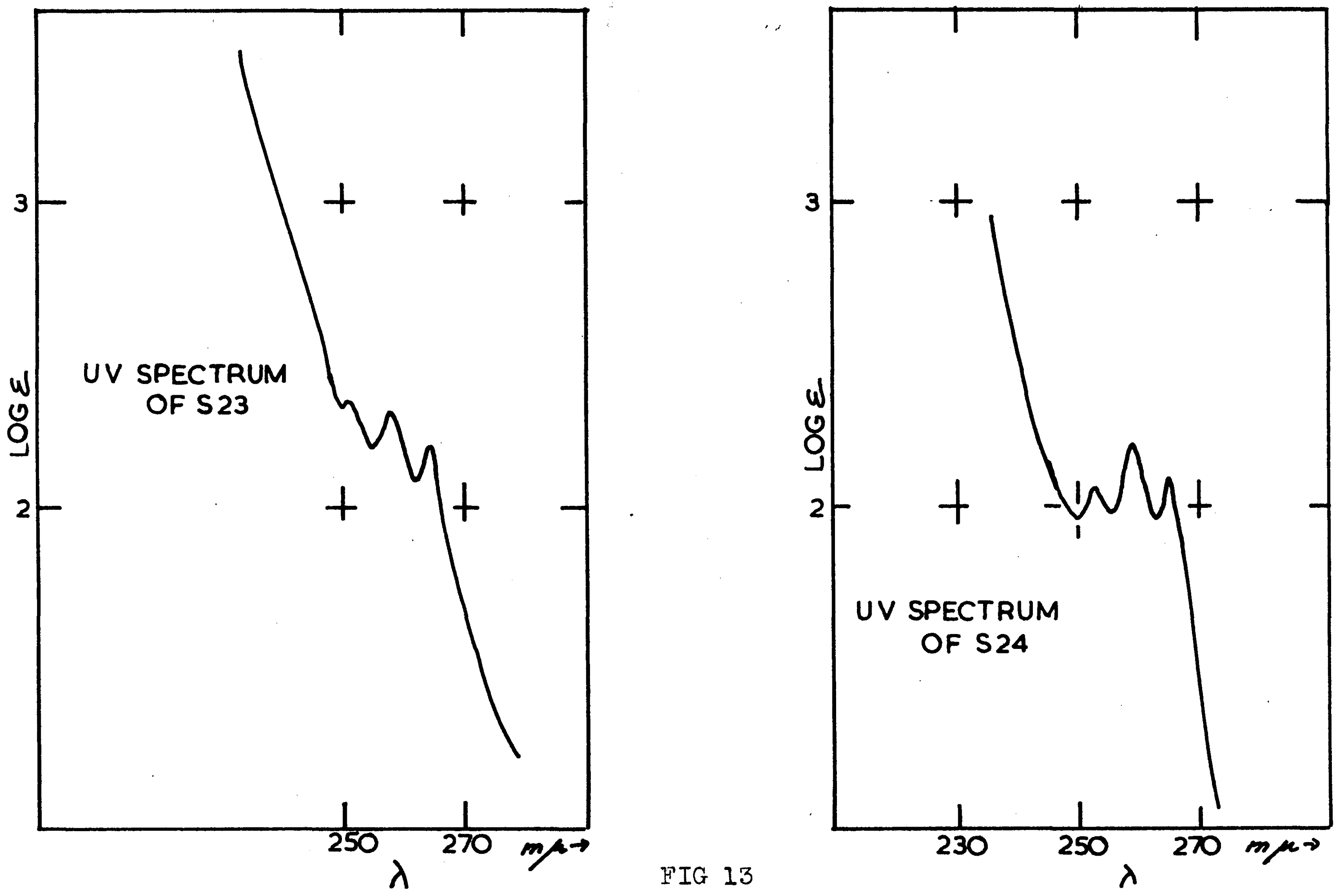
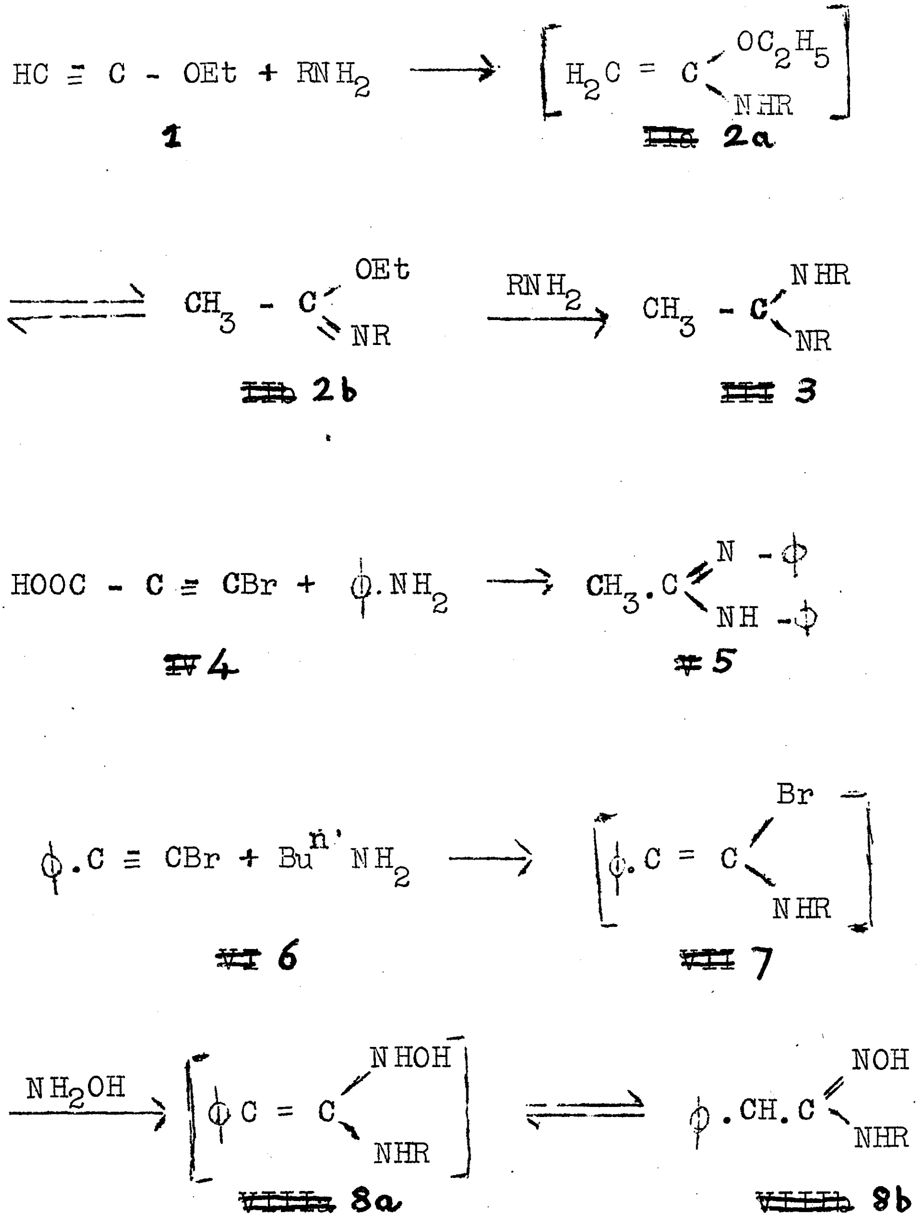

UV SPECTRUM
OF S23
LOG ε
3
2
250
270
mμ→
λ
UV SPECTRUM
OF S24
LOG ε
3
2
230
250
270
mμ→
λ

FIG 13

non bonded NH, and C=N. The ultra violet spectrum did not yield any information of structural interest, though it was consistent with the presence of a benzene ring in the compound. We therefore assigned the amidoxime structure (S23) which was later proved by synthesis.

Since the yield of the amidoxime hydrochloride only accounted for about 30% of the bromoacetylene used, the experiment was repeated and the acid layer examined. This gave a thick oil which accounted for the remainder of the bromoacetylene used. This oil partially crystallised to give a product which could be obtained more readily and in purer form when hydrazine was substituted for hydroxylamine in the coupling reagent. In this latter reaction, as expected, no amidoxime was isolated. This second product was also found to be a hydrochloride with an analysis in conformity with the empirical formula $C_{16}H_{26}N_2O.HCl$. The free base showed absorption bands in the infra red (CCl_4 solution) for unbonded NH and C=N, but nothing corresponding to OH bonded or free. Acid hydrolysis of this product yielded phenylacetic acid while mild alkaline treatment gave N-n-butylphenylacetamide. This latter product tied up a substantial part of the molecular structure, leaving only the assignment of a residual (C_4H_9NO) unit in doubt. It seemed fairly reasonable to assume that the C_4H_9N- was present as an integral **unit**, originating from the

M



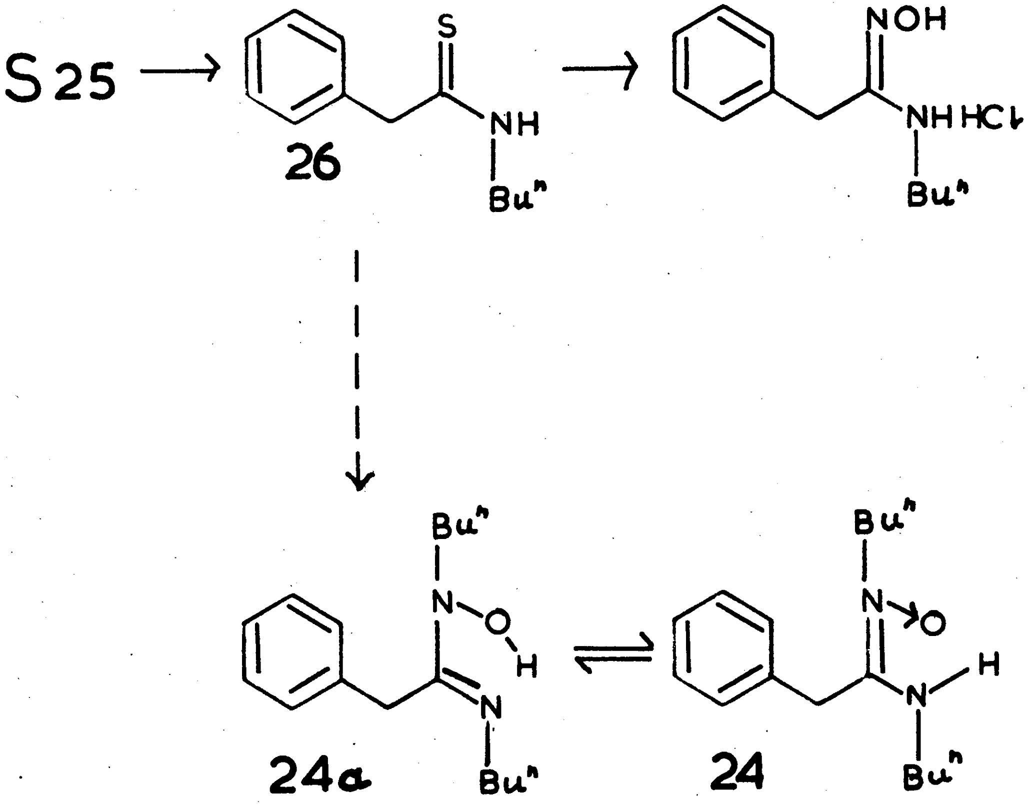
(S23)

butylamine. This left only the assignment of the lone oxygen, and this was accounted for by postulating the unusual but feasible amido-nitrone structure (S24) shown.

The formation of the amidoxime can be readily rationalised by the initial addition of butylamine to the β-carbon of bromophenylacetylene (M6), followed by addition of hydroxylamine to the same carbon with the elimination of the bromine as hydrogen bromide (M8a), a tautomer of the amidoxime (M8b). However, the mode of formation of the amidonitrone is less straightforward. One practical observation might be relevant in this respect. During the work up of the reaction conducted with hydrazine, the aqueous layer was made just alkaline with sodium carbonate and an intense blue colouration was observed. This was readily extracted into ether, and the solution on being allowed to stand in light at room temperature, in a stoppered flask for a few days, became virtually colourless. Such behaviour was identical with that reported for 1-chloro-1-nitrosoethanes[99]. One would expect a bromonitroso compound to behave similarly, and such a compound might possibly be an intermediate in the formation of the amido-nitrone (S24).

We have only two precedents to guide us as to the course of the reaction. Arens[89] (M1-M3) has reported that an amine and ethoxyacetylene gave a disubstituted amidine; Mabery and Kraus[90] (M4-M5) treated bromopropiolic acid

S



with aniline and p-toluidine, and isolated amidines in which the carboxyl group had been removed. It was thought desirable at this stage to confirm the postulated structure of the amidoxime (S23) by synthesis.

There are several possible routes to the formation of amidoximes, all involving the action of hydroxylamine hydrochloride on such substances as iminoethers[91], iminochlorides[92], nitriles[93], amidines[94] or thioamides[95]. The first two intermediates are rather unstable and difficult to handle, while the nitrile method, though extremely useful in many cases, does not work for phenylacetonitriles. As amidines are usually most readily prepared via the thioamide itself, it was decided to use N-butylphenylthioacetamide (S26) as starting material.

Sukurada[96] prepared a large series of analogous thioamides via thiocarboxylic orthoesters, which are not readily available. The neatest method, giving the highest yields is that due to Kindler and Findorf[97], in which the amide was heated in a sealed tube with aluminium sulphide and hydrated sodium sulphate. Since no aluminium sulphide was available to us, we used the method of Rivier and Schneider[98], in which crystalline phosphorus penta sulphide was added to a solution of N-butylphenylacetamide in hot xylene. The resultant malodorous N-butylphenylthioacetamide (S26) was used crude; treatment with hydroxylamine hydrochloride and sodium carbonate in ethanol yielded a crystalline compound identical with (S23), whose structure was thus considered to be confirmed.

