Some studies in the chemistry of reactive intermediates

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SOME STUDIES IN THE CHEMISTRY
OF REACTIVE INTERMEDIATES

A Thesis
Submitted to
Loughborough University of Technology
by
JOHN M. SKETCHLEY, A.R.I.C.

Supervisors: Dr. H. Heaney
Dr. K.G. Mason

In Partial Fulfilment of the
Requirements for the Degree of
Doctor of Philosophy
September 1970
The reactions of tetrafluorobenzyne and tetrachlorobenzyne with styrene have been investigated and found to give predominantly or exclusively 1,2,3,4-tetrahalogeno-9,10-dihydrophenanthrenes or 1,2,3,4-tetrahalogenophenanthrenes in good yield. Similar reactions are reported in which the arynes were generated in the presence of α-methyl-, trans-β-methyl-, 2-methyl-, 3-methyl-, 4-methyl, and 2,4-dimethylstyrene. Reactions were also carried out with trans-stilbene, 1,1-diphenylethylene, 1-phenylcyclohexene, and 1-vinylnaphthalene. The mechanism of formation of 1,2,3,4-tetrafluoro-9,10-dihydrophenanthrene has been studied by use of suitably deuteriated compounds. A discussion of the mechanism of formation of 1,2,3,4-tetrafluorophenanthrene and of 9,10-dihydro-9-phenylphenanthrene in the reaction of benzyne with styrene, is based on reactions with deuteriated styrenes.

Tetrabromobenzyne and tetraiodobenzyne have been generated efficiently from the corresponding tetrahalogenoanthranilic acids and have been shown to undergo cycloaddition reactions in solution with aromatic substrates. Competition data have been compared with those obtained previously for tetrachlorobenzyne and tetrafluorobenzyne. Certain substituted tetrabromobenzobarrelenes have been converted into naphthalene derivatives in the presence of 3-methylbutyl nitrite.
The reactions of the tetrahalogenobenzynes with biphenylene have been investigated and found to give 1,4-cycloaddition products in moderate yields. Naphthalene derivatives have also been obtained from the reactions of tetrachlorobenzyne and tetrafluorobenzyne with biphenylene which appear to be derived from an initially formed cycloadduct.
ACKNOWLEDGEMENT

I would like to express my gratitude to Dr. H. Heaney and Dr. K.G. Mason for their help and encouragement throughout the course of this work.

I would also like to thank Mrs. Rita Greenwood for her tremendous effort in typing this manuscript.

I am indebted to the Science Research Council for a research studentship for this work and to Loughborough University of Technology for the privilege of working in their laboratories. Thanks are also due to the Science Research Council through P.C.M.U., to Imperial Smelting Corporation for generous supplies of fluorinated chemicals, and to Chemische Fabrik Kalk, Köln, for a gift of tetrabromophthalic anhydride.

I finally acknowledge the help and understanding of my wife, without which this work would not have been possible.
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The chemistry of o-dehydrobenzene or benzyne, the parent aryne, has become well established during the past twenty years. Early workers in this field interpreted the rearrangements, which occurred in the reactions of non-activated aryl halides with strong nucleophiles, in terms of a benzyne mechanism. More recent evidence for the existence of aryne intermediates has been the preparation of a nickel carbonyl complex of both benzyne and tetrafluorobenzyne and the observation of appropriate peaks in the mass spectra of known aryne precursors. The half-life of benzyne itself has been measured by time of flight mass spectrometry and by the flash photolysis of benzene-diazonium-2-carboxylate.

The structure of benzyne has been discussed extensively during the past ten years and a number of representative structures have been proposed.

The aromatic character of the system is thought to be undisturbed with the two electrons of the "third-bond" at right angles to the pi-cloud (lb). The most commonly used formulation is structure la which accounts most satisfactorily for the products obtained in the cycloaddition reactions of arynes.
Benzyne, in the majority of its reactions with both cyclic and acyclic dienes, forms predominantly or exclusively the 1,4-cycloadduct.\textsuperscript{1,8} 1,2-cycloaddition reactions have also been observed. Recent calculations predict that o-dehydrobenzene is a ground state singlet species with the two electrons of the "third-bond" in the lower symmetric orbital.\textsuperscript{9} Thus the thermal cycloaddition reaction of benzyne with 1,3-dienes is an allowed concerted process by the conservation of orbital symmetry.\textsuperscript{10,11} Conversely the thermal cycloaddition reactions of benzyne with mono-olefins should occur by a step-wise process. The expected stereospecificity has been observed in the reactions of benzyne with \textit{trans-trans}-hexa-2,4-diene and with \textit{cis-and trans}-1,2-dichloroethylene.\textsuperscript{8} The results obtained in the reactions of tetrahalogenobenzenes with arenes leads to the conclusion that the tetrahalogenobenzenes have the same structure as benzyne itself. Early theories, which postulated that benzyne generated from different precursors could have different structures, have now been discounted in the light of more recent evidence.\textsuperscript{12}

Arynes can be generated from a number of suitable precursors but the overall principle involves the elimination of atoms or groups from adjacent positions in the aromatic nucleus. The abstracted species are small, thermodynamically stable species such as metal halides, nitrogen and carbon dioxide. Metals such as lithium, sodium and magnesium react with o-dihalogenoaromatic compounds to give good yields of the organometallic precursor from which the aryne is formed by elimination of metal halide.
For a given metal, the order of ease of metal halide elimination is \( F > Cl = Br \) and for a given halogen the order of ease of metal halide elimination is \( Na > Li > Mg \).

A convenient method for the generation of arynes involves the oxidation of 1-aminobenzotriazole with lead tetraacetate.

The reaction is thought to proceed via a nitrene intermediate. Low temperature thermolysis of benzenediazonium-2-carboxylate with elimination of nitrogen and carbon dioxide results in a smooth generation of benzyne.
Benzenediazonium-2-carboxylate can also be formed and decomposed in situ by the aprotic diazotisation of anthranilic acid.\textsuperscript{17}

Less important methods of generating aryynes include the thermolysis of benzenediazonium-2-sulphinate,\textsuperscript{18} high temperature pyrolysis of phthalic anhydride\textsuperscript{19} and irradiation of 1,2,3-benzothiadiazole-1,1-dioxide.\textsuperscript{20}

The chemistry of benzyne, which has been reviewed extensively during the past fifteen years, is essentially that of a short-lived and highly electrophilic intermediate. It reacts with a large number of nucleophiles and behaves as a highly reactive dienophile in Diels-Alder reactions with 1,3-dienes. Typical reactions of benzyne with benzene,\textsuperscript{22} furan,\textsuperscript{23} and tetra-cyclone\textsuperscript{24} are shown overleaf. In the tetracyclone reaction the product isolated is the one formed by loss of carbon monoxide from the initial cycloadduct. A number of reactions of this type are observed in the reaction of aryynes with 1,3-dienes and the driving force for the reaction is evidently the aromatisation of the initial cycloadduct. However the thermodynamic stability of the leaving group is also important. Thus bridging groups such as \(-\text{N=N-}\) and \(\equiv C=O\) are lost spontaneously while \(-\text{CH=CH-}\) and \(-\text{S-}\) can be lost by pyrolysis of the appropriate adduct and groups such as \(-\text{CH}_2-\), \(-\text{NR-}\) and \(-\text{O-}\) are not normally lost.

Aryynes undergo 1,2-cycloaddition reactions with olefins to give cyclobutane derivatives. The reaction of benzyne with norbornene\textsuperscript{25} gives the exo-adduct shown below.
Cyclobutane derivatives are also obtained in the reaction of benzyne with enamines\textsuperscript{26} and in this case the mechanism probably involves nucleophilic attack by the olefin on the aryne followed by ring closure as shown.

Azides\textsuperscript{27} add to arynes as 1,3-dipoles in the same way that they add to reactive olefins and acetylenes. The products are derivatives of benzotriazole.
Eenzyne reacts with olefins having an allylic hydrogen atom in a concerted 'ene' reaction.\(^{25}\)

When benzyne is generated in the absence of an aryne trap, the product obtained depends upon the method of generation. Benzene-diazonium-2-carboxylate decomposes smoothly on heating in ethylene chloride to give biphenylene\(^{28}\) in high yield. However benzyne generated from o-fluorophenyl lithium reacts with its precursor and this procedure has been utilised in the formation of triphenylene derivatives.\(^{30}\)

The work described in this thesis is concerned with the chemistry of the tetrahalogenobenzynes; the presence of four electron withdrawing substituents significantly increasing the electrophilicity of the aryne compared with that of benzyne. Pentafluorophenylmagnesium halides\(^{31}\) and pentachlorophenylmagnesium chloride\(^{32}\) are analogous to the benzyne precursors, the o-halogenophenylmagnesium halides. Pentafluorophenyl lithium eliminates lithium fluoride to generate tetrafluorobenzyne\(^{33}\) and pentachlorophenyl lithium\(^{34}\) similarly acts as a precursor for
tetrachlorobenzene. Although pentafluorophenyl lithium is more stable than o-fluorophenyl lithium, this has not proved to be a disadvantage. This is not unexpected because although the 6-halogeno-2-benzenesulphonylphenyl lithium\textsuperscript{35} derivatives are unusually stable, they are aryne precursors.

Polyfluoroarenes form charge-transfer complexes with electron-rich arenes\textsuperscript{36} and it was hoped that the precursors of the tetrachlorobenzynes would similarly form charge-transfer complexes with aromatic compounds and thus enable reactions with these compounds to be studied. Benzyne itself, generated from Grignard or organolithium reagents is not amenable to this type of study since the precursor is itself a strong nucleophile and adds to benzyne.\textsuperscript{30} The tetrachlorobenzynes are sufficiently electrophilic for these reactions to be less important. Benzyne has been generated from anthranilic acid\textsuperscript{17} and since the tetrachloroanthranilic acids are all compounds reported in the literature (F\textsuperscript{37}, Cl\textsuperscript{38}, Br\textsuperscript{39}, I\textsuperscript{40}) they constitute a series of potential precursors for the tetrachlorobenzynes.