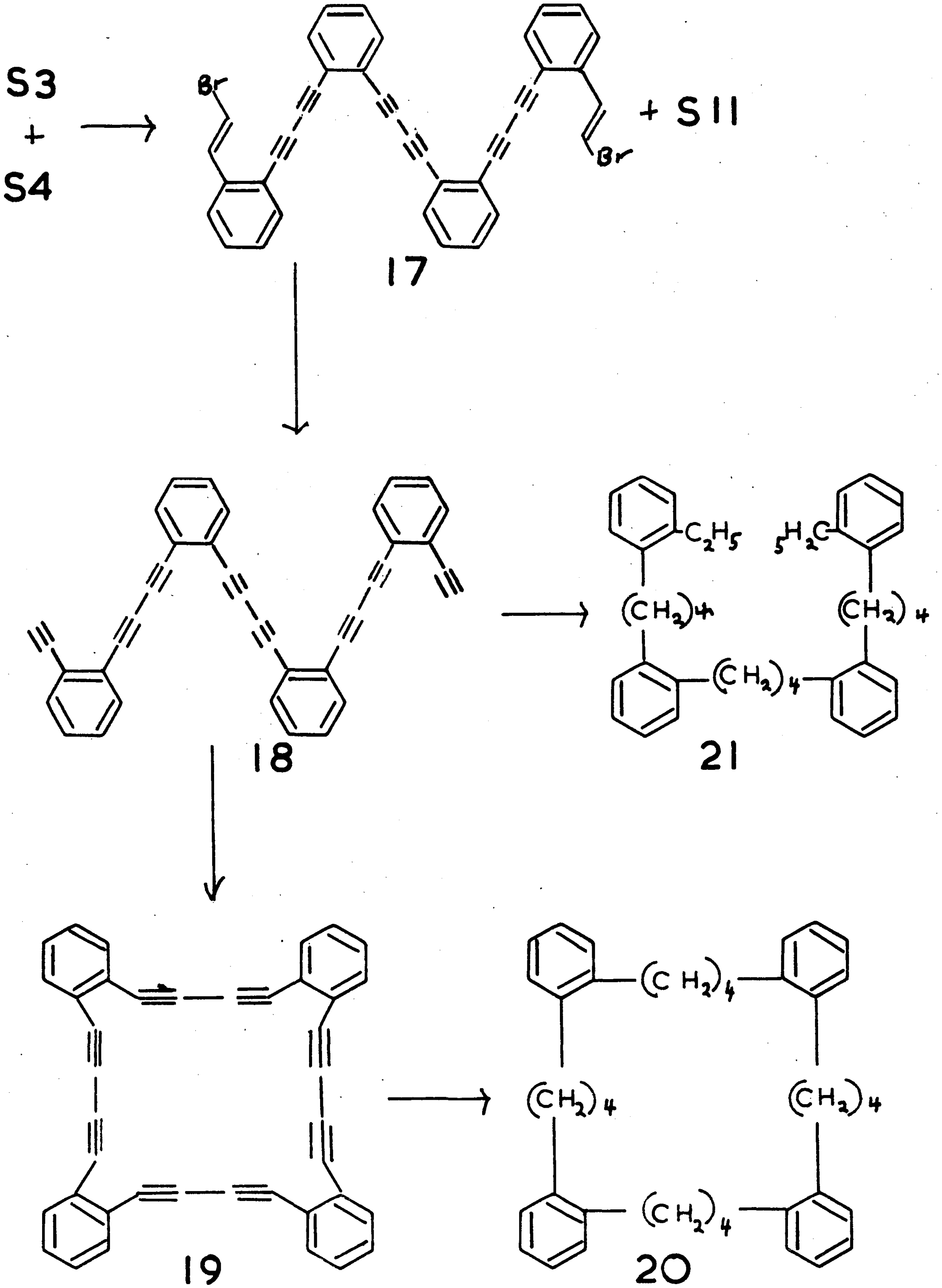
It is permissible to suggest an analogous route to the amidonitrone (S24) involving the action of the thioamide (S26) and N-butylhydroxylamine and subsequent rearrangement of the substituted amidoxime (S24a) to the amidonitrone. It will be remembered that while the amidoxime (S23) (as the base) contained interbonded hydroxyls which were shown by infra red studies to become free on dilution, the aldonitrone contained no trace of hydroxyl, bonded or otherwise in its infra red spectrum. From the diagrams shown (S24a and S24) it will be apparent that tautomerisation from one form to the other would not be difficult, and the aldonitrone (S24) might well be the most stable form.

Section 3. Possible routes to the trimer (S6).

There have been several postulated routes to the elusive trimer (S6). We will, however, only mention the two which now appear to be feasible. The dibromovinyldiyne (S11) was readily obtainable and appeared as an unwanted by-product in the formation of (S17). It was found that one mole of hydrogen bromide could be removed and the monobromotriyne (S16) isolated by careful chromatography.

The product thus obtained was self coupled to give (S17). However, since it contains but one free ethynyl group, there should be no great difficulty in solvating its copper derivative under standard Chodkiewicz conditions, thus eliminating the excess amine trouble discussed in Section 2. It could therefore be coupled with the bromovinyl bromoyne (S14) to give the desired precursor (S15) of the trimer (S6). Alternatively, a mixed coupling could be effected between excess bromovinylethynylbenzene (S3) and (S16), from which it might be possible to isolate the trimer precursor (S15).

S


S3
+
S4
Br
Br
+ S11
17
18
C_2H_5
$_5H_2C$
$(CH_2)_4$
$(CH_2)_4$
$(CH_2)_4$
21
19
$(CH_2)_4$
$(CH_2)_4$
$(CH_2)_4$
$(CH_2)_4$
20

PART C: The synthesis of the 'tetramer' 1,2:7,8:13,14:19,20-tetrabenzocyclotetracosa-1,7,13,19-tetraene-3,5,9,11,15,17,21,23-octayne (S19).

When the tetrayne (S12) was made it was thought that on high dilution coupling it might well dimerize to give (S19), as mentioned in Part A, Section 2 of this discussion, it merely ring closed to give the cyclic tetrayne (S5) in good yield.

The third false prediction of the course of the coupling reactions occurred when (S4) was coupled with a large excess of the enebromyne (S3) with the intention of forming (S15) the precursor of the trimer (S6). We were unable to detect this compound, which may well have been formed. Apart from (S16) the expected dimer of (S3), the only compound which was isolated was a yellow powder (S17) which darkened in colour fairly rapidly on exposure to light and air. The infra red spectrum showed bands due to $C\equiv C$ and trans $C=CBr$ as well as the aromatic bands. The analytical figures for this compound were rather poor, as were those of the dehydrobromination product (S18) and, to a lesser extent, those of the cyclic product (S19). There are two reasons for this, namely, the difficulty of accurate analysis due to explosion during combustion, and the more serious factor of contamination by benzene.

The second hypothesis is supported by the presence of an absorption band at 680 cm^{-1} of varying intensity in the infra red spectrum of several samples of all the above-mentioned products. Neither (S17) nor (S18) could be recrystallised, nor, since they were both low melting and unstable, could they be strongly heated to drive off the solvent. The only method remaining, pumping under vacuum, was not sufficiently powerful, even when the freeze drying technique was employed. In the case of the dibromovinylhexayne (S17) the analytical figures, C, 74.33; H, 3.10, were closer to those required by a C_{40} structure (C, 72.75; H, 3.05%) than those required by a C_{30} structure (C, 67.3; H, 2.98%): a C_{50} polymer was rather unlikely (required: C, 76.7; H, 3.06%), though it could not be dismissed on this evidence alone. The analytical figures for the open and cyclised acetylenes (S18) and (S19) were of no significance in structural determination. The results obtained for their hydrogenation products (S,21, S20) were, however, very important. The microanalytical figures for (S21) showed without a doubt that the compound had the empirical formula proposed for it, and the mass spectroscopic molecular weight for both was absolutely correct, showing no further peak on the trace for more than 120 mass units above the required value. Due to the gummy nature of the hydrogenation product of (S19) it was not possible to obtain enough (S20) to obtain a microanalysis. The different solubilities observed in this crude hydrogenation product indicated that transannular reaction had again taken place, though substantiation of this postulate must await the isolation of more material.

The disappearance of bands due to ethynyl absorption in the infra red spectrum of the product of the high dilution coupling of (S18) was taken as evidence of the cyclic nature of (S19), and this was supported by the rise in intensity of the ultraviolet absorption spectrum of (S19) compared to (S18).

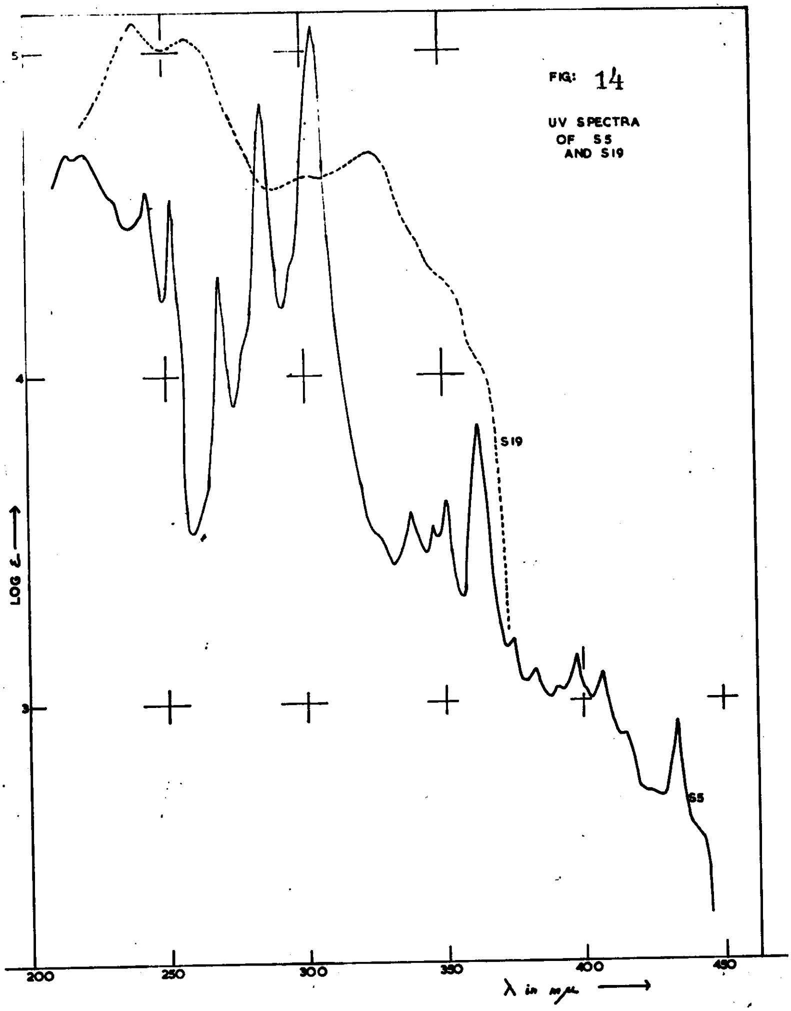


FIG: 14

UV SPECTRA
OF S5
AND S19

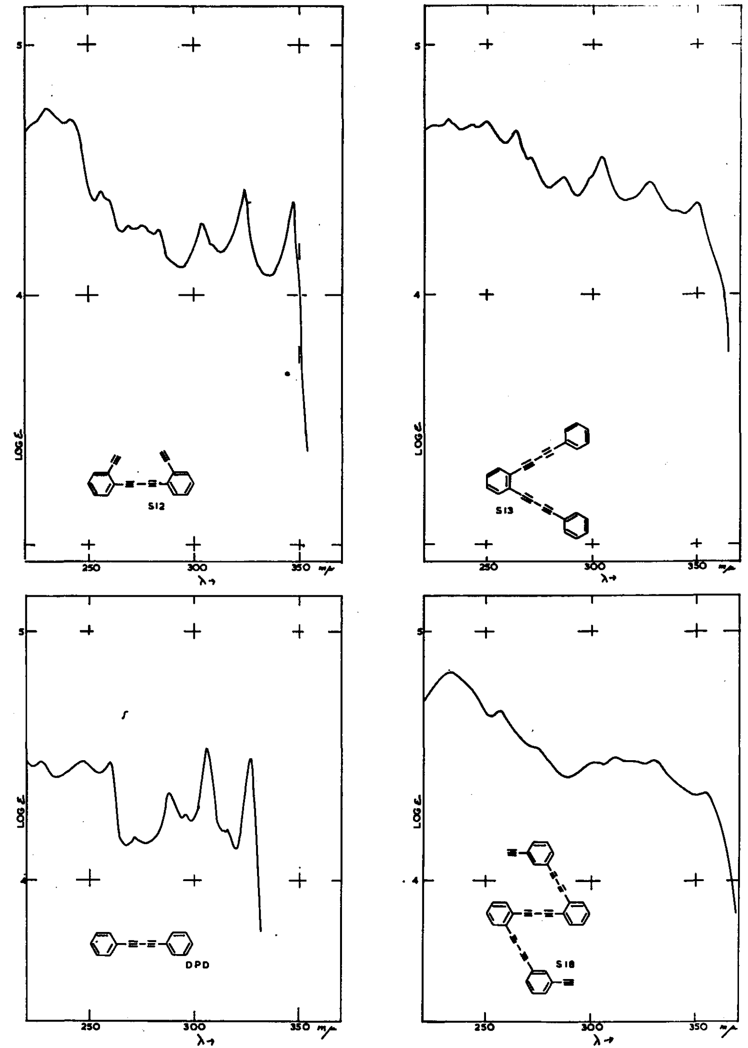


FIG: U.V. SPECTRA
15

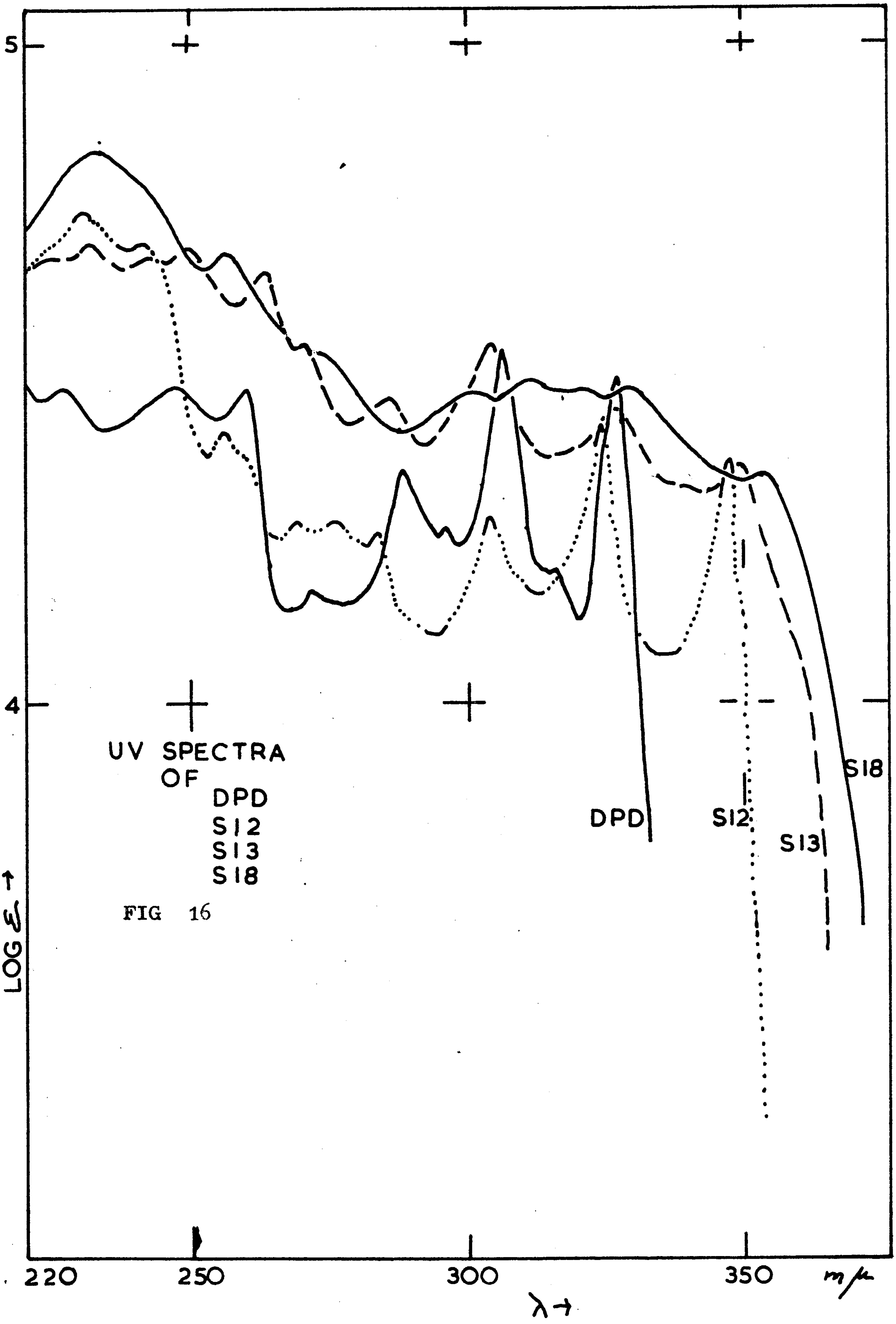

UV SPECTRA
OF
DPD
S12
S13
S18
DPD
S12
S13
S18
5
4
LOG ε ↑
220
250
300
350
mμ
λ →

FIG 16

PART D. The Ultra Violet Spectra of some polyaromatic αγ -diacetylenes.

The spectra tabulated here (with the exception of that of diphenyldiacetylene) are those of new polyaromatic αγ -diynes which have been prepared in ths course of this work. The spectra of Diphenyldiacetylene, S12, S13, and S18 are drawn out separately (Fig.15) and together for comparative purposes (Fig.16). The spectra of S5 and S19, the cyclic compounds, are drawn on Fig.14).

Diphenyldiacetylene in Ethanol			S12 in Cyclohexane		
$\lambda_{\text{min.}}$	$\lambda_{\text{max.}}$	log ε	$\lambda_{\text{min.}}$	$\lambda_{\text{max.}}$	log ε
223		4.46		231	4.75
	228	4.48	239		4.69
235		4.42		242	4.70
	247	4.48	253		4.28
256		4.43		256	4.41
	260	4.48	266		4.25
267.5		4.14		269	4.28
	271	4.18		276	4.28
	288	4.36		284	4.26
	296	4.27	294		4.10
299		4.22		304	4.29
	306	4.54	312		4.16
	316	4.20		324	4.42
320		4.13	336		4.02
	327	4.50		347	4.37

S13 in Cyclohexane			S18 in Ether		
$\lambda_{min.}$	$\lambda_{max.}$	log ε	$\lambda_{min.}$	$\lambda_{max.}$	log ε
	232	4.69		232.5	4.84
238		4.65			
	243	4.67			
	250	4.68			
258		4.60	252		4.64
	263	4.65		257	4.68
	271	4.54			
278		4.42			
	286	4.46			
292		4.38	288		4.41
	304	4.57		300	4.47
				311	4.49
314		4.37	326		4.47
	327	4.44		330	4.48
342		4.31	351		4.34
	349	4.36		354	4.35

S5 in Cyclohexane			S19 in Ether		
$\lambda_{\text{min.}}$	$\lambda_{\text{max.}}$	log ε	$\lambda_{\text{min.}}$	$\lambda_{\text{max.}}$	log ε
	192	4.68			
204		4.62			
	215	4.69			
217		4.68			
	221	4.69			
237		4.46			
	244	4.57		239	5.09
249.5		4.24	249		5.00
	252	4.55		257	5.04
260		3.52			
	269	4.31			
274.5		3.91			
	285	4.84			
292		4.21	288		4.58
	304	5.08		303	4.61
				324	4.69

S5 in Benzene		
λ min.	λ max.	log ε
332		3.41
	338	3.57
345		3.45
	346	3.53
348		3.50
	351	3.61
356		3.32
	362	3.83
372		3.15
	374.5	3.18
379.5		3.05
	382.5	3.08
387		2.999
	392	3.13
402		2.99
	406	3.07
412		2.88
	415	2.89
428		2.69
	433	2.92

S19 in Ether (contd.)		
λ min.	λ max.	log ε
	347	4.31
	354	4.26
	365	4.00

EXPERIMENTAL

General.

The following conditions for the physico-chemical measurements apply throughout the work reported unless otherwise stated. Melting points were measured on a Kofler hot stage and are corrected; ultraviolet spectra were generally measured on solutions in cyclohexane using a Unicam SP 500 spectrometer; infra red survey measurements were recorded on a Perkin-Elmer Model 13 or 117 and precise measurements on a Unicam SP 100 prism-grating spectrometer (only significant peaks in the IR region are reported). Nuclear magnetic resonance measurements, which are on the H_2O scale, were kindly made on a Varian 40 M/cs machine by Dr. N. Sheppard of the University Chemical Laboratories, Cambridge. Micro-Rast molecular weight determinations were made on 1.0 to 1.3 mg. of substance in *ca.* 11 mg. of camphor. Standard substances, e.g., 1,2:5,6:9,10-tribenzododeca-1,5,9-triene[101] and 1,4-diphenylbutane, gave results *ca.* 15% below the theoretical value. Other molecular weight measurements, kindly performed by Dr. V.M. Clark of Cambridge[71], were made in specially purified methylene chloride. Standardisation with 1,4-diphenylbutane gave values *ca.* 4% below theory. Gas-liquid chromatograms[102] were run on a Pye "Argon" chromatograph with a

4' column of 100-120 mesh Celite using 5% Apiezon 'L' as stationary phase, at ca. 220°, at flow rates of ca 30-50 ml./min.. The relative amounts of eluates were based on measurement of peak areas, not weight standardisation, and the quantitative results are therefore dependent on uniform detector response. The alumina for chromatography was acid washed, neutralised and standardised according to Brockmann's method; Grade I was used. Light petroleum was of b.p. 40-60°.

1,2-Divinylbenzene.

A slight modification of the literature route was used[57]. In the preparation of 1,2-di(ethoxycarbonylmethyl)benzene from 1,2-di(cyanomethyl)benzene, the pure nitrile was not isolated; this raised the overall yield from 1,2-di(bromomethyl)benzene from 58% to 82%. It was also found unnecessary to purify the 1,2-di(β-hydroxyethyl)-benzene prior to dehydration; thorough ether extraction of the diol was important. Contrary to previous reports[12], 1,2-divinylbenzene was found to polymerise slowly to a viscous glass.

1,2-Di($\alpha\beta$-dibromoethyl)benzene (S1).

Bromine (610 g.) in carbon tetrachloride (830 ml.) was added dropwise to a solution of 1,2-divinylbenzene (250 g.) in carbon tetrachloride (250 ml.). The reaction flask was cooled in an ice bath and stirred with a vibromixer. After addition of about 85% of the bromine, no further reaction appeared to take place. When all the bromine had been added, one third of the solvent was removed under reduced pressure and the residue left overnight at -10°. The resultant crystalline deposit was collected, the volume of solvent again reduced and a further crop obtained. The crude crystalline product was washed with light petroleum to give the tetrabromide (565 g., 66%) as light pink crystals. These were recrystallised from light petroleum (b.p. 60-80°) to give colourless plates m.p. 72-74° (Deluchat[12] reports m.p. 71-74°). (Found: C, 26.85; H, 2.45; Br, 70.9%. $C_{10}H_{10}Br_4$ requires C, 26.65; H, 2.40; Br, 70.9%). Further treatment of the residues from the mother liquors with ethanol/ether, and cooling to -10° yielded additional tetrabromide (80 g., 9%) of satisfactory purity. The remaining mother liquors appeared to contain partially brominated and polymeric material.

1-α-Bromovinyl-2-trans-β-bromovinylbenzene (S2).

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 vigorously stirred, ice-cooled solution of the tetrabromide (23.5 g., 52 m.mol.) in dioxan (50 ml.), the temperature being kept below 7°, a pale brown precipitate was formed almost immediately. The solvents were then removed under reduced pressure under nitrogen (55 mm., bath temp. 25-30°). The residue was treated with dilute (1.5%) hydrochloric acid, and thoroughly extracted with ether. The extract was washed, dried (sodium sulphate) and evaporated under reduced pressure to give the <u>dibromo-compound</u> (S2) (15.0 g.) as a pale orange oil of satisfactory purity. The infra red spectrum and a gas-liquid chromatogram (177°) showed this material, which was used as such in the next experiment, to be almost pure. A portion was distilled, b.p. 80° (bath)/4 x 10^{-4} mm., n_D^{22} 1.6385 (Found: C, 41.95; H, 3.1; Br, 55.25. $C_{10}H_8Br_2$ requires C, 41.7; H, 2.8; Br, 55.5%). (Deluchat[12] recorded b.p. 125-216°/2 mm., n_D^{23} 1.6366 for the dibromo-compound obtained by the action of sodium ethoxide on the tetrabromide (S1)) $\nu_{max.}$ (film), 3040 w, 1620 sh., 1605 m, 1218 m, 935 s (trans-CH=CHBr), 901 s (C=CH_2), 762 s, 730 m.br. cm^{-1}.

When sodium ethoxide in ethanol was employed[12] in the dehydrohalogenation, the reaction mixture being heated under reflux only briefly (1 min.), the product was found to be less homogeneous. Attempts to carry the dehydrohalogenation (potassium t-butoxide) through to the diyne in one step were unsuccessful.

1-trans-β -bromovinyl-2-ethynylbenzene (S3).

Dibromodivinylbenzene (6.17 g., 21.4 m.Moles) was dissolved in dioxan (ca. 10 ml.). A solution of potassium t-butoxide in t-butanol (0.356 N, 60 ml.) was added and the mixture warmed up slowly on a water bath to reflux temperature, and allowed to boil under reflux for fifteen minutes, a copious precipitate of potassium bromide was given. (In preliminary runs, e.g., using 5 ml. base, the solution was worked up with hydrochloric acid (0.1 N, 25 ml.) and distilled water, back titration with sodium hydroxide (0.1 N) gave a titre of 24.25, i.e., 97% reaction.) The reaction mixture was worked up with dilute acid, extracted with ether, washed thoroughly with water, and after drying and evaporation of solvent, gave a dark red mobile oil (4.04 g., 19.6 m.Moles, 91%), which was used without further purification. Gas liquid chromatography (168°, R.T. 6 mins.) showed that the product contained 1-trans-β -bromovinyl-2-ethynylbenzene (S3) (> 90%), unchanged dibromodivinylbenzene and diethynylbenzene. Distillation at 100° (bath)/2 mm. yielded a pale yellow oil n_D^{25} 1.6218 (Found: C, 58.3; H, 3.60; Br, 38.35. $C_{10}H_7Br$ requires C, 58.0; H, 3.4; Br, 38.5%). $\nu_{max.}$ (film) 3260 (≡CH), 3050, 2100 w. (C≡C), 1605, 952, 934 (trans. C=CBr) cm^{-1}. (trace band at 901 cm^{-1})).

1,2-Diethynylbenzene (S4).