The increased electrophilicity of the tetrachlorobenzynes compared to that of benzyne has resulted in significantly higher yields of products in reactions analogous to those of benzyne. It is also of interest to note that different products\textsuperscript{41} have been observed in analogous reactions and in certain instances, cycloaddition reactions have occurred with systems\textsuperscript{42} which did not react with the parent aryne.
SECTION 1

The Reactions of Tetrahalogenobenzynes with Styrene and Substituted Styrenes.
INTRODUCTION

The 1,3-diene formed by the exocyclic double bond and one of the aromatic double bonds in styrene has been recognised for many years as a system which reacts with dienophiles in the Diels-Alder reaction.43 A number of papers describing the reaction of benzyne with substituted styrenes have appeared in the literature and the products obtained were substituted phenanthrenes. The reaction of benzyne, generated from o-fluorophenyl lithium, with 1-vinyl-4-naphthalene gave chrysene in low yield. No comment was made by the authors on the nature of the dehydrogenation of the initial cycloadduct which produced the observed product. Corbett45 and his co-workers also obtained chrysene from the reaction of benzyne with 1-vinyl-naphthalene and suggested that the initial cycloadduct, 4b, 12-dihydrochrysene, would be rapidly dehydrogenated by excess of benzyne. The nature of this dehydrogenation step is discussed at a later stage in this thesis. Aprotic diazotisation of anthranilic acid in the presence of isoeugenol methyl ether and isosafrole gave the corresponding isomeric 9-methylphenanthrenes in low yield.46 A 9,10-dihydro-9-methylphenanthrene was also observed in the reaction of benzyne with isosafrole which appeared to arise by a rearrangement of the initial cycloadduct. This type of product is important in the reaction of tetrahalogenobenzyne with styrene.

In view of the high yields obtained in cycloaddition reactions of tetrahalogenobenzynes,47,48 the reactions of tetrafluorobenzene and tetrachlorobenzene with styrene and some of
its derivatives have been investigated. The aryne could, in principle undergo several types of cycloaddition reactions. Addition to the 1,3-diene formed by the exocyclic double bond and one of the aromatic double bonds as described previously. Cycloaddition to the exocyclic double bond to give cyclobutane derivatives or 1,4-cycloaddition across the aromatic ring.

**DISCUSSION**

The first paper\textsuperscript{25} describing the reaction of benzyne with styrene concluded that no identifiable products could be isolated. However Dilling\textsuperscript{49} reported the reaction of benzyne generated from o-fluorophenylmagnesium bromide in tetrahydrofuran, in the presence of a five mole excess of styrene and obtained 9,10-dihydro-9-phenylphenanthrene in 87% yield. The mechanism proposed for this reaction involved a three-step ionic process.

\[ \text{Scheme 1.} \]
The mechanism proposed above seems unlikely since it is improbable that a proton would be first lost and then regained under the basic conditions of the reaction medium. Another explanation of the product obtained in the above reaction has been tentatively suggested by Hoffmann. He proposed that the 9,10-dihydro-9-phenylphenanthrene could arise by a mechanism analogous to that in which phenyl-azaphenanthrenes are formed in the reaction of benzyne with benzonitrile derivatives. By this mechanism the benzyne is thought to react initially with its precursor to give 2-fluorobiphenylyl-2'-magnesium bromide. This then undergoes a cyclisation reaction with a second molecule of styrene in which elimination of magnesium bromofluoride occurs to give the observed product. We decided to investigate the mechanism of formation of 9-phenyl-9,10-dihydrophenanthrene as part of our general investigation of the reactions of arynes with styrenes. The mechanism involving the reaction of 2-fluorobiphenylyl-2'-magnesium bromide with styrene was readily tested and eliminated. The Grignard reagent from 2-chloro-2'-iodo-biphenyl was treated with a five mole excess of styrene in tetrahydrofuran. Subsequent hydrolysis and work-up of the product gave a mixture of 2-chloro-2'-iodobiphenyl and 2-chlorobiphenyl, the latter being formed by hydrolysis of the Grignard reagent. The 9,10-dihydro-9-phenylphenanthrene (Scheme 1) was not detected. A similar reaction involving 2-fluoro-2'-iodo-4,4'-dimethylbiphenyl gave only 2-fluoro-4,4'-dimethylbiphenyl. No products analogous to 9,10-dihydro-9-phenylphenanthrene were observed. These results confirm that a mechanism analogous to the one observed in the reaction of benzyne with benzonitrile derivatives is not operating.
A concerted 'ene' type reaction between the initial Diels-Alder adduct (Scheme 1) and a second molecule of benzyne is possible.

Scheme 2.

In order to test the validity of this mechanism we prepared \[ 2,4,6-^2\text{H}_3 \] styrene with the deuterium content shown in Table 1 and carried out a reaction between benzyne, generated from o-fluorophenylmagnesium bromide in tetrahydrofuran, and a mixture of unlabelled styrene and the labelled styrene (4:1). The resulting 9,10-dihydro-9-phenylphenanthrene which was analysed by low voltage mass spectrometry (Table 1) had the same abundance of deuterium as the styrene used in the experiment. 9,10-Dihydro-9-phenylphenanthrene is reported by Dilling to fragment in the mass spectrometer to give an ion M-78. This ion in the mass spectrum determined at 70 e.V. corresponds to the loss of C\textsubscript{6}H\textsubscript{6} and most reasonably may arise by the loss of the 9-phenyl group. An analysis of the ions at m/e 176-182 in the spectrum of both the deuteriated and the unlabelled compound showed that, within experimental error, one third of the deuterium was lost in the fragments of M-77 and 78 (Table 1). Assuming that no scrambling of hydrogen occurs prior to fragmentation of the molecular ion, these results prove that the 9,10-dihydro-9-phenylphenanthrene arises by the concerted
### TABLE 1

Mass spectral data

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<tr>
<th>Ionisation voltage (ev)</th>
<th>M/e (Corrected abundance)</th>
<th>Result $^{2H_2}$</th>
<th>$^{2H_3}$</th>
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<tr>
<td><strong>[2-$^2H$] Styrene</strong></td>
<td>12.0</td>
<td>104 (330.0)</td>
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<tr>
<td></td>
<td></td>
<td>105 (1281.0)</td>
<td>$^{2H_1}$ 79.3%</td>
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<tr>
<td></td>
<td></td>
<td>106 (0.5)</td>
<td>$^{2H_2}$ 0.03%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>107 (3.6)</td>
<td>$^{2H_3}$ 0.2%</td>
</tr>
<tr>
<td><strong>[3-$^2H$] Styrene</strong></td>
<td>12.0</td>
<td>104 (315.0)</td>
<td>$^{2H_2}$ 15.5%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>105 (1712.0)</td>
<td>$^{2H_1}$ 84.5%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>106* (63.7)</td>
<td>$^{2H_1}$ 84.5%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>107 (126.6)</td>
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</tr>
<tr>
<td></td>
<td></td>
<td>108 (6.7)</td>
<td>$^{2H_3}$ 0.03%</td>
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<tr>
<td><strong>[2,4,6-$^2H_3$] Styrene</strong></td>
<td>12.0</td>
<td>105 (134.0)</td>
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<td>105 (1403.2)</td>
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<td></td>
<td></td>
<td>107 (4876.0)</td>
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<td></td>
<td>108</td>
<td>$^{2H_4}$ 0.2%</td>
</tr>
<tr>
<td><strong>1,2,3,4-Tetrafluoro-</strong></td>
<td>12.8</td>
<td>250 (84.0)</td>
<td>$^{2H_2}$ 16.8%</td>
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<td>9,10-dihydrophenanthrene</td>
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<td>251 (1.2)</td>
<td>$^{2H_1}$ 0.2%</td>
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<tr>
<td></td>
<td></td>
<td>252 (498.9)</td>
<td>$^{2H_3}$ 99.8%</td>
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<td></td>
<td></td>
<td>253</td>
<td>$^{2H_4}$ 0.2%</td>
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<tr>
<td></td>
<td></td>
<td>254</td>
<td>$^{2H_5}$ 0.2%</td>
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<td><strong>1,2,3,4-Tetrafluoro-</strong></td>
<td>12.8</td>
<td>250 (15.2)</td>
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<td>9,10-dihydrophenanthrene from [2-$^2H$] Styrene</td>
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<td>251 (18.7)</td>
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<td></td>
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<td>252 (2820)</td>
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<td></td>
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<td>253 (806.9)</td>
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<td></td>
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<td>254 (38.2)</td>
<td>$^{2H_5}$ 3%</td>
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<td></td>
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<td>255 (0.5)</td>
<td>$^{2H_6}$ 0.2%</td>
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<td></td>
<td></td>
<td>256</td>
<td>$^{2H_7}$ 0.2%</td>
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<tr>
<td><strong>9,10-Dihydro-</strong></td>
<td>14.0</td>
<td>256 (118.0)</td>
<td>$^{2H_2}$ 80.4%</td>
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<td>9-phenylphenanthrene from styrene and [2,4,6-$^2H_3$] styrene</td>
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<td>257 (0.5)</td>
<td>$^{2H_1}$ 0.3%</td>
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<td></td>
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<td>258 (5.7)</td>
<td>$^{2H_2}$ 3.9%</td>
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<td></td>
<td></td>
<td>259 (22.6)</td>
<td>$^{2H_3}$ 15.4%</td>
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<td></td>
<td></td>
<td>260</td>
<td>$^{2H_4}$ 0.2%</td>
</tr>
<tr>
<td><strong>70.0</strong></td>
<td>176 (13.6)</td>
<td>$^{2H_1}$ 12.15%</td>
<td>deuterium</td>
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<tr>
<td></td>
<td>177 (13.6)</td>
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<td>178 (100)</td>
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<td>179 (74)</td>
<td>$^{2H_4}$</td>
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<td>181 (10.5)</td>
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<td>deuterium</td>
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<tr>
<td></td>
<td>182 (1.1)</td>
<td>$^{2H_7}$</td>
<td>deuterium</td>
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<tr>
<th>Ionisation voltage (ev)</th>
<th>M/e</th>
<th>Corrected abundance</th>
<th>Result ([2H_n]^{+})</th>
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<td>70.0</td>
<td>176</td>
<td>(14)</td>
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<td>177 (12)</td>
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<td>181 (1.4)</td>
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<tr>
<td>182 (0.5)</td>
<td></td>
<td></td>
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</tbody>
</table>

| 20.0                   | 250 | (6200)             | 50.3%            |
| 251 (6056.4)           |     | \([2H_0]^{+}\)     |                  |
| 252 (58.2)             |     | \([2H_1]^{+}\)     | 49.2%            |
| 253 (5.7)              |     | \([2H_2]^{+}\)     | 0.5%             |