Potassium (6.32 g., 0.16 mol.) was dissolved in t-butanol (ca. 400 ml.). After the butanol had been removed under reduced pressure, the potassium t-butoxide was dissolved in dry benzene (ca. 600 ml.) and the opalescent solution then stirred vigorously (Hirshberg stirrer), and heated under reflux. A solution of 1-α-bromobinyl-2-trans-β-bromovinylbenzene (15.0 g., 52 m.mol.) in dry benzene (100 ml.) was then added and the mixture stirred and heated for 4 hours. During the course of the reaction, aliquots were removed, worked up and their infra red spectra inspected for the presence of absorption at 1650 cm^{-1} due to C=C; after 3.5 hours this absorption was found to have disappeared (continuing the reaction after the dehydrobromination was complete was detrimental to the yield). It is important, however, not to use more than 30% excess base otherwise too much polymeric material tends to be formed. The reaction mixture was cooled, ether (ca. 100 ml.) was added and the mixture shaken with dilute hydrochloric acid. The handling of the product after completion of the actual dehydrobromination requires great care and the final yield is very much dependent on it. The mixture of ether, benzene and crude product was evaporated on a waterbath whose temperature did not rise above 30°, under water pump vacuum, a pine splinter rather than a nitrogen bubbler was used to prevent bumping. Conditions more vigorous than these cause some of the product to codistil with the solvent; it was preferable to remove the last traces of benzene at not more than 20° after transference of the mixture to a smaller flask. A considerable amount of polymeric material was formed in the reaction which was not only undistillable, but appeared to occlude the desired product. Part of this polymer could be removed by precipitation with light petroleum. It was advisable to distil the crude product at the lowest possible temperature and pressure (bath temp. $40\text{-}60^{\circ}/10^{-4}$ mm) and employ a liquid air-cooled receiver. The product thus obtained was sometimes very slightly contaminated by solvent, but was quite pure enough for synthetic purposes. Redistillation gave 1,2-diethynylbenzene (4.6 g., 70%) as an almost colourless oil, b.p. $80\text{-}82^{\circ}/14$ mm., n_D^{20} 1.5900 (Deluchat[12] reported b.p. $80\text{-}82^{\circ}/14$ mm., $n_D^{17.5}$ 1.5915). (Found: C, 94.95; H, 5.0. $C_{10}H_6$ requires C, 95.2; H, 4.8%). On one occasion the compound decomposed violently on attempted distillation. Light absorption $\lambda_{max.}$ (hexane) 217, 222, 227, 251, 256, 264 mμ (log ε 4.54, 4.50, 4.71, 4.13, 4.10, 4.10) $\nu_{max.}$ (CCl_4) 3312 <u>s</u>, 2107 <u>w</u>; (CS_2) 756 cm^{-1}. 1,2-Diethylbenzene was formed on catalytic hydrogenation of a small portion over palladium-charcoal (10%) in ethyl acetate and was identified by comparison of its infra red spectrum with spectrum number 1419, API project 44.

1,2:7,8-Dibenzocyclododeca-1,7-diene-3,5,9,11-tetrayne (S5).

Anhydrous cupric acetate (12.1 g., 67 m.mol.) was dissolved in a mixture of dry pyridine (600 ml.), and methanol (600 ml.), and ether (100 ml.), then added to the solution. 1,2-Diethynylbenzene (1.97 g., 15 m.mol.) in a mixture of pyridine and methanol (1:1, 400 ml.) was added over 5.5 hrs. to the copper acetate solution, using the high-dilution technique[53]. The dark green solution was heated under reflux for a further 45 mins., set aside overnight and filtered through a sintered-glass funnel. It was then poured on to a stirred mixture of sulphuric acid (700 ml., 50 v/v%), chopped ice (ca. 1 kg.), and ether (500 ml.), more ice being added to maintain the temperature below 15°. Three layers were formed - the upper ether layer, a brown-green emulsion, and the aqueous layer. The last two were thoroughly extracted with ether and the combined ether extracts washed with dilute sulphuric acid, water, sodium carbonate solution, and dried (Na_2SO_4). The bulk of the solvent was removed under reduced pressure in a stream of nitrogen (bath temp. less than 30°) and the last 50 ml. were removed at room temperature. Benzene (40 ml.) was then added, the mixture warmed gently and filtered from an insoluble cream residue (ca. 100 mg.). The filtrate was immediately chromatographed on alumina (Type H; 190 g.). Elution of the bright yellow band with benzene (250 ml.) gave a dark orange solution of the hydrocarbon S5 (842 mg., 43%, spectroscopic estimation based on the intensity of the 304 mμ absorption band). Slow crystallisation from benzene at ca. 0° yielded the pure hydrocarbon as canary yellow needles. /Found: C, 96.8; H, 3.55; M (thermistor drop)[71] 245. $C_{20}H_8$ requires C, 96.75; H, 3.25%; M, 248/. $\nu_{max.}$ (CCl_4; grating spectrometer) 3112, 3085, 3063, 3026, 2187, 2116, 1953, 1920, 1889, 1852, 1816, 1747, 1698; (CS_2) 1270, 1163, 1035, 947, 754, 692; (KBr prism) 476 cm^{-1} $\lambda_{max.}$ (cyclohexane) 192, 215, 221, 244, 252, 269, 285, 304 mμ (log ε 4.68, 4.69, 4.69, 4.57, 4.55, 4.31, 4.84, 5.08); (benzene) 338, 346, 351, 362.5, 374.5, 382.5, 392, 406, 415, 433 mμ (log ε 3.57, 3.53, 3.61, 3.83, 3.18, 3.08, 3.13, 3.07, 2.89, 2.92); $\lambda_{min.}$ (cyclohexane) 204, 217, 237, 249.5, 260, 274.5, 292 (log ε 4.62, 4.68, 4.46, 4.24, 3.52, 3.91, 4.21); (benzene) 332, 342.5, 348.5, 356, 372, 379.5, 387, 402, 412.5, 428 mμ (log ε 3.41, 3.45, 3.50, 3.32, 3.15, 3.05, 2.999, 2.99, 2.88, 2.69). (Cary model 11;) we are indebted to Dr. R.S.M. Smellie for this determination. The yellow colour and associated long wave absorption (395-450 mμ) were established as being characteristic features of the pure hydrocarbon by examination of successive fractions eluted from a benzene chromatogram of the hydrocarbon over alumina, when the relative intensities of the peaks were found to be constant. Nuclear magnetic resonance measurements gave only one peak (with fine structure) at $\sigma = -1.80$ (dioxan), $\sigma = -1.75$ (CH_2Cl_2).

The best crystallisation solvent was benzene (solubility: 6 mg/ml. at 20°, 10 mg/ml. at 55°). The hydrocarbon is, however, moderately soluble in tetrahydrofuran and slightly soluble in ether, dioxan, carbon tetrachloride (2 mg/ml.), chloroform, methylene chloride (1 mg/ml.), ethyl acetate, n-hexane and cyclohexane (1 mg/100 ml.) and in pyridine. The hydrocarbon is unstable in the crystalline state, decomposing explosively when ground (e.g., during the preparation of a nujol mull), or when heated above 80°. After a few days at room temperature either in air or vacuum, in the light or in the dark, the crystals, though unchanged in shape, are black, insoluble, and no longer give a distinct X-ray diffraction pattern. Storage in the solid state is feasible for several weeks at -5°, though it is better to store the compound as a benzene solution. It is more stable in pyridine than in benzene; for instance, a dilute solution of the hydrocarbon (ca. 1 mg/2 ml.) in pyridine darkened only slowly at 100°, whereas a similar solution in benzene at 80° charred after a few minutes. The density of the hydrocarbon was determined by flotation of a large crystal (ca. 5 mm. x 0.1 mm.; very small crystals were unduly sensitive to convection effects) in an aqueous solution of zinc chloride whose density was then measured. Adsorbed and dissolved air were removed from the crystal and the solution respectively by pumping at the water pump for 15 mins. Found: d_4^{19} = 1.283 (from dioxan), 1.306 (from benzene). The dimensions of the unit cell were found[2] to be a = 28.3, b = 3.87, c = 11.5 Å, (β = 90°), and hence for four molecules of M. 248 the required density is d = 1.308.

The isolation procedure described was found to be superior to that involving the removal of the solvent under reduced pressure, acidification of the residue and extraction with ether, as less decomposition of the product occurred.

The hydrocarbon formed a 1:1 complex with trinitrofluorenone[103]; red needles, m.p. 160° (decomp.) (from acetic acid) (Found: C, 70.5; H, 2.8; N, 7.7. $C_{20}H_8.C_{13}H_5N_3O_7$ requires C, 70.4; H, 2.4; N, 7.5%). Hexanitrosobenzene[104] in ethanol-acetic acid (4:1) did not form a complex.

Catalytic hydrogenation of 1,2:7,8-dibenzocyclododeca-1,7-diene-3,5,9,11-tetrayne (S5).

A solution of the hydrocarbon (806 mg., 3.2 m.mol.) in tetrahydrofuran (40 ml.) was added to palladium charcoal (1643 mg., 10%, 'Baker') which had been prehydrogenated under ethyl acetate, and the hydrogenation carried out in the usual manner. The uptake was 382 ml. (16.1 m.mol.) of hydrogen (68% of theory) after five hours, most of the hydrogen (60% of theory) being taken up in the first ten minutes. Evaporation of the solvent, together with the hot chloroform used for extraction of the catalyst, left an oil (564 mg.), trituration of which with ether yielded a colourless crystalline solid. This solid, after sublimation, at 210°/10^{-4} mm. was identified as "trans-fluorenacene" /indeno (1,2-b)fluorene (S7)/, m.p. 300-302° (sealed tube; uncorrected). (Found: C, 94.3; H, 5.80. Calc. for $C_{20}H_{14}$ C, 94.45; H, 5.55%). $\nu_{max.}$ (KCl disc) 955 m, 870 m, 770 s, 730 s cm^{-1}. Infra red and ultraviolet absorption spectra (in ether) were identical with those of a genuine sample[15]; the mixed melting point, 298-300°, was undepressed. The residual oil was chromatographed on alumina (40 g.).

(a) Elution with light petroleum (60/80) yielded a colourless oil (263 mg.), trituration of which with methanol/ether led to the deposition of 1,2:7,8-dibenzocyclododeca-1,7-diene (S8) (ca. 100 mg.), which crystallised from ethanol in colourless needles, m.p. 103-105° [Found: C, 90.8; H, 8.95; M. 224 (micro Rast). $C_{20}H_{14}$ requires C, 90.85, H, 9.15%; M. 264]. $\nu_{max.}$ (CS_2) 765, 756, 740 cm^{-1}, [no absorption near 1370 cm^{-1}, (CH_3)]. $\lambda_{max.}$(cyclohexane) 266.5, 274 mμ (log ε 2.91, 2.88), $\lambda_{min.}$ 237, 271 mu (log ε 1.90, 2.72). Tetralin[105] has $\lambda_{max.}$(isooctane) 267, 273 mμ (log ε 2.77, 2.77). The nuclear magnetic resonance spectrum showed bands with fine structure at $\tau = -1.90$ (aromatic CH), + 2.37 (benzyl CH_2) and +3.45 (saturated CH_2), 1,4-diphenylbutane and tetralin had similar absorption.

(b) Benzene-light petroleum (1:9) yielded an oil (146 mg.), which after trituration with ether/ethanol deposited a crystalline material (ca. 30 mg.) recrystallisation of which from methanol gave a naphthalene probably (S9) as colourless plates, m.p. 117-119°. [Found: C, 93.6; H, 6.5; M. 235 (micro Rast). $C_{20}H_{16}$ requires C, 93.7; H, 6.3%; M. 256)]. The mass spectrogram showed peaks at mass numbers 91, 115, 141, 142, 166 and 256 (parent peak). Structure (S9) is consistent with this pattern in view of the known propensity for fission at benzylic carbons. Thus, the peaks at 115, 141 and 142 normally occur in the cracking pattern of a methylnaphthalene or a methylene naphthalene ($C_{11}H_9$, 141) fragment. Mass numbers 91 and 166 probably represent the benzyl (C_7H_7, 91) and benzindane ($C_{13}H_{10}$, 166) fragments respectively. $\nu_{max.}$ (CS_2) 870, 804, 766, 749, 741 cm^{-1}, $\lambda_{max.}$ (cyclohexane) 236, 268, 275, 310, 316, 324 mμ (log ε 4.82, 3.75, 3.82, 3.03, 2.92 and 3.09 respectively). $\lambda_{min.}$ 248 (log ε 3.37). 2,3-Benzindane[87b] has $\lambda_{max.}$ 322, 315, 310, 292, 285, 280, 276, 270, 264, 228 mμ (log ε 3.38, 3.03, 3.62, 3.65, 3.73, 3.70, 3.62, 3.54 and 4.99 respectively).

(c) Elution with benzene yielded a red oil (34 mg.), from which, on treatment with ether and very slow evaporation, a further small quantity of indeno(1,2,-b)fluorene (S7) separated.

The gas liquid chromatogram (214°, 40 ml./min.) of the crude reduction product, showed that the hydrocarbons (S8), m.p. 103° (R.T. 20 min.), and (S9), m.p. 117° (R.T. 35 min.), constitute 50 and 38% of the mixture respectively. Six other peaks were noted from the trace. The hydrocarbon (S7) m.p. 300°, which gave a broad peak (R.T. 47 min., 75 ml./min.) too weak to be measured, was estimated from the amount isolated, to constitute at least 3% of the product.

The two low-melting products, (S8) and (S9), are very soluble and tend to crystallise together, and consequently only relatively small amounts of pure material were isolated.

Sodium-liquid ammonia reduction of 1,4-diphenylbuta-1,3-diyne (with J.W. Purdie).

A solution of the diyne (1.10 g., 5 m.mol.) in dry tetrahydrofuran (50 ml.) was added slowly to a solution of sodium (920 mg., 40 m.mol.) in liquid ammonia (300 ml.), the colour changing from blue through violet and red to a dull orange. More sodium (1.84 g., 80 m.mol.) was then added, the mixture becoming green then blue. The volume was increased to 500 ml. with liquid ammonia and the mixture stirred for two hours, after which dry ammonium chloride was added slowly until the colour changed to pale yellow. After evaporation of the ammonia the residue was treated with dilute hydrochloric acid (6N., 50 ml.) and thoroughly extracted with ether. The neutral fraction was chromatographed on alumina (grade III, 30 g.). Elution with light petroleum yielded a colourless oil, the infra red spectrum of which demonstrated the presence of nonconjugated ethylenic material, $\nu_{max.}$ (film) 966 cm^{-1} (trans C=C), $\lambda_{max.}$ (cyclohexane) 260 mμ (log ε 2.77).

A portion of the oil (42 mg., 0.208 m.mol.) was hydrogenated in ethyl acetate over palladium-charcoal (10%) resulting in a hydrogen uptake of 0.114 m.mol. and the formation of 1,4-diphenylbutane [$\nu_{max.}$ (nujol) 745, 698 cm^{-1} /7.

Sodium-liquid ammonia reduction of 1,2:7,8-dibenzocyclododeca-1,7-diene-3,5,9,11-tetrayne (S5).

A solution of the hydrocarbon /̄1.3 g., 5.2 m.mol. (spectroscopic estimation) /7 in tetrahydrofuran (100 ml.) was added slowly to a solution of sodium (1.70 g., 74 m.mol.) in liquid ammonia (300 ml.). More sodium (4.9 g., 2.13 m.mol.) was then added and the volume of the reaction mixture increased to 750 ml., by addition of liquid ammonia. After stirring for two hours ammonium chloride (dried for 12 hours at 120°; omission of this precaution gave rise to increased carbonyl absorption in the product) was added slowly, the blue solution becoming colourless. The ammonia was allowed to evaporate overnight and the residue then dissolved in dilute hydrochloric acid (6N., 200 ml.), and thoroughly extracted with ether. The extract was washed with saturated sodium carbonate solution, dried (sodium sulphate) and evaporated. The residual yellow oil (1.367 g.), $\nu_{max.}$ (film) 1750 s, 1700 s cm^{-1} (carbonyl impurity) was dissolved in benzene/light petroleum (1:1) and chromatographed on alumina (type 'O'; 100 g.). Three fractions were obtained. Elution with (a) benzene/light petroleum (1:19, 400 ml.) yielded, on evaporation, a colourless gum (821 mg., 3.3 m.mol.; (b) benzene/light petroleum (1:2, 300 ml.) yielded a yellow gum (150 mg.), $\nu_{max.}$ 970 m cm^{-1}, and (c) with ether (200 ml.) yielded a brown gum (160 mg.). Fractions (b) and (c) were not further examined.

Fraction (a) on hydrogenation over platinum oxide (190 mg.) in ethyl acetate containing one drop of perchloric acid, absorbed only 2.28 ml. (94 μmol.) after 85 minutes. The resulting gum (760 mg.) when triturated with ether deposited a precipitate (40 mg.) which after crystallisation from chloroform/ether furnished *α-4b,5,5a,10b,11,11a-hexahydroindeno(1,2-b)fluorene*(S10) as rectangular plates, m.p. 230-231°. [Found: C, 92.4; H, 7.9; M (thermistor drop) 245 (in $CHCl_3$). $C_{20}H_{20}$ requires C, 92.25; H, 7.75%; M, 260], $\nu_{max.}$ (CS_2) 741 cm^{-1} [no absorption near 1370 cm^{-1} ($C-CH_3$)], $\lambda_{max.}$ (cyclohexane) 260.5, 266.5, 273 mu (log ε 3.18, 3.39, 3.41) $\lambda_{min.}$ 233, 262.5, 270 mμ (log ε 2.02, 3.15, 3.00). 1,2-Dimethylindane[70] (in *iso*octane) has $\lambda_{max.}$ 260, 267, 273 mμ (log ε 2.90, 3.10, 3.16) $\lambda_{min.}$ 232, 264, 270 (log ε 1.52, 2.85, 2.63). The ethereal mother liquor was concentrated and chromatographed on alumina (100 g.) and 50 ml. fractions were collected. Elution with light petroleum (60-80°, 650 ml.) yielded crystalline and partially crystalline fractions (468 mg.). The combined fourth and fifth fractions were recrystallised several times from methanol-ether to give <u>β-4b,5,5a,10b,11,11a-hexahydroindeno-(1,2-b)fluorene</u> (S10) as long needles, m.p. 120-122° /Found: C, 91.9; H, 8.05; M. (thermistor drop) 259 ($CHCl_3$), 246 (CH_2Cl_2)/, $\nu_{max.}$ (CS_2) 769, 741, 735, 722 cm^{-1} /no absorption near 1370 cm^{-1} ($C-CH_3$)/; $\lambda_{max.}$ (n-hexane) 260.5, 267, 273.5 mμ (log ε 3.33, 3.45, 3.45); $\lambda_{min.}$ 234, 262.5, 271 mμ (log ε 2.47, 3.30, 3.19). Nuclear magnetic resonance showed bands at σ = -1.65 (aromatic H) and diffuse absorption between σ = 2 and 4, with a maximum at σ = 2.7. The benzylic methylene in tetralin and 1,4-diphenylbutane shows absorption at σ = 2.7; the broad absorption regions are typical of rigid systems. Elution with increasing proportions of benzene up to pure benzene, provided a further 155 mg. of semi-crystalline material, which was not further examined. Gas-liquid chromatography (224°, 20 ml./min.) showed that the crude reaction product before alumina chromatography contained: α-isomer (R.T. 18 min. 21%), β-isomer (R.T. 16 min.; 48%), 1,2:7,8-dibenzocyclododeca-1,7-diene (S8) (R.T. 14 min.; 8%), and the naphthalene (S9) (R.T. 28 mins., 7%), and at least four other minor components. Immediately after this chromatogram had been run, a pure sample of the β-isomer was chromatographed to determine the inherent degree of isomerisation. The proportions given are therefore corrected.

Isomerisation of β-to α-4b,5,5a,10b,11,11a-hexahydroindeno-(1,2-b)fluorene (S10).

During gas liquid chromatography (4% Apiezon "L" on 100-120 mesh Celite at 214°) of the two hexahydrofluorenes (S10) it was noted that the α-form gave rise to one peak but the β-form gave two peaks, the retention time of the second peak of the β-form being the same as that for the α-form. Alteration of the flow rate of the carrier gas (100 ml./min. to 24 ml./min.) showed that the relative area of the second β-peak decreased as a function of retention time (from 10.5 min. to 30.5 min.). A later chromatogram run under identical conditions on an apparently similarly prepared column showed a α:β-ratio different from that in the previous experiment. In all experiments crystalline samples of the highest purity were used. Attempts (KOH, ethylene glycol, 244°, 3 hours; "Celite", 300°, 3 hours) to isomerise the β-(120°) to the α-(230°)-hydrocarbon were unsuccessful, the 120° compound being substantially unchanged.

Dehydrogenations.

(a) General. The following procedure was used for all the dehydrogenations[107]. The hydrocarbon to be dehydrogenated was placed in a tube (diameter ca. 7 mm.) which was sealed at one end. The hydrocarbon was then covered with thoroughly dried, granular palladium-charcoal (15%)[108], and the tube sealed under nitrogen. After total immersion in a silicone oil bath for two hours at 320°, during which time the tube was inverted to ensure the complete mixing of the components, the tube was cooled, opened, and the product sublimed out directly under high vacuum (ca. 5 x 10^{-5}mm.). The recovery in all cases was almost quantitative. Tetralin (5.2 mg.) after dehydrogenation with palladium-charcoal (43 mg.) gave crystalline naphthalene in high yield.

(b) Dehydrogenation of the β-hexahydrofluorene (S10). The hydrocarbon (7.1 mg.) after dehydrogenation with palladium-charcoal (63 mg.) followed by sublimation at 230° (block) yielded indeno(1,2-b)fluorene (S7) m.p. 300-302°, undepressed mixed m.p., infra red (KCL disc) and ultraviolet (ether) absorption spectra were identical with those of a genuine sample[72].

(c) Dehydrogenation of the α-hexahydrofluorene (S10). Similar treatment of this hydrocarbon (25 mg.) furnished indeno(1,2-b)fluorene (S7) of slightly lower purity.

(d) Dehydrogenation of dibenzocyclododecadiene (S8). The hydrocarbon (6.9 mg.) was dehydrogenated with palladium charcoal (70 mg.) for five hours;

sublimation (230°) then yielded gummy crystals (5.1 mg.), $\lambda_{max.}$ (cyclohexane) 274, 280 mμ (log ε 3.59, 3.60), $\lambda_{min.}$ 257 mμ (log ε 3.58). Gas liquid chromatography (214°, 40 ml./min.) showed that the product consisted of unchanged (S8) (R.T. 23 min., 57%) and the naphthalene (S9), m.p. 117° (R.T. 39 min., 43%).

5,6-Benzo-1,10-diphenyldec-5-ene-1,3,7,9-tetrayne (S13).

Hydroxylamine hydrochloride (1.04 g., 15 m.Moles) and freshly prepared cuprous chloride (21 mg., 106 μ Moles) were dissolved under nitrogen in a mixture of n-butylamine (17 ml.) and ethanol (4 ml.) to form a colourless solution. Diethynyl benzene (630 mg., 5 m Moles) was added, the solution became pale yellow, and a very small amount of solid was noted in suspension. The 1-bromophenylacetylene (2.0 g., 10.5 m.Moles) in n-butylamine/ethanol (15 ml./3 ml.) was added very slowly, with vigorous stirring and ice cooling, the temperature being held between 14° and 18°. After two hours, an aliquot was extracted from the mixture, and found to show strong ethynyl absorption in the infra red. More bromoacetylene (300 mg., 1.6 m.Moles) was therefore added, and, after stirring for a further thirty minutes, examination of a second aliquot showed negligible ethynyl absorption. Potassium cyanide (ca. 1 g.), was added, the solvents evaporated under reduced pressure, and the residue extracted with ether. The neutral fraction, a brown gum, was chromatographed on alumina (grade H, 150 g.). Elution with light petroleum (300 ml.) yielded unreacted bromoacetylene, and elution with benzene/light petroleum (1:4) yielded a yellow gum, recrystallisation of which gave *5,6-benzo-1,10-diphenyldec-5-ene-1,3,7,9-tetrayne* (1.05 g., 3.2 m.Moles, 64%) as almost colourless needles, m.p. 130-132^{o} (from benzene/light petroleum) (Found: C, 95.45; H, 4.65. $C_{26}H_{14}$ requires C, 95.7; H, 4.3%). $\nu_{max.}$ (CS_2) 3080, 3062, 3032, 3020, 2211, 1492, 1481, 1444, 1111, 1071, 1030, 945, 913 cm^{-1}; (KCl disc) 760, 751, 683 cm^{-1}. $\lambda_{max.}$ (cyclohexane) 349, 327, 304, 286, 271, 263, 250, 243, 232 mμ (log ε 4.36, 4.44, 4.57, 4.46, 4.54, 4.65, 4.68, 4.67, 4.69). $\lambda_{min.}$ (342, 314, 292, 278, 258, 238 mμ (log ε 4.31, 4.37, 4.38, 4.42, 4.60, 4.65).

5,6-Benzo-1,10-diphenyldec-5-ene.

The parent tetrayne (52.2 mg., 157 μ Moles) was hydrogenated over palladium charcoal (10%) in ethyl acetate. Initial uptake was rapid (905 μ Moles in 30 mins.), though the final uptake (1.21 m.Moles) was only absorbed overnight. Evaporation followed by distillations under high vacuum gave substantially pure *5,6-benzo-1,10-diphenyldec-5-ene* as a pale yellow oil, b.p. 165^{o} (block)/ 8 x 10^{-5} mm. (Found: C, 90.6; H, 8.95. $C_{26}H_{30}$ requires

C, 91.15; H, 8.85%). $\nu_{max.}$ (film) 3010, 2930, 2850, 1600, 1490, 1450, 1080, 1034, 747, 698 cm^{-1}. $\lambda_{max.}$ (cyclohexane) 269, 265.5, 262.5 mu (log ε 2.98, 3.00, 3.04), $\lambda_{min.}$ 242 mu (log ε 2.73). Gas liquid chromatography indicated that the oil was a single substance (192°, R.T. 15 mins.).

Sodium/liquid ammonia reduction of 5,6-benzo-1,10-diphenyldec-5-ene-1,3,7,9-tetrayne.

A solution of the hydrocarbon (925 mg., 2.84 m. Moles) in tetrahydrofuran (50 ml.) was slowly added, with stirring to a solution of sodium (1.03 g., 45 m.Moles) in dry liquid ammonia (250 ml.). On completion of the addition, the solution became grey-green. Sodium (3.15 g., 137 m.Moles) was added and the volume of the solution made up to one litre with liquid ammonia: after about half an hour the solution had become a dark green blue. After three hours, the mixture was decomposed with dry ammonium chloride, and the ammonia allowed to evaporate. The neutral fraction was a pale yellow oil (930 mg.) $\nu_{max.}$ (film) 1605, 970 cm^{-1}. This on hydrogenation over palladium charcoal (10%, 335 mg.) in ethyl acetate, absorbed (after 20 hours) 0.94 ml. (38.8 µ Moles) of hydrogen. The resulting oil (786 mg.) had no infra red absorption band at 970 cm^{-1}. $\lambda_{max.}$ (hexane) 273, 268, 266.5, 262 mμ (log ε 2.76, 2.90, 2.94, 2.95). The oil was chromatographed on alumina (75 g.), three main fractions being obtained. Elution with

a) benzene/light petroleum (1:49) yielded 5,6-benzo-1,10-diphenyldec-5-ene as a colourless oil (485 mg.) b.p. (block) $140^{\circ}/10^{-4}$ mm. (Found: C, 91.31; H, 8.54%) $\lambda_{max.}$ (hexane) 268.5, 265, 262 mμ (log ε 2.80, 2.84, 2.87). These values differ only very slightly from those obtained from the catalytically hydrogenated product;

b) benzene/light petroleum (1:9) yielded a colourless oil (238 mg.) $\lambda_{max.}$ (hexane) 273, 266, 262 mμ (log ε 2.82, 2.97, 2.96);

c) benzene yielded a yellow oil (95 mg.) $\nu_{max.}$ 970 cm^{-1}.