* A small amount of ethylbenzene was detected by gas chromatography and is assumed to be responsible for the ions at m/e 106, 107, and 108.
'ene' reaction of the initial Diels-Alder adduct with benzyne (Scheme 2). Although the scrambling of hydrogen has been detected in certain aromatic compounds, this is normally observed in low voltage spectra\textsuperscript{51} and not at 70 e.V.

In order to gain further proof of the mechanism proposed above, an attempt was made to oxidise the 9,10-dihydro-9-phenyl phenanthrene, derived from the labelling experiment, with alkaline potassium permanganate. The oxidation products were extracted into ether and treated with diazomethane. Gas liquid chromatography indicated the presence of methyl benzoate and dimethyl phthalate in the reaction mixture but an attempt to determine the deuterium content of the esters by mass spectrometry was unsuccessful.

The concerted 'ene' reaction described above in the reaction of benzyne with styrene has been discussed more recently by Ciganek\textsuperscript{52} who has also carried out a reaction of benzyne, generated by aprotic diazotisation of anthranilic acid, with a fifty mole excess of styrene. He obtained a mixture of the threo and erythro forms of 9,10-dihydro-9-(\(\alpha\)-methylbenzyl) phenanthrene in a ratio of 1:1 (Scheme 3a). This product was derived by a concerted 'ene' reaction of the initial Diels-Alder adduct with styrene, the threo and erythro forms resulting from exoid and endoid attack by the styrene in the 'ene' reaction. The two centres of the allylic system involved in the 'ene' reaction, namely the \(\pi\)-orbitals of the exocyclic double bond in styrene and the \(C_{4b}-H\) bond in the Diels-Alder intermediate,
Scheme 3.
are almost co-planar and thus are well oriented for a concerted reaction. Exoid or endoid type transition states are possible and the allylic hydrogen may be transferred to the carbon carrying the phenyl group or to the methylene carbon of styrene. The former course appears to be of no significance since the product of such a transfer, namely 9,10-dihydro-9-(β-phenylethyl) phenanthrene is not observed in the reaction. Models show that there is very little difference in non-bonded interactions between the transition states of paths (a) and (b) (Scheme 3). It therefore seems likely that the 'ene' reaction in this case is not completely synchronous and that in the transition state, carbon-hydrogen bond formation has proceeded to a larger extent than carbon-carbon bond formation, resulting in a partial carbonium, carbanion or radical character of the carbon carrying the phenyl group. A two-step process, involving complete transfer of the allylic hydrogen prior to carbon-carbon bond formation seems unlikely since the allylic anion, cation or radical (Scheme 3c) should undergo side reactions such as aromatisation or hydrogen abstraction, unless recombination of the two fragments is favoured by occurring in a cage.

The results obtained in the reactions of tetrahalogenobenzynes with styrenes differ somewhat from those obtained in the analogous reactions with benzyne. When styrene (5 mole) was added to a solution of pentafluorophenyl lithium in ether at -60° and the mixture was allowed to warm rapidly to room temperature, 1,2,3,4-tetrafluoro-9,10-dihydrophenanthrene (IV) was obtained in 60% yield. When styrene was added to a solution of pentachlorophenyl
<table>
<thead>
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<th>Compound</th>
<th>( R^1, R^2, R^3, R^4, R^5 )</th>
<th>( R^6 )</th>
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<tr>
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<td></td>
</tr>
<tr>
<td>(II)</td>
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<td></td>
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<tr>
<td>(III)</td>
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<td></td>
</tr>
<tr>
<td>(IV)</td>
<td>( R^1=R^2=R^3=R^5=H )</td>
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<tr>
<td>(V)</td>
<td>( R^1=R^2=R^3=R^5=H )</td>
<td></td>
</tr>
<tr>
<td>(VI)</td>
<td>( R^1=R^2=R^3=R^5=H )</td>
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<tr>
<td>(VII)</td>
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</tr>
<tr>
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<td>( R^1=R^2=R^3=R^5=H )</td>
<td></td>
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<tr>
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<td></td>
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<td>(X)</td>
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<tr>
<td>(X)</td>
<td>( R^1=R^2=CH_2 _4, \quad R^3=R^4=H )</td>
<td></td>
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</tbody>
</table>
lithium in ether and the mixture was heated at 50°C, 1,2,3,4-tetrachloro-9,10-dihydrophenanthrene was obtained in 33.5% yield. In an attempt to force the reaction towards the formation of the 9-aryl derivative analogous to the product obtained in the reaction of benzyne with styrene, a reaction was carried out in which the ratio of pentafluorophenyl lithium to styrene was 1:0.5. Column chromatography of the crude reaction mixture on neutral alumina and elution with light petroleum gave two products which were shown to be (IV) and 1,2,3,4-tetrafluoro-phenanthrene (V) in a ratio of 1:0.75. When pentafluorophenyl lithium was allowed to warm to room temperature over a period of eighteen hours, (V) was obtained as the major product. With the prolonged reaction period and 0.5 mole of styrene, (V) was the only product isolated.

1,2,3,4-Tetrachlorophenanthrene (I) was the only product isolated when tetrachlorobenzyne, generated by aprotic diazotisation of tetrachloroanthranilic acid, was reacted with styrene. The compound (I) was also the only product isolated when tetrachlorobenzyne was generated from tetrachloroanthranilic acid in the presence of phenylacetylene. This latter result differs somewhat from the observations made on the reaction of benzyne with phenylacetylene. In addition to phenanthrene, which is analogous to the product observed in the reaction of tetrachlorobenzyne with phenylacetylene, a second product was observed. This was the major product and was shown to be 5,6-diphenyldibenzo[a,e]cyclooctatetraene which arises by (2+2)π cycloadDITION of the benzyne with the triple bond of the phenylacetylene, dimerisation of the resulting benzocyclobutadiene and rearrangement leading to the
observed product. The failure to observe this type of product in the reaction of tetrachlorobenzyne with phenylacetylene was undoubtedly due in some part to the reluctance with which tetrahalogenobenzynes undergo (2+2)π cycloaddition reactions.

In view of the results obtained in the reaction of tetrafluorobenzyne with styrene, it has been possible, by selecting the appropriate experimental conditions, to prepare a series of 9,10-dihydrophenanthrene or phenanthrene derivatives [(I) → (XX)] in reactions between tetrahalogenobenzynes and substituted styrenes. The reaction of tetrafluorobenzyne with 1-phenylcyclohexene gave both 1,2,3,4-tetrafluoro-8b,9,10,11,12,12a-hexahydrotriphenylene (XVIII) and 1,2,3,4-tetrafluoro-9,10,11,12-tetrahydrotriphenylene (XIX). Catalytic dehydrogenation of (XVIII) and (XIX) over palladium charcoal gave 1,2,3,4-tetrafluorotriphenylene (XX).

The reaction of tetrafluorobenzyne with α-methylstyrene gave three products analogous to the products observed in the reaction of benzyne with α-methylstyrene. They were α-(2,3,4,5-tetrafluorobenzyl) styrene (XV), 1,2,3,4-tetrafluoro-9,10-dihydro-9-methylphenanthrene (XVI) and 1,2,3,4-tetrafluoro-9-methylphenanthrene (XVII). Product (XV) arises by way of an 'ene' reaction of tetrafluorobenzyne with the allylic system in α-methyl styrene.

![Scheme 4](image-url)
It was possible, by carrying out the reaction under conditions leading either to the 9,10-dihydrophenanthrene or to the phenanthrene derivatives, to obtain products (XV), (XVI) and (XVII) in significantly different ratios. Under conditions leading to the 9,10-dihydrophenanthrene derivatives the percentage of products obtained was (XV) 28%, (XVI) 21% and (XVII) 5% and under conditions leading to the phenanthrene derivatives the percentage was (XV) 29%, (XVI) 15% and (XVII) 14%.