Fraction (b) was rechromatographed on alumina (25 g.). On elution with ether/light petroleum (1:199), fifteen column volumes were collected, and the elution followed by recording the optical density of the 266 mμ band. Appropriate fractions were re-examined for the presence of the 273 mμ side band. The first five (containing 92 mg.) contained decreasing amounts of the benzodiphenyldecene. The remaining fractions contained little if any of this hydrocarbon, and apparently consisted of a single substance (136 mg.) b.p. (block) $170^{\circ}/10^{-4}$ mm. (Found: C, 91.47; H, 8.43. $C_{26}H_{28}$ requires C, 91.71; H, 8.29%). $\lambda_{max.}$ (hexane) 273, 266, 261 mμ (log ε

3.01, 3.10, 3.07). Gas liquid chromatography later showed that this substance has two components (228°, R.T. 35, 38 mins. resp., ratio 13:2).

Di-(1-trans β-bromovinyl-2-ethynylbenzene) mercury.

Mercuric acetate (3.8 g., 12 m.Moles) was dissolved in n-butylamine (15 ml.) to give a cloudy solution, 1-trans β-bromovinyl-2-ethynylbenzene (4.95 g., 80% pure, 19.1 m. Moles) was added, and the mixture poured into water, immediately extracted with ethyl acetate and the extract washed with dilute acid and water. A yellow insoluble material was noted in the solvent layer: this was filtered off and discarded. The pale brown filtrate was dried overnight, filtered and evaporated to give the crude <u>mercury salt</u> (4.5 g., 7.33 m.Moles, 78%). Recrystallisation from ethyl acetate gave the salt as colourless needles m.p. 187-189°. $\nu_{max.}$ (nujol) 2130 ($C\equiv C-Hg-C\equiv C$), 1580, 1590, 950, 935, 758 cm^{-1}.

1-trans β-bromovinyl-2-ω bromoethynylbenzene (S14).

The bromovinyl ethynyl mercury salt (3.4 g., 5.54 m. Moles) was dissolved in benzene (150 ml.) and a solution of bromine (1.81 g., 22.6 m.Moles) in benzene added dropwise to it, with stirring. After most of the bromine solution (<u>ca.</u> 80%) had been added, the red colour persisted. The remainder was then added, the mixture stirred for ten minutes; after removal of the solvent, the residue was dissolved in a minimal amount of petrol, filtered and poured through a column of charcoal (1.5 g.) containing palladium charcoal (10%, 300 mg.). Evaporation of the petroleum eluent gave *1-trans β -bromovinyl-2- ω bromoethynylbenzene* b.p. 60° (bath)/10^{-4} mm. (Found: C, 42.1; H, 2.19. $C_{10}H_6Br_2$ requires C, 42.0; H, 2.10%) $\nu_{max.}$ (CCl_4) 3060, 3220 m (C≡CBr), 1605, 952, 939 cm^{-1}. Gas liquid chromatography showed the oil to be a single substance (171°, R.T. 14 mins.). After standing in a refrigerator for about one week, the oil became crystalline. It was not possible, however, to recrystallise it or to obtain a sharp melting point.

o-,o'-Di(trans-β -bromovinyl)-1,4-diphenylbutadiyne (S11)

Bromovinylethynylbenzene (S3) (4.04 g., 19.6 m. Moles) was dissolved in methanol (25 ml.) and a solution of cupric acetate (7.0 g., 3.9 m.Moles) in pyridine/methanol (1:1, 160 ml.) was added. After addition of about one third of this solution, the flask was warmed gently and the solution then changed from deep blue to green. The rest of the cupric complex solution was then added and the mixture heated, on a water bath, under reflux for five minutes, allowed to cool to room temperature, and worked up by acidification with hydrochloric acid, and extraction with ether. The ethereal solution was shaken with a solution of silver nitrate in aqueous ethanol to remove traces of uncoupled ethynyl material. A large quantity of water was then added, the organic material extracted with ether, the ethereal layer washed several times with water, dried and evaporated to give a yellow oil (3.84 g.); trituration with ether/methanol gave white crystals. Filtration through alumina (150 g.) in benzene/light petroleum yielded *o-,o'-di(trans-β-bromovinyl)-1,4-diphenylbutadiyne* (2.0 g., 9.8 m.Moles, 50%) as feathery needles (from methanol), m.p. 107-108° (Found: C, 58.56; H, 3.10; Br, 38.55. $C_{20}H_{12}Br_2$ requires C, 58.30; H, 2.90; Br, 38.80%). $\nu_{max.}$ (CCl_4) 3060, 2220 (C≡C), 1605, 955, 938 (trans C=CBr) cm^{-1}.

o-,o'-Diethynyl-1,4-diphenylbutadiyne (S12).

The dibromodivinyldiyne (S11) (1.35 g., 3.05 m.Moles) was dissolved in dioxan (*ca.* 10 ml.), and a solution of potassium t-butoxide in butanol (0.356 N, 25 ml.) added, the mixture then being heated under reflux for fifteen minutes. A copious precipitate of potassium bromide and slight darkening were noted. The mixture was worked up in the usual way. Evaporation of the solvent left brown crystals (768 mg.), which after purification by boiling with animal charcoal in light petroleum solution (60/80) crystallised from this solvent to give o-,o'-diethynyl-1,4-diphenylbutadiyne (610 mg., 2.44 m.Moles) as pale yellow needles m.p. 124-124.5° (Found: C, 95.61; H, 4.37. $C_{20}H_{10}$ requires C, 95.97; H, 4.03%) $\nu_{max.}$ (CCl_4) 3280 (C≡CH), 3050, 2220, 2110, 952 cm^{-1}. $\lambda_{max.}$ (cyclohexane) 347, 324, 304, 284, 276, 269, 256, 242, 231 mμ (log ε 4.37, 4.42, 4.29, 4.26, 4.28, 4.28, 4.41, 4.70, 4.75); $\lambda_{min.}$ 336, 312, 294, 266, 253, 239 mμ (log ε 4.08, 4.16, 4.10, 4.25, 4.38, 4.69). Previous to this experiment, attempts were made to dehydrobrominate the starting material with sodamide in liquid ammonia. It was not found possible to isolate an identifiable product.

Coupling of o-,o'-diethynyl-1,4-diphenylbutadiyne (S12).

Diethynyldiyne (S12) (2 51 mg., 1.0 m.Moles) was dissolved in pyridine/methanol (1:1, 20 ml.) and added dropwise to a solution of cupric acetate (837 mg., 4.3 m.Moles) in pyridine/methanol/ether (7:7:4, 90 ml.), via a high dilution system with ether as the circulating phase, over two hours. An aliquot (5 ml.) was taken after the mixture had been heated under reflux for a further half hour. It was worked up in the usual way and the residue after ether evaporation was dissolved in carbon tetrachloride (2 ml.) and the infra red spectrum recorded using 5.0 mm cells. Trace ethynyl absorption was noted as well as bands characteristic of the cyclotetrayne (S5). The main bulk was then worked up, washed with ethanolic silver nitrate, dissolved in benzene and filtered through an alumina column. An aliquot was evaporated and the residue recrystallised from benzene to give yellow needles dec. p. ca. 80°. $\lambda_{max.}$ (benzene) as for cyclotetrayne (S5). The crude solution gave a similar ultra violet absorption spectrum. A 1 ml. fraction of the crude benzene solution (total vol. 70 ml.) was diluted (1:99) and the optical density measured at 304 mμ in a 1.0 mm. cell. This gave $O.D._{304}$: 0.80, hence the 1 ml. fraction contained 1.67 mg. of the cyclotetrayne (S5), and the total yield, 115 mg. (46%).

1,24-Dibromo-3,4:9,10:15,16:21,22-tetrabenzotetracosa-1,3,9,15,21,23-hexaene-5,7,11,13,17,19-hexyne (S17).

1-Transbromovinyl-2-ethynylbenzene (S3)(8890 mg., 42.9 mM) and 1,2-diethynylbenzene (880 mg., 6.9 mM) were added to a previously filtered solution of cupric acetate (53 g., 292 mM) in a mixture of pyridine and methanol (1:1, 800 ml.). The mixture was allowed to stand at room temperature for 18 hours and then poured into a mixture of ether (500 ml.) and hydrochloric acid (1 l., 6N) and ice. The ethereal layer was washed with HCl (200 ml., 6N), then with water and saturated salt solution, dried and evaporated to give a red oil (ca. 9.84 g.). The oil was dissolved in benzene (30 ml.) and chromatographed on alumina (100 g.): elution with petrol/benzene (1:1) gave a pale yellow solution which on treatment with petrol (b.p. 40/60) yielded a very pale brown precipitate (400 mg.) m.p. 76-78°. The solution, after standing overnight at -12°, yielded another batch of the solid (400 mg.). The column was eluted with benzene and ether and a further quantity of the solid (80 mg.) was obtained in similar manner.

The combined mother liquors were evaporated, the residue dissolved in benzene (15 ml.) and diluted to 150 ml. with petrol. A red oil (1.6 g.) was precipitated and separated from the mother liquor. This red oil was chromatographed on alumina (120 g.). Elution with petrol benzene (7:3) yielded a pale yellow oil which, after standing in ether in the cold for some time, yielded a white crystalline material which was found to be identical with (diBr open rectangle). The bulk of the mother liquor (ca. 6.7 g. residue content) probably contains this material as well.

It was not found possible to purify the precipitated solid well. Found: C, 74.33; H, 3.10%. $C_{40}H_{20}Br_2$ requires C, 72.75; H, 3.05%.

$_{\text{max.}}$ (Nujol) 2200 *w* ($C\equiv C$), 1600, 1570, twinned *w* (ar and $C=C$), 935 *m* (trans $C=CBr$) and 755 *s* (ar) cm^{-1}. The 935 band is much weaker here relative to the 755 band than in the dibromovinyldiphenylbutadiyne (S11)

3,4:9,10:15,16:21,22-Tetrabenzotetracosa-1,7,13,19-tetraene-1,5,7,11,13,17,19,23-octyne (S18).

The dibromide (402 mg., 610 μM) was dissolved in dioxan (10 ml.), and a solution of potassium t-butoxide in butanol/dioxan (6 ml., 0.345 N, 2.06 mM) was added and the mixture heated under reflux on a steam bath for twenty minutes, after which time the solution was almost black. The solution was acidified with dilute hydrochloric acid, extracted with ether, thoroughly washed with water and evaporated to give a brown solid (360 mg.). This solid was dissolved in benzene and chromatographed on alumina (40 g.). Elution with benzene (70 ml.) yielded a white/brown solid (300 mg.). Further elution (170 ml.) yielded a further 36 mg. of the same material, but brown.

The evaporate from the chromatogram was dissolved in a little benzene and reprecipitated with petrol. $\nu_{\text{max.}}$ 3280 ($C\equiv CH$) *s*, 3020 *m* (Ar), 2220 *w* ($C\equiv C$) cm^{-1}, aromatic substitution bands. Light absorption in ether showed bands at $\lambda_{\text{max.}}$ 232.5, 257, 300, 311, 330, 354 mμ (log ε 4.84, 4.68, 4.47, 4.49, 4.48, 4.35); $\lambda_{\text{min.}}$ 252, 288, 326, 351 mμ (log ε 4.64, 4.41, 4.47, 4.34) (cary).

The acetylene was obtained as a pale yellow powder freeze dried from benzene, m.p. 58-60°

Found: C, 95.37; H, 4.20%; $C_{40}H_{18}$ requires C, 96.38; H, 3.64%.

3,4:9,10:15,16:21,22-Tetrabenzotetracos-1,7,13,19-tetraene (S21).

The acetylene (S18) (14 mg., 28.2 μM) in benzene was added to prehydrogenated palladium charcoal cata list (Baker, 10%, 15 mg.) in benzene at 20°. The uptake of hydrogen was 10.8 ml. (theory: 11.1 ml.). The product, on evaporation, was a pale yellow gum which was chromatographed on alumina (1 g.). Elution with benzene petrol (1:19, 40 ml.) yielded a colourless gum which crystallised on standing and gave colourless needles (from ethanol), m.p. 53-55° (Found: C, 90.40; H, 9.88%; M.W. (Mass Spec.) 530. $C_{40}H_{50}$ requires C, 90.50; H, 9.50%; M.W. 530).

1,2:7,8:13,14:19,20-Tetrabenzocyclotetracosa-1,7,13,19-tetraene-3,5,9,11,15,17,21,23-octyne (S19).