During the course of the work on the reactions of tetrafluorobenzyne with substituted styrenes, a number of results have been observed which warrant further discussion. Although the product of the 'ene' reaction (Scheme 4) was obtained in the reaction of tetrafluorobenzyne with α-methylstyrene, this product was not observed in the reaction with trans-β-methyl styrene. This may be due to the fact that the double bond produced in such a reaction would not be conjugated with an aryl group. A transition state leading to such a product would undoubtedly be of higher energy than the analogous transition state in the reactions with α-methyl styrene. In the reaction of tetrafluorobenzyne with 1-vinylnaphthalene, the only product isolated was 1,2,3,4-tetrafluoro-11,12-dihydrochrysene (XI), even though dehydrogenation of the expected Diels-Alder intermediate might have been predicted to be especially easy, leading to the corresponding tetrafluorochrysene. This would be analogous to the results observed in the reaction of benzyne with 1-vinyl-4-naphthalene when the only product isolated was chrysene. The
very low yield of (XI) obtained in this reaction was undoubtedly due, in part, to the rapid polymerisation of 1-vinylnaphthalene under the conditions of the reaction. Tetrahalogenobenzenes do not appear to form cycloadducts readily with styrenes which are substituted at the 3-position. The reaction of tetrafluorobenzyne with 3-methylstyrene gave only a low yield of 1,2,3,4-tetrafluoro-7-methylphenanthrene (VI). Two isomers are possible in this reaction but the 1,2,3,4-tetrafluoro-5-methylphenanthrene was ruled out by the failure to observe splitting of the methyl group in the $^1\text{H}$ n.m.r. spectrum which would have resulted from long-range $^1\text{H}-^{19}\text{F}$ spin-spin coupling. 2,5-Dimethylstyrene, prepared by the reduction and subsequent dehydration of 2,5-dimethylacetophenone, was expected to exhibit long-range $^1\text{H}-^{19}\text{F}$ spin-spin coupling but did not, in fact, form a cycloadduct. It is surprising that tetrafluorobenzyne does form a cycloadduct with 2,3,4,5,6-pentafluorostyrene.\(^{55}\) Dehydrofluorination of the first intermediate occurs to form 1,2,3,4,5,6,7,8-octafluorophenanthrene. Tetrafluorobenzyne was reacted with $\beta\beta$-dimethylstyrene, which was prepared from isobutyraldehyde. Reaction with phenyl lithium in ether and hydrolysis gave the expected carbinol which was dehydrated over fused potassium hydrogen sulphate at 200° to give the required styrene. No cycloadducts were obtained in the reaction which leads to the conclusion that the steric requirements of the cis-$\beta$-methyl group prevents the formation of the transition state leading to the cycloadduct. Evidently the steric control of the reactions of the tetrahalogenobenzenes with substituted styrenes is more exacting than in the analogous cycloadditions involving
benzyne. This is not surprising.

A number of interesting observations have been made by other research workers on the reaction of tetrafluorobenzyne with styrene. Massey\textsuperscript{56} and his co-workers carried out a reaction of tetrafluorobenzyne, generated from pentafluorophenyl lithium, in the presence of a large excess of styrene and obtained (V) as the major product. A very small quantity of (IV) was also produced. This result differs from our observations on this particular reaction. The mechanism of the reaction was explained in terms of dehydrogenation of (IV), once formed, by tetrafluorobenzyne. In a similar paper,\textsuperscript{57} tetrafluorobenzyne, generated from pentafluorophenylmagnesium bromide, in the presence of a large excess of styrene, gave a mixture of (IV) and 1,2,3,4-tetrafluoro-9,10-dihydro-9-(\beta-phenylethyl)phenanthrene in approximately equal proportions. This result is in marked contrast to the observations made by Ciganek\textsuperscript{52} on the reaction of benzyne with a large excess of styrene. The authors proposed an ionic mechanism analogous to that proposed by Dilling for the reaction of benzyne with styrene. The carbanion (5c; \(R=H\)) attacks a second molecule of styrene and the resulting carbanion is reprotonated to give the observed product. An alternative mechanism, which would account for the observed product, would be the concerted 'ene' reaction between the initial Diels-Alder intermediate (5b; \(R=H\)) and a second molecule of styrene.

A number of mechanisms could account for the results which we obtained in our experiments and we therefore investigated the
mechanisms of the reactions between tetrafluorobenzyne and styrenes leading to dihydrophenanthrene and phenanthrene derivatives. A concerted, disrotatory cycloaddition with, for example, trans-$\beta$-methylstyrene, leading to the intermediate with the stereochemistry shown (5b; $R=\text{Me}$), is possible and in accord with the Woodward-Hoffmann rules.\(^5^8\)

\[ \text{(a)} \quad \begin{array}{c}
\text{F} \\
\text{F} \\
\text{F} \\
\text{F}
\end{array} \quad \rightarrow \quad \begin{array}{c}
\text{F} \\
\text{F} \\
\text{F} \\
\text{F}
\end{array} \quad \text{(b)} \quad \begin{array}{c}
\text{F} \\
\text{F} \\
\text{H} \\
\text{R}
\end{array}
\]

\[ \text{(d)} \quad \begin{array}{c}
\text{F} \\
\text{F} \\
\text{F} \\
\text{F}
\end{array} \quad \begin{array}{c}
\text{F} \\
\text{F} \\
\text{F} \\
\text{F}
\end{array} \quad \text{(c)} \quad \begin{array}{c}
\text{F} \\
\text{F} \\
\text{F} \\
\text{F}
\end{array}
\]

Scheme 5.

However an electrocyclic rearrangement of such an intermediate to a dihydrophenanthrene (5d; $R=\text{Me}$) which involves a 1,3-proton transfer is not allowed. The base-catalysed prototropic rearrangement to the carbanion (5c; $R=\text{Me}$) is possible and would be analogous to the mechanism proposed for the reaction of benzyne with styrene. In order to establish the existence or otherwise of the carbanion (5c; $R=\text{H}$) in the reaction of tetrafluorobenzyne with styrene, tetrafluorobenzyne was generated from pentafluorophenyl lithium in the presence of a five mole excess of styrene.
and the reaction was quenched with deuterium oxide. Investigation of the product (IV) by $^1$H n.m.r. and mass spectrometry showed no incorporation of deuterium. Similarly when tetrafluorobenzyn was generated in the presence of a five mole excess of styrene and a ten mole excess of deuteriopentafluorobenzene (prepared by the hydrolysis of pentafluorophenylmagnesium bromide with deuterium oxide), the product obtained (IV) again showed no incorporation of deuterium. These results prove that the carbanion ($5c; R=H$) can have no more than a transient existence in reactions between tetrafluorobenzyn and styrenes in which $1,2,3,4$-tetrafluoro-$9,10$-dihydrophenanthrenes are the observed products. In order to further elucidate the mechanism of the formation of dihydrophenan-

threnes from tetrafluorobenzyn and styrenes, we prepared $[2-^2\text{H}]$ styrene. A number of potential routes to the required $[2-^2\text{H}]$ styrene were investigated. The first involved, as an initial step, the conversion of o-dibromobenzene, by n-butyl lithium, to o-bromophenyl lithium and hydrolysis by deuterium oxide to $[2-^2\text{H}]$ bromobenzene. Subsequent conversions, by standard procedures, were expected to give the required labelled styrene. Difficulties were encountered in the initial conversion of o-dibromobenzene to $[2-^2\text{H}]$ bromobenzene due to aryne formation prior to hydrolysis of the o-bromophenyl lithium by deuterium oxide. The second route utilised as the starting material o-chlorobromobenzene. In this experiment it was hoped to convert the o-chlorobromobenzene to $[2-^2\text{H}]$ chlorobenzene by the procedure described in the first experiment above. Formation of the Grignard reagent of the labelled chlorobenzene in tetrahydrofuran, which has been described
in the literature, and reaction with acetaldehyde was expected to give, after hydrolysis, [2-2H] phenyl methyl carbinol. Dehydration would have given the required [2-2H] styrene. Unfortunately it was not found possible to prepare the Grignard reagent from chlorobenzene with the required consistency. The third route which proved to be successful involved conversion of 2-bromoaniline to [2-2H] aniline by n-butyl lithium (3 equiv.) and hydrolysis by deuterium oxide (4 mole). The 2-bromoaniline was converted to [N,N-2H2]-2-bromoaniline by deuterium oxide (3 mole) in the presence of deuterium chloride prior to the conversion to [2-2H] aniline. This procedure was necessary in order to avoid transfer of hydrogen derived from the amino group prior to the hydrolysis of the reagent prepared from 2-bromoaniline and n-butyl lithium. Evidence for this transfer was obtained by taking an aliquot from the reaction in which [N,N-2H2]-2-bromoaniline was converted to [N,N-2H2]-2-lithioaniline. Hydrolysis of the aliquot by water and investigation of the product by infra-red spectroscopy showed the presence of a C-D stretching frequency (2260 cm⁻¹). This indicated that a transfer of the following type had occurred:

\[
\begin{align*}
\text{ND}_2^+ + \text{Li}^- & \rightarrow \text{ND}^- + \text{Li}^+ \\
\text{ND}^- + \text{H}_2\text{O} & \rightarrow \text{NH}_2^- + \text{D}_2 \text{O}
\end{align*}
\]

The [2-2H] aniline was converted to [2-2H] styrene by the sequence of reactions described in the experimental section. The product was analysed by mass spectrometry (Table 1). The reaction of tetrafluorobenzylene with [2-2H] styrene would be expected to produce
an initial Diels-Alder intermediate (5b; R=H) which can have either hydrogen or deuterium at the ring junction position. Consequently the intermolecular or intramolecular nature of the transfer of the ring junction proton in the intermediate (5b; R=H) to the 9-position in the dihydrophenanthrene (IV) should be reflected in the deuterium content of the product. The reaction between tetrafluorobenzyne and \([2\cdot ^2\text{H}]\) styrene was carried out under the conditions found to give the dihydrophenanthrene. The product obtained (IV) was analysed by mass spectrometry (Table 1) which showed that the distribution of \([2\cdot ^2\text{H}_2]\), \([2\cdot ^2\text{H}_1]\) and \([2\cdot ^2\text{H}_0]\) in the product was almost identical to that observed in the starting material, indicating a high degree of intramolecularity for the reaction.

A number of base catalysed intramolecular 1,3 proton transfer reactions have been observed previously and a 'conducted-tour' mechanism proposed. An analogous mechanism would account for the results of the labelling experiment in the reaction of tetrafluorobenzyne with styrene, in which pentafluorophenyl lithium acts as the base. The highly intramolecular character of the reaction may result from the ability of the migrating conjugate acid, which in this instance would be pentafluorobenzene, to exist as a charge-transfer complex with the extended pi-electron system containing negative charge. The failure to observe the chlorinated analogue in the reaction in which tetrachlorobenzyne was generated by aprotic diazotisation of tetrachloroanthranilic acid would therefore result from the absence of a suitable base.
which could act as a catalyst in the proton transfer. A similar explanation would account for the failure to observe 9,10-dihydrophenanthrene in the reaction of benzyne, generated from o-fluorophenylmagnesium bromide, with styrene. Although o-fluorophenylmagnesium bromide could remove the analogous proton from the ring junction position, fluorobenzene would not be capable of acting as the acid in the subsequent reprotonation step.

In the reactions in which a formal dehydrogenation occurred to form phenanthrene derivatives, a number of experimental observations are significant. Both α-methylstyrene and trans-β-methyl styrene did yield the appropriate phenanthrene derivatives in reactions with tetrafluorobenzyne. The possibility that the dihydrophenanthrene, once formed, could be dehydrogenated by excess of tetrafluorobenzyne has been tentatively suggested and the feasibility of this proposal has been investigated by generating tetrafluorobenzyne, generated from pentafluorophenyl lithium, in the presence of 1,2,3,4-tetrafluoro-9,10-dihydro-6,8-dimethylphenanthrene (IX). Investigation of the reaction mixture by gas liquid chromatography showed only unchanged (IX). In a similar experiment, which reproduced more exactly the conditions under which phenanthrene derivatives were formed, tetrafluorobenzyne was generated in the presence of styrene (2.5 mole) and compound (IX). Examination of the reaction mixture by gas liquid chromatography showed unchanged (IX) together with (IV) and (V) in the expected ratio. Thus dehydrogenation of the 9,10-dihydrophenanthrenes by excess tetrafluorobenzyne does not occur. An alternative mechanism which must be considered is the dehydro-
eneration of the initial Diels-Alder adduct (5b; R-H) by tetrafluorobenzene. In order to test the validity of this mechanism, a reaction was carried out between tetrafluorobenzene and cis-β-deuteriostyrene under the conditions which had been shown to give phenanthrene derivatives. The cis-β-deuteriostyrene was prepared by electrolytic reduction of β-deuteriophenylacetylene and shown by 'H n.m.r. to have 93% of the deuterium cis. Mass spectrometry showed a total deuterium content of 84.5% (Table 1). A concerted disrotatory cycloaddition of tetrafluorobenzene and cis-β-deuteriostyrene would produce an initial Diels-Alder adduct having the stereochemistry shown in Scheme 6(a).

\[
\text{Scheme 6.}
\]

Cis-dehydrogenation of the intermediate (6a) would result in a phenanthrene having no deuterium. The phenanthrene (V) produced in the experiment was shown by mass spectrometry (Table 1) to contain \( ^2\text{H}_0 \) 50.3% and \( ^2\text{H}_1 \) 49.2% which proved that the
deuterium had not been removed stereospecifically. Thus the intermediate (6a), if formed in a concerted reaction, is not dehydrogenated by tetrafluorobenzene. The most reasonable explanation of the observed result is that tetrafluorobenzene abstracts a hydride ion from the intermediate (Scheme 6). This type of reaction, involving the formal transfer of a hydride ion to an aryne has been recently reported.\textsuperscript{62} An alternative mechanism, involving the removal of a hydride ion from the carbanion (5c; R=H) is unlikely since (V) was produced in a significant amount in the reaction in which no deuterium incorporation was detected in (IV) in the presence of deuteriopentafluorobenzene. Since pentafluorobenzene would be expected to form a charge-transfer complex with the extended pi-electron system of the intermediate (6a), it is not surprising that the phenanthrene (V) was produced and this suggests that the hydride ion is removed from the methylene group rather than from the ring junction methine group in the intermediate (6a). In addition, the approach of tetrafluorobenzene to remove a hydride ion from the ring junction position would set up a favourable geometry for an 'ene' reaction, the transition state for which would presumably be of lower energy than that involving the removal of a hydride ion. The failure to observe the 'ene' product indicates that the hydride ion is, in fact, removed from the methylene group with the formation of a resonance stabilised carbonium ion (Scheme 6). Subsequent loss of a proton would give the observed phenanthrene (V).
Phenanthrene derivatives were the only products isolated in the reaction of tetrafluorobenzyn with certain styrene derivatives. 3-Methylstyrene, trans-β-methylstyrene, and 1,1-diphenylethylene gave only the phenanthrenes (VI), (XIV), and (XIII) respectively, even under conditions found in other systems to give the dihydrophenanthrene as the major product. These results are difficult to rationalise except in the case of 1,1-diphenylethylene where conjugation of the 9-aryl group might be expected to be the driving force towards aromaticity.
EXPERIMENTAL

1. General Methods

Analytical gas chromatography was carried out on Pye 104 gas chromatographs, using a hydrogen flame ionisation detector.

Infrared spectra were determined using potassium bromide discs for solids or thin films in the case of liquids on Perkin-Elmer 237 or 257 grating spectrophotometers. U.V. spectra for methanolic solutions were determined on a Unicam S.P. 800 spectrophotometer.

$^1$H n.m.r spectra were determined at 60 MHz for solutions in deuteriochloroform, using tetramethyl silane as internal standard with a Perkin-Elmer R10 spectrophotometer. Mass spectra were determined with A.E.I. MS9 and MS12 spectrometers.

All compounds described are colourless solids unless otherwise specified. Melting points are uncorrected. All reactions involving lithio-compounds or Grignard reagents were carried out under an atmosphere of dry, oxygen-free nitrogen.

Hydrolyses were effected by dilute hydrochloric acid or distilled water. All reactions involving the formation of adducts between tetrahalobenzenes from the organo-metallic compounds and liquids, were carried out using dry diethyl ether as solvent. Reactions with solids were carried out using dry diethyl ether or light petroleum (b.p. 60-80$^\circ$) as
Solvent. Solutions of products were dried with anhydrous sodium or magnesium sulphate.

Light petroleum, diethyl ether, and cyclohexane were dried over sodium wire. Tetrahydrofuran was dried by heating under reflux over sodium, distilled onto potassium, and distillation from potassium when required for use.

n-Butyl lithium was obtained commercially in hexane solution and standardised by titration with acid. It was stored in the refrigerator and removed through a serum-cap by means of a syringe. All reactions involving the preparation of lithio-compounds were cooled by means of an acetone/liquid nitrogen bath. Silver nitrate T.L.C. plates were prepared by the method of Berg. Column chromatography was carried out with 'CAMAG' alumina, Brockmann activity 1. Filtrations of crude products to remove polymeric material were carried out on deactivated alumina.

**Reaction of Tetrachlorobenzene with Styrene**

Tetrachloroanthranilic acid (2.5 g., 0.009 mole) in dry diethyl ether (50 ml.) was added slowly to a stirred solution of 3-methylbutyl nitrite (10 ml) and styrene (10.4 g., 0.1 mole.) in cyclohexane (150 ml) at 45°. Heating was continued for 0.5 hr. after the addition. The ether, pentyl alcohol and excess of styrene were distilled off to leave a viscous brown oil. Elution from alumina with light petroleum gave 1,2,3,4-tetrachlorophenanthrene (I) (1.0 g., 75%), m.p. 170° (from ethanol).

(Found: C, 53.3; H, 2.1; Cl, 44.6. \( \text{C}_{14}\text{H}_{6}\text{Cl}_{4} \) requires C, 53.2; H, 1.9; Cl, 44.9%), \( \gamma \) 0.25-0.4 (m, 1H), 1.75-1.9 (m, 1H), 2.15-2.45 (m, 4H), \( \lambda_{\text{max}} (\text{MeOH}) \) 256 (log e 4.54), 267 (4.74).
Reaction of Tetrafluorobenzyne with 2-Methylstyrene

Method I 2-Methylstyrene (11.8 g., 0.1 mole) was added slowly (0.5 hr.) to a solution of pentafluorophenyl-lithium (0.02 mole) at -70°C. The mixture was allowed to warm to ambient temperature immediately after the addition. The ether solution was washed with water and dried. Removal of the ether and excess of 2-methylstyrene left a viscous brown oil which when eluted from neutral alumina with light petroleum gave 1,2,3,4-tetrafluoro-9,10-dihydro-8-methylphenanthrene (II) (930 mg., 37.5%), m.p. 81°C (from ethanol).

(Found: C, 67.5; H, 3.65; F, 28.3. C_{15}H_{10}F_{4} requires C, 67.65; H, 3.75; F, 28.6%), ν 2.1-2.4 (m, 1H), 2.7-3.0 (m, 2H), 7.25 (s, 4H), 7.7 (s, 3H), λ_{max} (MeOH) 266 (log ε 3.98), 300 (2.85) n.m.

Method II 2-Methylstyrene (5.9 g., 0.05 mole) was added slowly to a solution of pentafluorophenyl-lithium (0.02 mole) at -70°C. The mixture was allowed to warm to ambient temperature during ca. 18 hr. The ether solution was washed with water and dried. Evaporation of the ether left a yellow oil which crystallised when cooled and gave 1,2,3,4-tetrafluoro-8-methylphenanthrene (III) (1.48 g., 56%), m.p. 189°C (from ethanol-benzene).

(Found: C, 68.3; H, 3.10; F, 28.3. C_{15}H_{10}F_{4} requires C, 68.2; H, 3.05; F, 28.8%), ν 1.0-1.2 (m, 1H), 1.9-2.05 (m, 2H), 2.3-2.5 (m, 2H), 7.25 (s, 3H), λ_{max} (MeOH) 240 (log ε 4.67), 247 (4.79), 262 (4.23), 280 (3.91), 291 (4.07), 303 (4.13), 330 (2.69), 350 (2.57) n.m.
Reaction of Tetrafluorobenzene with Styrene

The procedure described in Method I above was followed and the reaction was carried out on the same molar scale to give 1,2,3,4-tetrafluoro-9,10-dihydrophenanthrene (IV) (5.02 g., 60.5%), m.p. 89° (from ethanol).