Tetrabenzotetracosoctyne (S18) (500 mg., 1 m.Mole) was dissolved in ether/methanol/pyridine (150 ml., 4:7:7) and added to a solution of cupric acetate (900 mg., 4.96 m.Moles) in a similar solvent mixture (150 ml.) via the high dilution method, over five hours. The mixture was heated under reflux for a further two hours, left overnight, filtered and worked up in the usual manner. The residue, a brown powder (340 mg.), was dissolved in warm benzene and chromatographed on alumina (40 g.). Elution with benzene (80 ml.) yielded a pale yellow solution, which on evaporation left a pale brown powder (200 mg., 0.4 m.Moles, 40%). Recrystallisation gave 1,2:7,8:13,14:19,20-tetrabenzocyclotetracosa-1,7,13,19-tetraene-3,5,9,11,15,17,21,23-octyne as rhombs (from benzene) Decomp. p. 198-200° (Found: C, 96.10; H, 3.96. $C_{40}H_{16}$ requires C, 96.75; H, 3.25%) $\nu_{max.}$ ($CHCl_3$) no absorption 3500 to 3200; 2211 (C≡C); 1959, 1930, 1900, 1852, 1819, 1780 (ar. subst.); (KCl disc) 1465, 1440; (nujol) 1195, 1159, 1110, 1035, 950 all w.; 755 (ar. 1,2-subst.), 685 m. (benzene contamination). $\lambda_{max.}$ (ether) 365, 354, 347, 324, 303, 257, 239 mμ (log ε 4.00, 4.26, 4.31, 4.69, 4.61, 5.04, 5.09) $\lambda_{min.}$ 288, 249 mμ (log ε 4.58, 5.00).

Catalytic hydrogenation of 1,2:7,8:13,14:19,20-tetrabenzocyclotetracosa-1,7,13,19-tetraene-3,5,9,11,15,17,21,23-octyne (S19).

Cyclooctyne (S19) (56 mg., 113 μ Moles) was dissolved in benzene and hydrogenated over palladium charcoal (Baker, 10%, 75 mg.) in benzene at 19°. Uptake after two hours: 36 ml. (82%). Evaporation of the solvent left a yellow oil (ca. 45 mg.) which on trituration with ether/ethanol yielded a gummy crystalline material. This was washed in ether to give the tetrabenzocyclotetracosatetraene (S20) as white crystals m.p. 125-127° (Found: (Mass spec.) M.W. 528, clear to above 650 mass numbers. $C_{40}H_{48}$ requires M.W. 528). $\lambda_{max.}$ (ether) 272, 264, 232 (shoulder) mμ (log ε 3.14, 3.18, 3.19); $\lambda_{min.}$ 270, 241 mμ (log ε 3.04, 2.83).

Partial Dehydrobromination of the Dibromodiyne (S11).

Dibromodiyne (S11) (425 mg., 1.035 m.Mol.) was dissolved in dioxan (5 ml.) and heated under reflux with potassium t-butoxide in t-butanol (0.345 N, 3 ml.) for thirty minutes. The mixture was then cooled, acidified with hydrochloric acid (0.1 N, 20 ml.), and extracted with ether. The aqueous layer was then titrated against sodium hydroxide solution (0.1 N), titre: 18.85. Therefore, 0.115 m.Moles or 11% of the dibromide had not reacted. The ether layer was evaporated to give a red oil (314 mg.); infra red absorption showed bands at 3290 ($C\equiv CH$), and 935 (trans $C=CHBr$) cm^{-1}.

Preliminary experiments had shown that a mixture of the tetrayne (S12) and the dibromide (S11) may be separated by chromatography on alumina. (S12) was eluted by benzene/light petroleum (1:19) and (S11) by benzene/light petroleum (3:17). The red oil was chromatographed on alumina (30 g.) and fractions of one column volume (30 ml.) were collected. Elution with benzene/light petroleum (3:47) (210 ml.) yielded oils (36 mg.). The infra red spectra showed high absorption at 3290 and very low absorption at 935 cm^{-1}. Elution with benzene/light petroleum (1:9) (120 ml.) yielded crystalline material (90 mg.). The infra red spectrum showed low absorption at 3290 cm^{-1} relative to that at 935 cm^{-1}. Further elution with the same eluant (200 ml.) yielded a dark brown oil (126 mg.), probably (S16). The infra red spectra of these fractions showed high absorption at 3290 as well as at 935 cm^{-1}.

Elution with benzene/light petroleum (3:17) (180 ml.) yielded oils (52 mg.). The infra red spectrum showed very low absorption at 3290 cm^{-1}, and high absorption at 935 cm^{-1}.

Oxidative self-coupling of (S16).

The oils (126 mg.) which were presumed to contain a high proportion of the bromovinylethynyl compound (S16) were dissolved in pyridine (5 ml.) and added to a solution of cupric acetate (244 mg.) in pyridine/methanol (1:1, 10 ml.). The blue solution immediately became green. It was left overnight and heated under reflux for fifteen minutes, then worked up in the normal way. The crude product (144 mg.) was dissolved in benzene/light petroleum (7:3) and filtered through an alumina column (2 g.) with benzene/light petroleum (1:1). Light petroleum (200 ml.) was added to the eluate, and the mixture left overnight at -12°. A white powdery precipitate was obtained. This was filtered off and found to be identical with a sample of the dibromovinylhexayne (S17) obtained by the route mentioned previously.

The anomalous Bromoacetylene/n-Butylamine Reactions.

General. The 'standard reaction mixture' referred to in the following reactions consisted of a mixture of ethanol/n-butylamine (1:4) in which was dissolved a trace of cuprous chloride (ca. 1% per mole of bromoacetylene). The resultant blue solution was rendered colourless by the addition of a reducing agent, in most cases, hydroxylamine hydrochloride.

Unsuccessful Cadiot couplings of o-diethynylbenzene with 1-ω bromovinyl-2-ω bromoethynylbenzene (S14).

a). Diethynylbenzene (S4) was added to the standard reaction mixture and stirred vigorously under nitrogen at 30, 18, and -10° respectively. A solution of the bromoacetylene (S14) was added slowly over two hours and the mixture stirred for a further hour. The greenish colour was immediately removed by the addition of more hydroxylamine hydrochloride. The reaction mixture was worked up by pouring it into water and isolating the neutral fraction. The product was in all cases an oil. $\nu_{max.}$ (film) 3290 s ($C{\equiv}CH$), and 2230 v.w. ($C{\equiv}CBr$) , 935 s (trans $C{=}CHBr$) cm^{-1}. Except in one case (b), mentioned below, no identifiable product was isolated.

b). The bromoacetylene (S14) (327 mg.) was added to diethynylbenzene (63 m.) in the standard reaction mixture over fifteen minutes, the mixture was stirred for one hour and worked up. The product, a brown oil (150 mg.) was dehydrobrominated by heating under reflux in a mixture of dioxan (5 ml.) and t-butoxide in butanol (5 ml., 0.272 N) for twenty minutes. A semi-crystalline mass (86 mg.) was isolated. This was chromatographed on alumina (5 g.). Elution with light petroleum yielded an oil (10 mg.). Elution with benzene/light petroleum (1:9, 150 ml.) yielded colourless crystals (52 mg.). Mixed melting point and infra red spectra showed these to be identical with the tetrayne (S12).

Action of the standard reaction mixture on (S14).

The bromovinylbromoacetylene (S14) (84 mg.) in ether (1 ml.) was added, over ten minutes, to the standard reaction mixture (5 ml.) under nitrogen at 18°. Hydroxylamine hydrochloride was added as required: after ninety minutes the mixture was worked up by pouring into water, acidified with dilute hydrochloric acid, whereupon a crystalline solid appeared in the ether layer. This was separated by centrifugation. (Evaporation of the ether layer yielded an oil (6 mg.)). The crystalline material (50 mg.) was washed with ether and dried under vacuum. This compound was found to be soluble in ethanol, methanol, chloroform and hot water. Recrystallisation yielded the hydrochloride (S22) as colourless needles (from hot water) m.p. 154-155°. (Found: C, 55.3; H, 6.75; N, 7.15 (O; 0.62)%. $C_{18}H_{27}N_2Br.HCl$ requires C, 55.7; H, 7.26; N, 7.25%). $\nu_{max.}$ (Nujol) 1645 (C=N) cm^{-1}, and aromatics. $\lambda_{max.}$ (ethanol) 250 mμ (log ε 4.13).

Treatment of the hydrochloride with saturated sodium carbonate solution yielded the base of an oil (from which the hydrochloride could be regenerated). $\nu_{max.}$ (CCl_4) 3400 (free NH), 1645 (C=N), 1250, 950, 935 (trans C=CBr) cm^{-1}.

Action of the standard reaction mixture on bromophenylacetylene.

a). Bromophenylacetylene (111 mg.) in ether (1 ml.) was added to the standard reaction mixture (4.2 ml.) at -10° under nitrogen: an excess of hydroxylamine hydrochloride was used. After stirring thirty minutes the mixture was poured into water, acidified and extracted with ether. Evaporation of the ether layer yielded crude 1,4-diphenylbut-1,3-diyne (27 mg.) contaminated with bromophenylacetylene. The aqueous layer was evaporated to dryness under vacuum, treated with saturated sodium carbonate solution, extracted with ether, washed with water, dried and evaporated to give an oil (74 mg.) (Base of S23).

b). The experiment was repeated using bromophenylacetylene (815 mg.) in the standard reaction mixture (21 ml.). The mixture was poured into water, acidified and extracted with ether; the aqueous layer was made alkaline with solid sodium carbonate and extracted with ether. This latter ether layer was washed with water and treated with hydrochloric acid (6N). Insoluble crystals (340 mg.) were formed in the ether layer and these were isolated by centrifugation. The crystals were recrystallised to give the hydrochloride (S23) as colourless plates (from ethanol) m.p. 182-184° (sublime on melting) (Found: C, 59.3; H, 7.6; N, 11.65; Cl, 14.42%. $C_{12}H_{18}N_2O.HCl$ requires C, 59.55; H, 7.85; N, 11.6; Cl, 14.6%). $\nu_{max.}$ (Nujol) 3000 cm^{-1} region (broad band), 1660 (C=N), 1550, 1225, 1180, 1150, 1080, 1055 cm^{-1}, and aromatic bands. $\lambda_{max.}$ (ethanol) 264, 258, 251 mμ (log ε 2.18, 2.31, 2.34, and rising end absorption).

Treatment of the hydrochloride with saturated aqueous sodium carbonate yielded an oil (Base of S23), $\nu_{max.}$ (CCl_4) 3600 (free OH), 3400 (free NH), 3200 (broad, H bonding), 1645 (C=N) cm^{-1}, 1500 cm^{-1} and below - complex band structure and aromatics. Studies on the Unicam S.P. 100 infra red spectrometer show that the hydrogen bonding is intermolecular since it disappears on dilution.

c) As above, with different isolation procedure.

Bromophenylacetylene (856mg..) was reacted as in (b) above. After two hours the mixture was evaporated to dryness under vacuum on a water bath, treated with hydrochloric acid (6N), extracted with ether (the ether layer together with the crystals in it were set aside), and the aqueous layer treated with solid sodium carbonate. A red oil (787 mg.) was given (in the light of further investigations the appearance of this oil was probably due to a salting out effect), which was insoluble in ether and benzene, but was soluble in chloroform and methanol. The infra red spectrum was identical with that of the solid crystalline material obtained in section (d). A seed of this latter caused the oil to become semi-crystalline: it was not found possible to recrystallise it.

d) As above using hydrazine hydrochloride as the reducing agent.

The experiment was carried out twice. Bromophenylacetylene (906 mg.) was reacted with the standard reaction mixture (21 ml.) which contained hydrazine hydrochloride (41 mg.). An olive green colouration appeared, more hydrazine hydrochloride was added and the colour changed slowly to a pale yellow brown: the temperature rose from -7° to +1°. (Since 4 ml. of the solution were added to the reaction mixture it is not certain if the temperature rise was due to insufficient cooling of the added solution.) The mixture was stirred for ninety minutes and evaporated on an oil pump at ice bath temperature; ether and hydrochloric acid (6N) were added: when water was added an insoluble oil separated out. The mixture was extracted with ether and the ether layer set aside.

The aqueous layer was made just alkaline with solid sodium carbonate, more oil separated out and the aqueous layer turned blue: ether extraction removed the colouration into the ether layer, which was set aside. The aqueous layer (together with the oil) was extracted with chloroform: evaporation yielded a red oil (1180 mg.). This oil was triturated with a mixture of benzene and light petroleum (60/80) to give dirty white crystals (870 mg.). Recrystallisation at low temperature gave the hydrochloride (S24) as colourless plates (from ethanol/ether) m.p. 84-85°. (Found: C, 64.7; H, 8.9; N, 9.5; Cl, 11.7%. $C_{16}H_{26}N_2O.HCl$ requires C, 64.3; H, 9.1; N, 9.4; Cl, 11.9%). $\nu_{max.}$ (film) 3000 cm^{-1} region (broad band), 1645 (C=N) 1580 cm^{-1} and aromatics. $\lambda_{max.}$ (ethanol) 264, 258, 252 mμ ($\log\varepsilon$ 2.07, 2.19, 2.05 and rising end absorption).

Treatment of the hydrochloride (S24) with saturated carbonate solution yielded the base as an oil which gave a red brown ferric chloride colouration (not very conclusive). $\nu_{max.}$ (film) 3400 (free NH) 3250 (bonded NH), 1650 (C=N), 1540-1510 (unresolved) cm^{-1}, $\nu_{max.}$ (CCl_4) 3400 (free NH), no OH bands, 1650 (C=N) cm^{-1}.