(Found: C, 66.4; H, 3.15; F, 30.2. $\text{C}_{14}\text{H}_{6}\text{F}_{4}$ requires C, 66.7; H, 3.2; F, 30.15%). $\gamma$ 1.97-2.31 (m, 1H), 2.6-2.87 (m, 3H), 7.05-7.35 (s, 4H). $\lambda_{\text{max}}$ (MeOH) 264 (log $\varepsilon$ 4.22), 290 (3.35) n.m.

When the procedure described in Method II was followed, the product obtained was 1,2,3,4-tetrafluorophenanthrene (V) (500 mg., 20%), m.p. 175° (from ethanol).

(Found: C, 67.85; H, 2.6; F, 29.6. $\text{C}_{14}\text{H}_{6}\text{F}_{4}$ requires C, 67.2; H, 2.4; F, 30.4%). $\gamma$ 0.9-1.25 (m, 1H), 1.5-2.4 (m, 5H)

$\lambda_{\text{max}}$ (MeOH) 236 (4.66), 244 (4.83), 257 (4.36), 273 (4.19), 283 (4.20), 295 (4.21), 330 (2.94) n.m.

Reaction of Tetrafluorobenzene with 3-Methylstyrene

The only product obtained from Method I or II was 1,2,3,4-tetrafluoro-7-methylphenanthrene (VI) (422 mg., 16%), m.p. 130° (from methanol).

(Found: C, 68.2; H, 2.95; F, 28.9. $\text{C}_{15}\text{H}_{8}\text{F}_{4}$ requires C, 68.2; H, 3.05; F, 28.8%). $\gamma$ 1.1-1.3 (m, 1H), 2.2-2.6 (m, 4H), 7.45 (s, 3H). $\lambda_{\text{max}}$ (MeOH) 244 (4.78), 249 (4.87), 259 (4.36), 275 (4.04), 285 (3.98), 318 (2.53), 332 (2.62), 348 (2.53) n.m.

Reaction of Tetrafluorobenzene with 4-Methylstyrene

Method I gave 1,2,3,4-tetrafluoro-9,10-dihydro-6-methylphenanthrene (VII) (1.76 g., 33%), m.p. 72° (from
ethanol).

(Found: C, 67.55; H, 3.60; F, 28.4. C\textsubscript{15}H\textsubscript{10}F\textsubscript{4} requires C, 67.65; H, 3.75; F, 28.6%). \(\gamma\) 2.2-2.35 (m, 1H), 2.9-3.0 (m, 2H), 7.25 (s, 4H), 7.6 (s, 3H), \(\lambda\)\textsubscript{max} (MeOH) 265 (4.22), 298 (3.50) n.m.

Method II gave \(1,2,3,4\)-tetrafluoro-6-methylphenanthrene (VIII) (1.53 g., 58%) m.p. 147\(^\circ\) (from ethanol).

(Found: C, 68.1; H, 3.15; F, 28.1. C\textsubscript{15}H\textsubscript{8}F\textsubscript{4} requires C, 68.2; H, 3.05; F, 28.8%). \(\gamma\) 1.2-1.3 (m, 1H), 2.05-2.15 (m, 3H), 2.3-2.5 (m, 1H), 7.4 (s, 3H), \(\lambda\)\textsubscript{max} (MeOH) 240 (4.7), 259 (4.35), 276 (3.88), 287 (4.02), 299 (4.12), 319 (2.77), 334 (3.03), 349 (3.07) n.m.

Reaction of Tetrafluorobenzyne with 2,4-Dimethylstyrene.

Method I gave \(1,2,3,4\)-tetrafluoro-2,10-dihydro-6,8-dimethylphenanthrene (IX) (1.46 g., 26%), m.p. 95\(^\circ\) (from ethanol).

(Found: C, 68.8; H, 4.25; F, 27.1. C\textsubscript{16}H\textsubscript{12}F\textsubscript{4} requires C, 68.6; H, 4.3; F, 27.1%). \(\gamma\) 2.4-2.5 (m, 1H), 3.0-3.1 (m, 1H), 7.3 (s, 4H), 7.7 (s, 6H), \(\lambda\)\textsubscript{max} (MeOH) 265 (4.21), 305 (3.48) n.m.

Method II gave \(1,2,3,4\)-tetrafluoro-6,8-dimethylphenanthrene (X) (1.45 g., 52%), m.p. 179\(^\circ\) (from ethanol-benzene).

(Found: C, 69.2; H, 3.6; F, 27.5. C\textsubscript{16}H\textsubscript{10}F\textsubscript{4} requires C, 69.1; H, 3.6; F, 27.4%). \(\gamma\) 1.25-1.35 (m, 1H), 2.0-2.1 and 2.55-2.7 (m, 3H), 7.25 (s, 3H), 7.4 (s, 3H), \(\lambda\)\textsubscript{max} (MeOH) 240 (4.63), 249 (4.78), 263 (4.32), 272 (4.21), 295 (4.05), 307 (4.10), 338 (3.02), 352 (2.95) n.m.

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Reaction of Tetrafluorobenzynne with 1-Vinylnaphthalene

Method I gave 1,2,3,4-tetrafluoro-11,12-dihydrochrysene (XI) (60 mg., 1%) m.p. 133° (from methanol).

(Found: C, 71.5; H, 3.5; F, 25.1; C_{18}H_{10}F_{4} requires C, 71.5; H, 3.35; F, 25.1%), \( \tau \) 1.6-1.7 and 1.8-2.5 (m, 6H), 6.6-7.2 (m, 4H), \( \lambda_{\text{max}} \) (MeOH) 245 (4.40), 253 (4.69), 263 (4.83), 297 (4.01), 309 (3.97), 323 (3.47), 340 (3.14) n.m.

Reaction of Tetrafluorobenzynne with trans-Stilbene.

trans-Stilbene (2.7 g., 0.015 mole) in cyclohexane (100 ml.) was added to pentafluorophenylmagnesium chloride (0.01 mole). The ether was removed by distillation until the temperature of the vapour reached 80°. Heating under reflux was continued for 5 hr., the cyclohexane was removed by distillation, and the residue was distilled with steam. The residual material was partially purified by chromatography on alumina; finally preparative layer chromatography on silver nitrate-impregnated silica and recrystallisation gave 1,2,3,4-tetrafluoro-9,10-dihydro-10-phenylphenanthrene (XII) (1.84 g., 32%) m.p. 89° (from methanol).

(Found: C, 73.3; H, 3.6; C_{20}H_{12}F_{4} requires C, 73.2; H, 3.7%), \( \tau \) 1.8-2.0 (m, 1H), 2.7-3.0 (m, 8H), 5.3 (t, 1H), 6.8 (d, 2H [\( \text{J} = 6 \text{ Hz} \) ] ), \( \lambda_{\text{max}} \) (MeOH) 266 (4.19), 293 (3.34) n.m.

Reaction of Tetrafluoroobenzynne with 1,1-Diphenylethylene

The only product obtained from both Methods I and II was 1,2,3,4-tetrafluoro-9-phenylphenanthrene (XIII) (1.37 g., 42%) m.p. 203° (from benzene-light petroleum).
Reaction of Tetrafluorobenzyne with trans-β-Methylstyrene.

The only product obtained from both Methods I and II was 1,2,3,4-tetrafluoro-10-methylphenanthrene (XIV) (1.58 g., 60%), m.p. 142°C (from ethanol).

(Found: C, 68.2; H, 3.1; F, 28.9. C_{15}H_{10}F_{4} requires C, 68.2; H, 3.05; F, 28.6%), \( \gamma \) 1.0-1.2 (m, 1H), 2.3-2.5 (m, 4H), 7.2 (d, 3H [J= 9Hz \text{ } \text{ } \text{ } \text{ } \text{ } \text{ } \text{ } \text{ } \text{ } \text{ } \text{ } \text{ } \text{ } \text{ } \text{ } \text{ } \text{ } \text{ } \text{ } \text{ } \text{ } \text{ ] }, \lambda_{max}^{(\text{MeOH})} 240 (4.69), 246 (4.81), 260 (4.26), 276 (3.96), 287 (4.02), 299 (4.07), 336 (3.08), 351 (3.14) n.m.

Reaction of Tetrafluorobenzyne with α-Methylstyrene

The reaction was carried out as described in Method I and the crude reaction mixture was shown by gas liquid chromatography to contain three major components. Column chromatography of the oil on neutral alumina with light petroleum as eluent gave (a) α-(2,3,4,5-tetrafluorobenzyl) styrene (XV) (1.49 g., 28%), colourless oil.

(Found: C, 67.25; H, 3.9; F, 28.45. C_{15}H_{10}F_{4} requires C, 67.7; H, 3.8; F, 28.55%), \( \gamma \) 2.5-2.88 (m, 5H), 2.98-3.47 (m, 1H), 4.49 (s, 1H), 4.94 (t, 1H), 6.19 (s, 2H), \( \lambda_{max}^{(\text{MeOH})} 244 (4.00), 284 (2.80), 297 (2.49) n.m. (b) 1,2,3,4-tetrafluoro-9,10-dihydro-9-methylphenanthrene (XVI) (1.12 g., 21%) m.p. 93°C (from ethanol).

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(Found: C, 67.8; H, 3.85; F, 28.4. \( \text{C}_{15} \text{H}_{10} \text{F}_{4} \) requires C, 67.7; H, 3.8; F, 28.5%). \( \gamma \) 1.97-2.25 (m, 1H), 2.58-2.9 (m, 3H), 6.83-7.4 (m, 3H), 8.6-8.9 (d, 3H \( J = 6 \text{Hz} \)), \( \lambda_{\text{max}} \) (MeOH) 267 (4.26), 293 (3.35) n.m. (c) 1,2,3,4-tetrafluoro-9-methylphenanthrene (XVII) (132 mg., 5%) m.p. 179° (from ethanol).

(Found: C, 68.4; H, 3.35; F, 28.4. \( \text{C}_{15} \text{H}_{10} \text{F}_{4} \) requires C, 68.2; H, 3.05; F, 28.8%). \( \gamma \) 0.9-1.25 (m, 1H), 1.8-2.12 (m, 1H), 2.17-2.55 (m, 3H), 7.38 (s, 3H), \( \lambda_{\text{max}} \) (MeOH) 240 (4.65), 246 (4.76), 259 (4.32), 274 (4.12), 285 (4.13), 297 (4.11), 348 (2.90) n.m.

The reaction of tetrafluorobenzylene with \( \alpha \)-methylstyrene was repeated using Method II. The three products obtained were identical to those obtained using Method I but the product ratios were significantly different. \( \alpha \)-(2,3,4,5-tetrafluorobenzyl) styrene (29%), 1,2,3,4-tetrafluoro-9,10-dihydro-9-methylphenanthrene (15%) and 1,2,3,4-tetrafluoro-9-methylphenanthrene (14%).

Reaction of Tetrafluorobenzylene with 1-Phenylcyclohexene

Method I gave 1,2,3,4-tetrafluoro-9,10,11,12,12a-hexahydrotriphenylene (XVIII) (857 mg., 14%) m.p. 107° (from ethanol).

(Found: C, 70.3; H, 4.45; F, 24.6. \( \text{C}_{18} \text{H}_{14} \text{F}_{4} \) requires C, 70.6; H, 4.6; F, 24.8%). \( \gamma \) 1.9-2.1 (m, 1H), 2.5-2.8 (m, 3H), 6.8-7.0 (m, 2H), 8.3-8.6 (m, 8H), \( \lambda_{\text{max}} \) (MeOH) 268 (4.20), 295 (3.39) n.m.

Method II gave 1,2,3,4-tetrafluoro-9,10,11,12-tetrahydrotriphenylene (XIX) (669 mg., 22%) m.p. 205° (from ethanol-benzene).

(Found: C, 70.8; H, 4.0. \( \text{C}_{18} \text{H}_{12} \text{F}_{4} \) requires C, 71.0; H, 4.0%). \( \gamma \) 0.9-1.1 (m, 1H), 1.8-1.95 and 2.2-2.4 (m, 4H), 6.7-7.0 (m, 4H),
Dehydrogenation of (XIX)

The adduct (25 mg.) and palladium-charcol (10%; 10 mg.) were heated together at 300° for 15 min. under nitrogen. The residue was extracted with benzene and the extract, after evaporation and recrystallisation from methanol, gave 1,2,3,4-tetrafluorotriphenylene (XX) (20 mg., 81%), m.p. 229°.

(Found: C, 72.2; H, 2.8. \( \text{C}_{18} \text{H}_{2} \text{SF}_{4} \) requires C, 72.0; H, 2.7%), 0.9-1.15 (m, 2H), 1.3-1.45 (m, 2H) and 2.2-2.4 (m, 4H), \( \lambda_{\text{max}} \) (MeOH) 245 (4.68), 252 (4.91), 259 (4.97), 276 (4.20), 286 (4.15), 317 (2.88), 332 (3.02) and 347 (2.91) n.m.

Dehydrogenation of 1,2,3,4-tetrafluoro-8b,9,10,11,12,12a-hexahydrotriphenylene under the same conditions also gave (XX).

Preparation of Deuterium-labelled Styrene Intermediates.

\[
\begin{align*}
[2,4,6 - ^2\text{H}_2] \text{Styrene.} \\
\end{align*}
\]

(a) \[
\begin{align*}
[2,4,6 - ^2\text{H}_2] \text{Aniline hydrochloride} \quad \text{Aniline hydrochloride (43.2 g., 0.33 mole) was heated in a sealed tube with deuterium oxide (20 g., 1.0 mole) for 12 hr. at 100°. The water was then removed by distillation under reduced pressure and the aniline hydrochloride dried in a vacuum desiccator over phosphorus pentoxide. After four additional treatments with deuterium oxide, the aniline hydrochloride was dried and weighed (36.8 g., 81.4%). A sample of the final product (40 mg.), after generation of the free base, was converted to acetonilide and the \( ^1\text{H} \) n.m.r spectrum recorded. The spectrum showed the presence of aromatic protons,}
\]

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NH protons and methyl protons in the ratio of 2:1:3, indicating the incorporation of three deuterium atoms into the aromatic nucleus.

(b) \[ [2,4,6-^2\text{H}_3] \text{Iodobenzene} \rightarrow [2,4,6-^2\text{H}_3] \text{aniline} \]

hydrochloride (36.8 g., 0.27 mole) was dissolved in concentrated hydrochloric acid (50 ml.) and water (73 ml.). The solution was then cooled to 5° with stirring. A solution of sodium nitrite (18.6 g., 0.27 mole) in water (100 ml.) was added dropwise with continuous stirring and the temperature was maintained at 0-5° during the addition. The aqueous diazonium salt was stirred for 15 min. at 5° then a solution of potassium iodide (47.8 g., 0.28 mole) in water (53 ml.) was added dropwise with stirring. After complete addition of the potassium iodide solution, during which time a vigorous evolution of nitrogen occurred, the temperature was allowed to rise to ambient, followed by heating at 70° on a water bath for 2 hr. until evolution of nitrogen ceased completely. The crude product, after decantation of the supernatant liquors was washed with sodium bisulphite solution (100 ml., 10%) and distilled water (100 ml.). Treatment of the crude product with 20% sodium hydroxide (50 ml.) and distillation with steam gave a pale yellow distillate which was extracted into ether. Removal of the ether and distillation of the residual liquid (b.p. 61-62°/8 mm.) gave \[ [2,4,6-^2\text{H}_3] \text{iodobenzene} \] (40.1 g., 71.7%).

(c) \[ [2,4,6-^2\text{H}_3] \text{Phenyl methyl carbinol} \rightarrow \text{A solution of} \]

\[ [2,4,6-^2\text{H}_3] \text{iodobenzene} (40.1 g., 0.20 mole) in dry ether (200 ml.) was added dropwise with stirring to a stirred
suspension of lithium wire (3.15 g., 0.45 g. atom) in dry ether (10 ml.) under an atmosphere of nitrogen. The addition was controlled to maintain a gentle reflux. After complete solution of the lithium, stirring was continued for 30 min. before the solution was cooled to 5° and redistilled acetaldehyde (28.5 g., 0.65 mole) was added at a slow drop rate. The temperature was allowed to rise to ambient after complete addition of the acetaldehyde and hydrolysis was effected by the addition of 10% sulphuric acid (50 ml.). The ether solution was washed with sodium bisulphite solution (100 ml., 10%) and dried. Removal of the solvent and distillation of the crude product (b.p. 62°/2 mm.) gave \( [2,4,6-^2\text{H}_3] \) phenyl methyl carbinol (14.6 g., 58.4%).

(d) \( [2,4,6-^2\text{H}_3] \) Styrene - The \( [2,4,6-^2\text{H}_3] \) phenyl methyl carbinol (14.6 g., 0.12 mole) prepared above was added in small portions to fused potassium bisulphate (10.2 g.) and picric acid (12 mg.) in a flask equipped for distillation at a temperature of 200° and a pressure of 85 mm. The styrene, which co-distilled with the water, was extracted into ether and the ether solution dried. Removal of the ether and distillation of the residue (b.p. 20°/0.4 mm.) gave \( [2,4,6-^2\text{H}_3] \) styrene (6.2 g., 48.4%). The product was redistilled and shown to be pure by gas liquid chromatography. The styrene was analysed by mass spectrometry (Table I).

Preparation of \( [2-^2\text{H}] \) Styrene

(a) \( [N,N-^2\text{H}_2] -2\text{-Bromoaniline} \) - 2-Bromoaniline (80.0 g., 0.465 mole) was dissolved in dry ether (200 ml.) and stirred vigorously with deuterium oxide (10.0 g., 0.5 mole) for 6 hr. in presence of deuterium chloride (0.2 ml.). The ether solution was then filtered through a core of anhydrous sodium carbonate.
An aliquot (0.5 ml.) of the solution was removed and the ether evaporated on a water pump. The $^1$H n.m.r. spectrum of the sample showed an 84% conversion of the protons on the nitrogen to deuterium. The experiment was repeated when the conversion was found to be 89.5%. A third exchange gave $[N, N - ^2H_2]$-2-bromoaniline having a conversion of 93.7% which was acceptable for the subsequent stages of the synthesis.

(b) $[2-^2H]$ Styrene - The ether solution from the above experiment was diluted to a total volume of 1.5 litres with dry ether. n-Butyl lithium (600 ml., 3 equiv.) was added at a slow drop rate with stirring in an atmosphere of dry nitrogen. After complete addition, stirring was continued for a further 3 hr. Hydrolysis was then effected by the dropwise addition of deuterium oxide (40.0 g., 2.0 mole) and the solution was subsequently stirred for 12 hr. The precipitated lithium deuterioxide was redissolved by the addition of water (500 ml.). The ether layer was separated and washed with water (100 ml.) and saturated sodium chloride solution (250 ml.). The washings were extracted with ether and this extract was combined with the original ether extract. The combined extracts were then dried. Distillation of the ether gave $[2-^2H]$ aniline which, without further purification, was converted to $[2-^2H]$ iodobenzene (56 g., 58.7% yield based on 6-bromoaniline) by the Sandmeyer procedure described above for the preparation of $[2,4,6-^2H_3]$ iodobenzene. The $[2-^2H]$ iodobenzene (56 g., 0.27 mole) was converted to $[2-^2H]$ phenyl methyl carbinol (24.2 g., 74.2%) by the procedure described above for the preparation of $[2,4,6-^2H_3]$ phenyl methyl carbinol.