Degradation of the aldonitrone (S24).

a) With concentrated hydrochloric acid. The hydrochloride (S24) (50 mg.) was sealed in a Carius tube with concentrated hydrochloric acid (5 ml.): the tube was heated in an electrical furnace at 220° for six hours. The resultant solution was poured into water and extracted with ether. The ether extract was washed with water and treated with saturated sodium carbonate. The ether layer was set aside and the aqueous layer made acid and extracted with ether. Evaporation yielded a pale brown crystalline material (20 mg.): recrystallisation from light petroleum yielded phenyl acetic acid m.p. 74-75°. This sample gave no depression of melting point when mixed with a genuine sample m.p. 76-77°.

b) With sodium hydroxide solution. The hydrochloride (S24) (58 mg.) was dissolved in aqueous ethanol (50%, 10 ml.), sodium hydroxide (250 mg.) added, and the mixture left standing overnight. The solution was then saturated with sodium chloride and extracted with ether, washed with water, dried and evaporated to give a pale brown crystalline material (27 mg.). Recrystallisation from light petroleum (100/120) at low temperature gave N-n-butyl-1-phenyl acetamide (S25) as colourless plates m.p. 54-55°. These gave an undepressed m.p. 53-55° with a genuine synthetically obtained sample m.p. 55-56°.

Preparation of N-n-butylphenylacetamide. n-Butylamine (38.6 g., 0.53 Moles) was added to aqueous sodium hydroxide (10%, 600 ml.), and phenyl acetylchloride (comml., 88.6 g., 0.53 Moles) added slowly. After all the acid chloride had been added, the mixture was shaken in the stoppered flask for fifteen minutes and cooled under running water. The supernatant, crystalline mass was dissolved in ether, washed with sodium hydroxide solution, water, and dilute hydrochloric acid, dried and evaporated. The brown mass was recrystallised from light petroleum (100/120) to give the amide (S25) as white plates (60 g., 0.32 Moles), m.p. 55 - 56°

Attempted formation of N-n-butylphenylthioamide. Phosphorus pentasulphide (comml. 4.58 g.) and the amide (3.5 g.) were mixed with dry xylene (25 ml.) and heated under reflux for fifteen minutes. The xylene was decanted off, but it was noted that the pentasulphide did not appear to have reacted. Evaporation of the xylene yielded a yellow oil which showed strong absorption in the carbonyl region of the infra red spectrum.

Formation of the thioamide (S26).

Commercial phosphorus pentasulphide was recrystallised from carbon disulphide using an acetone/dricold bath for cooling. The pale yellow crystalline powder was washed with ether and dried on a water pump at room temperature, m.p. 235-260°, the major portion of the material melting at the higher temperature. This material was considered pure enough for reagent purposes. Amide (S25) (2.00 g.) was dissolved in xylene (25 ml.) and heated to reflux temperature: phosphorus pentasulphide (1.83 g.) was added in small portions, there being marked effervescence at each addition. The mixture was then heated under reflux for 10 minutes and the xylene solution decanted from the yellow gum coating the sides of the flask. The solution was cooled and light petroleum (40/60, 10 ml.) added: a yellow oil (1.47 g.) separated. This oil was separated and dissolved in methanol and used in the next stage. In a further run under similar conditions the xylene was evaporated off entirely and the residual oil set into a crystalline mass. It was found impossible to recrystallise this from any of the normal solvents or mixtures thereof.

However, the slow evaporation of a benzene solution yielded the thioamide (S2[illegible]) as crystals which, on pressing on filter paper, were found to be colourless plates m.p. 64.5-66° (Found: C, 68.74; H, 7.74%. $C_{12}H_{17}NS$ requires C, 69.54; H, 8.27%). $\nu_{max.}$ (Nujol) 3150 (bonded NH) 1595 (ar) 1520 (amide II), various CH bands, 1290 (amide III) 1182 m, 1138 m, 1045 ms (thioamide) cm^{-1}.

Formation of N-n-butylphenylacetamidoxime.

Crude thioamide (1.47 g.) was dissolved in ethanol (25 ml.) and hydroxylamine hydrochloride (693 mg.) and sodium carbonate (497 mg.) added. The mixture was heated under reflux for fourteen hours and evaporated to dryness on an oil pump. Ether and hydrochloric acid (6N) were added to the residual mass. An insoluble layer appeared at the interface. This was separated by centrifugation, washed with ether and dissolved in ethanol leaving an insoluble yellow residue. The amidoxime hydrochloride was reprecipitated from the ethanol solution with ether, and recrystallised from ethanol/ether to give colourless plates m.p. 181-182°, (mix m.p. with S23 180-182°). The infra red absorption spectrum is identical with that of S23. The postulated structure of S23 is therefore presumed to be correct.

REFERENCES.

1) Eglinton & Galbraith, Proc.Chem.Soc., 1957, 350.

2) Grant & Speakman, Proc.Chem.Soc., 1959, 231.

3) Glaser, Ber., 1869, 2, 422.

4) McCrae, Ph.D. Thesis, Glasgow, 1960.

5) Baeyer, Ber., 1882, 15, 50.

6) Bowden, Heilbron, Jones & Sargent, J., 1947, 1579.

7) Heilbron, Jones & Sondheimer, J., 1947, 1586.

8) Armitage, Cook, Entwhistle, Jones & Whiting, J., 1952, 1998.

9) Bruun, Haug, Sorensen, Acta Chem.Scand., 1950, 4, 850.

10) Eglinton & Galbraith, Chem. and Ind., 1956, 737.

11) Bohlman & a) Pollitt, Ber., 1957, 90, 130.
b) Inhoffen & Herbst, Ber., 1957, 90, 1661.

12) Deluchat, Comptes Rendus, 1931, 192, 1387.

13) Toda & Nakagawa, Bull.Chem.Soc.Japan, 1960, 33, 223, 230.

14) Akiyama & Nakagawa, Chem. and Ind., 1960, 346.

15) Jones, Proc.Chem.Soc., 1960, 199.

16) Klebanski, Grachev & Kusnetsova, J.Gen.Chem. (USSR), (Transl.), 1957, 27, 3008.

17) a) Hay, J.Org.Chem., 1960, 25, 1275.
b) Hay, J.Org.Chem., 1960, 25, 637.

18) Chodkiewicz, Ann.Chim., 1957, 2, 819.

19) Armitage, Jones & Whiting, J., 1952, 2014.

20) Black, Horn & Weedon, J., 1954, 1704.

21) Bergelson, Molotkowsky & Shemyakin, Chem.and Ind., 1960, 558.

22) Carnduff, Eglinton, McCrae & Raphael, Chem. and Ind., 1960, 559.

23) Sondheimer *et al.*, Part II, Proc.Chem.Soc., 1957, 22.

24) Sondheimer *et al.*, Part I, J.A.C.S., 1956, 78, 4178.

25) idem Part III, J.A.C.S., 1957, 79, 5817.

26) idem Part IV, J.A.C.S., 1957, 79, 6263.

27) idem Part V, J.A.C.S., 1957, 79, 4247.

28) idem Part VI, J.A.C.S., 1959, 81, 1771.

29) idem Part VII, J.A.C.S., 1959, 81, 1771.

30) idem Part VIII, J.A.C.S., 1959, 81, 4600.

31) idem Part IX, Tet.Lett., 1959, No.3, 3.

32) idem Part X, J.A.C.S., 1959, 81, 6301.

33) idem Part XI, J.A.C.S., 1959, 81, 4755.

34) idem Part XII, J.A.C.S., 1960, 82, 754.

35) idem Part XIII, J.A.C.S., 1960, 82, 755.

36) Ruzicka, Hurbin & Boekenoogen, Helv.Chim.Acta, 1933, 16, 498.

37) Blomquist, Liu & Bohrer, J.A.C.S., 1952, 74, 3643.

38) Blomquist & Liu, J.A.C.S., 1953, 75, 2153.

39) Jaffe, Diss.Abs., 1957, 17, 2815.

40) Treibs & Pester, Tet.Lett., 1960, No.17, 5.

41) Prelog, Helv.Chim.Acta, 1955, 38, 1786.

42) Domnin, J.Gen.Chem. (USSR), 1938, 8, 851.

43) Blomquist, Burge & Sucsy, J.A.C.S., 1952, 74, 3636.

44) Cram & Cordon, J.A.C.S., 1955, 77, 4090.

45) Cram & Dewhirst, J.A.C.S., 1959, 81, 5963.

46) Ruggli, *Ann.*, 1912, *392*, 92.

47) Ruggli, *Ann.*, 1913, *399*, 174.

48) Epsztein & Marzak, *Comptes Rendus*, 1956, *243*, 283.

49) Cram & Allinger, *J.A.C.S.*, 1956, *78*, 2518.

50) Lespieau, *Comptes Rendus*, 1929, *188*, 502.

51) Reppe, *et al.*, *Ann.*, 1955, *596*, 1.

52) Sworski, *J.Chem.Phys.*, 1948, *16*, 550.

53) Eglinton & Galbraith, *J.*, 1959, 889.

54) Galbraith, Ph.D. Thesis, Glasgow, 1958.

55) Hueckel, *Z.Phys.*, 1931, *70*, 204.

56) Mislow, *J.Chem.Phys.*, 1952, *20*, 1489.

57) Halford & Weismann, *J.Org.Chem.*, 1952, *17*, 1646.

58) Finan, Personal communication.

59) Bourguel, *Ann.Chim.*, 1925, *3*, 191.

60) Hazeldine, *Nature*, 1951, *168*, 1028.

61) Kitzon, *Analyt.Chem.*, 1953, *25*, 1470.

62) Akhtar & Weedon, *Proc.Chem.Soc.*, 1958. 303.

63) Katritzky & Jones, *J.*, 1959, 3670.

64) a) Whiffen, *Spectrochim.Acta*, 1955, *7*, 253.
    b) Cava & Napier, *J.A C.S.*, 1958, *80*, 2255.

65) a) Bellamy, Infra red Spectra of Complex Molecules, Methuen & Co., Ltd., London, 1958, p.77.
    b) Dannenberg & Rahman, *Ber.*, 1955, *88*, 1405.

66) Raphael, Acetylenic compounds in organic Synthesis, Butterworth, London, 1955; a) pp.203-4, b) p.163.

67) Hueckel & Bretschneider, Ann., 1939, 540, 157.

68) Straus, Ann., 1905, 342, 190.

69) Klages, Ber., 1904, 37, 2301.

70) Entel, Ruof & Howard, Analyt.Chem., 1953, 25, 1303.

71) Iyengar, Rec.Trav.Chim., 1954, 73, 789.

72) Deuschel, Helv.Chim.Acta, 1951, 34, 2403: we are indebted to Prof. L. Chardonnens for a sample.

73) Cook & Linstead, J., 1934, 946.

74) a) Campbell & Eby, J.A.C.S., 1941, 63, 216.

b) Henne & Greenlee, J.A.C.S., 1943, 65, 2020.

c) Birch, Quart.Rev., 1950, 69.

75) Ziegler & Schaeffer, Ann., 1930, 479, 150.

76) Wooster & Ryan, J.A.C.S., 1932, 54, 2419.

77) Birch, J., 1944, 430.

78) Hueckel & Schwen, Ber., 1956, 89, 481.

79) Cope, Fenton & Spenser, J.A.C.S., 1952, 74, 5884.

80) Prelog, Schenker & Kueng, Helv.Chim.Acta, 1953, 36, 471.

81) a) Prelog & Schenker, Helv.Chim.Acta, 1952, 35, 2044.

b) Prelog, Ureh, Bothner-By & Würsch, Helv.Chim.Acta, 1955, 38, 1695.

c) Cope, Colter & Roller, J.A.C.S., 1955, 77, 3590.

82) Prelog & Boarland, Helv.Chim.Acta, 1955, 38, 1776.

83) Prelog & Polyak, Helv.Chim.Acta, 1957, 40, 816.

84) Hansche, Chem.Rev., 1953, 53, 353.

85) Leonard & Little, J.A.C.S., 1958, 80, 4111.

86) Mozingo, Org.Synth., Coll. Vol.III, p.685.

87) Friedel & Orchin, Ultra violet spectra of aromatic Compounds, Chapman & Hall, Ltd., London, 1951, 9,10,13,14,15,17,20,23.

88) Prevorsek, Bull.Soc.Chim.France, 1958, 5 E.S., 788.

89) Arens & Rix, Proc.K.Ned.Acad.Wetenschap, 1954, B57, 275.

90) Mabery & Kraus, Ber., 1889, 22, 3305.

91) Lossen, Ber., 1884, 17, 1587.

92) Houben & Kaufmann, Ber., 1913, 46, 2821.

93) Eitner & Wetz, Ber., 1893, 26, 2840.

94) Lottermoser, J.Prakt.Chem., 1896, 54, 113.

95) Tiemann, Ber., 1886, 19, 1668.

96) Sukurada, Bull.Chem.Soc.Japan, 1927, 2, 307.

97) Kindler & Findorf, Ber., 1921, 54, 1079.

98) Rivier & Schneider, Helv.Chim.Acta, 1920, 3, 115.

99) Rodd, Chemistry of Carbon Compounds, Elsevier Publishing Co., London, 1951, IA, p.603.

100) D.B.P. 951, 933.

101) We are indebted to Dr. F.G. Mann, Cambridge University, for a sample.

102) Eglinton, Hamilton, Hodges & Raphael, Chem. and Ind., 1959, 955.

103) Newman & Lutz, J.A.C.S., 1956, 78, 2469.

104) Bailey & Case, Proc.Chem.Soc., 1957, 176.

105) A.P.I. Project 44, U.V. No.133.

106) Friedel & Orchin, Ultra violet spectra of aromatic Compounds, Chapman & Hall, London, 1951, No.214.

107) We are indebted to Professor V. Prelog, ETH Zurich for the experimental details.

108) Newman & Zahm, J.A.C.S., 1943, 65, 1097.

109) Newman & Reid, J.Org.Chem., 1958, 23, 665.

110) Cram, Allinger & Steinberg, J.A.C.S., 1954, 76, 6132.

111) Gouterman & Wagniere, Tet.Lett., 1960, No.11, 22.

112) Bohlman, Ber., 1952, 85, 386.

... and part on the square,

... and may the blessings of the
Grand Architect of the Universe
fall on all our undertakings.