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Subsequent dehydration of the \([2-^2\text{H}]\) phenyl methyl carbinol by the procedure described for the dehydration of \([2,4,6-^2\text{H}_3]\) phenyl methyl carbinol gave \([2-^2\text{H}]\) styrene (4.6 g., 21.9%). The styrene was again analysed by mass spectrometry (Table 1).

**Preparation of Deuteriopentafluorobenzene**

**Method I.** n-Butyl lithium (40 ml., 0.1 mole) was added dropwise to a stirred solution of bromopentafluorobenzene (24.7 g., 0.1 mole) in dry ether (150 ml.) at -70\(^\circ\) under an atmosphere of nitrogen. Stirring was continued for 15 min. after complete addition, then the solution of pentafluorophenyl-lithium was treated with deuterium oxide (4 g., 0.2 mole) at -60\(^\circ\). Stirring was continued and the reaction mixture was allowed to warm slowly to ambient temperature. The lithium deuterioxide formed was dissolved by the addition of 4N hydrochloric acid solution (25 ml.) and the ether layer separated. Gas liquid chromatography of the ether solution and comparison with an authentic sample of pentafluorobenzene showed the absence of deuteriopentafluorobenzene.

**Method II.** Bromopentafluorobenzene (49.4 g., 0.2 mole) in dry ether (250 ml.) was added to a stirred suspension of magnesium turnings (4.9 g., 0.2 g. atom) in dry ether (25 ml.) under an atmosphere of nitrogen. The addition was controlled to maintain gentle reflux. Stirring was continued for 2 hr. after complete addition of the bromopentafluorobenzene then deuterium oxide (4 g., 0.2 mole) was added dropwise to the solution of pentafluorophenylmagnesium bromide which was then heated under reflux for 3 hr. The reaction mixture was set aside for 12 hr. then shaken successively with 1N hydrochloric acid solution (50 ml.), water (50 ml.) and saturated sodium chloride solution (50 ml.).
The ether solution was then dried and the ether distilled off using a 15" Vigreux fractionating column. A further fraction (b.p. 60-80°) was then collected. Redistillation from a flask equipped with a 12" vacuum-jacketed fractionating column packed with glass helices gave deuteriopentafluorobenzene (9.6 g., 25.4%), b.p. 85° (lit. 63 b.p. 85°).

Reaction of Styrene with the Grignard reagents from (a) 2-chloro-2'-iodobiphenyl and (b) 2-fluoro-2'-ido-4',4'-dimethylbiphenyl.

(a) Styrene (5.2 g., 0.05 mole) was added to a stirred solution of the Grignard reagent (0.01 mole) in tetrahydrofuran (50 ml.) at ambient temperature. The solution was heated at 60° for 3 hr. in an atmosphere of nitrogen. Hydrolysis with water (1 ml.) and distillation to dryness gave an oily residue which was extracted into ether. Examination of the ether solution by gas liquid and thin layer chromatography showed the presence of two compounds which, by comparison with authentic compounds, were found to be 2-chloro-2'-iodobiphenyl and 2-chlorobiphenyl. The absence of 9,10-dihydro-9-phenylphenanthrene was also demonstrated by comparison with an authentic sample.

(b) Styrene (5.2 g., 0.05 mole) was again added to a stirred solution of the Grignard reagent (0.01 mole) in tetrahydrofuran (50 ml.) at ambient temperature. The reaction mixture was worked up as described in (a) above and shown to contain 2-fluoro-4',4'-dimethylbiphenyl and 2-fluoro-2'-ido-4',4'-dimethylbiphenyl by comparison with authentic samples.
Reaction of Benzyne with $\left[2,4,6-^2H_3\right]$ Styrene.

O-Bromofluorobenzene (0.01 mole) was added to magnesium turnings (0.01 g. atom) and a mixture of styrene (0.04 mole) together with $\left[2,4,6-^2H_3\right]$ styrene (0.01 mole) in dry tetrahydrofuran at 60°. Hydrolysis with water and removal of excess of styrene left a viscous yellow oil, which when eluted from neutral alumina with hexane gave 9,10-dihydro-9-phenylphenanthrene, m.p. 80° (lit. 49 m.p. 80°). The product was analysed by mass spectrometry (Table 1).

Reaction of Tetrachlorobenzylene with Phenylacetylene

A solution of tetrachloroanthranilic acid (2.75 g., 0.01 mole) in dry diethyl ether (50 ml.) was added dropwise to a stirred solution of phenylacetylene (5.1 g., 0.05 mole) in methylene chloride (30 ml.) containing 3-methylbutyl nitrite heated at 40°. Stirring was continued for 1 hr. after complete addition. Removal of methylene chloride and excess of phenylacetylene by distillation left a viscous oil which was examined by thin layer chromatography and shown to contain two products. Comparison with an authentic sample showed one of the products to be 2,3,4,5-tetrachlorophenetole which arises by cleavage of diethyl ether by tetrachlorobenzylene. The crude product was eluted from a neutral alumina column in light petroleum and gave (a) 2,3,4,5-tetrachlorophenetole (0.21 g., 8%) and (b) 1,2,3,4-tetrachlorophenanthatrene (0.9 g., 28.6%) m.p. 171° (from ethanol) (lit. 41 m.p. 170°).
SECTION 2

The Reactions of Tetrahalogenobenzynes with Arenes.
INTRODUCTION

The first reported reaction of an aryne with a simple aromatic compound was by Miller and Stiles who generated benzyne from benzenediazonium-2-carboxylate in the presence of an excess of benzene and obtained a mixture of three products. These were shown to be the 1,4-cycloadduct, benzobarrelene, the valence-bond isomerised 1,2-cycloadduct, benzocyclo-octatetrane, and the product of insertion into a carbon-hydrogen bond, biphenyl in 2, 8, and 6% yields respectively. When benzyne was generated by the oxidation of 1-aminobenzotriazole with lead tetraacetate in an excess of benzene the only product detected was biphenylene which was isolated in 83% yield. A number of explanations have been put forward to explain the reason for the predominance of dimerisation in this oxidative method of generating benzyne. One is the possibility of co-ordination to lead of some intermediate, possibly benzyne itself, in such a way as to enhance the probability of dimerisation. Another is that the benzyne is generated in a triplet state, is thus much less reactive towards nucleophiles, and is able to build up to concentration where one triplet with $\alpha$-spins and another with $\beta$-spins can combine with the virtually simultaneous formation of two new covalent bonds. This latter explanation is that given for the quantitative dimerisation of dimesitylcarbene on photolysis of dimesityldiazomethane. This latter explanation can now be discounted on the basis of recent calculations (see later).

When tetrafluorobenzyne and tetrachlorobenzyne were generated from their organometallic precursors and also by
aprotic diazotisation of the appropriate tetrahalogenoanthranilic acid in benzene solution, the only products isolated were tetrafluorobenzobarrelene\textsuperscript{66}, and tetrachlorobenzobarrelene\textsuperscript{67} in high yield. The fact that no insertion or 1,2-cycloaddition products were produced in these reactions was initially surprising, particularly in view of the fact that the 1,4-cycloadduct, benzobarrelene, was formed in a lower yield than the other two isomers in the reaction of benzyne with benzene. However, in a re-investigation of the reaction of benzyne with benzene\textsuperscript{68}, it was shown that the original method of isolating benzenediazonium-2-carboxylate resulted in the contamination of the zwitter-ion with silver salts. In the absence of silver ions, biphenylene, benzobarrelene, benzocyclo-octatetraene, and biphenyl were obtained in 2, 17, 0.05 and 2\% yields respectively. It was suggested that a benzyne-silver complex is formed in the presence of the silver ions and that the reactions of the complex, which is more electrophilic than benzyne, led to the increased yields of benzocyclo-octatetraene and biphenyl (Scheme 7). This result led to the re-investigation of the reaction of tetrafluorobenzyne and tetrachlorobenzyne with benzene in the presence of silver salts.\textsuperscript{69} Pentafluorophenyl lithium was prepared in benzene solutions containing traces of silver oxide, bromide and nitrate. The only product isolated, after decomposition to the aryne, was the 1,4-cycloadduct of tetrafluorobenzyne and benzene. Analogous results were obtained in the reaction of tetrachlorobenzyne with benzene in the presence of silver salts. When the aryne was generated from pentachlorophenyl lithium and by aprotic diazotisation of tetrachloroanthranilic acid in benzene solutions containing silver salts, the only product
Scheme 7.
isolated was again the 1,4-cycloadduct of tetrachlorobenzylene and benzene. These results suggest that tetrahalogenobenzynes do not form the necessary silver complexes for 1,2-cycloaddition reactions to occur. This can be explained by the fact that benzyne itself is more electron rich than tetrahalogenobenzynes and can therefore more readily donate electrons to the silver ion to form a complex.

The mechanisms, by which the products observed in the reactions of benzyne and tetrahalogenobenzynes with benzene arise, can be discussed in the light of current theories on the structure of aryne intermediates. Recent calculations concluded that benzyne is a ground-state singlet species with the two electrons of the "third-bond" in the lower symmetric orbital. Thus the thermal cyclo-addition reactions of arynes with 1,3-dienes is an allowed, concerted process by the conservation of orbital symmetry. Orbital symmetry analysis of various modes of cyclo-addition to the benzene ring shows that thermal 1,4-cycloaddition reactions are orbital symmetry controlled but photochemical cycloadditions are not. No positive evidence has been adduced so far which supports the idea that benzyne intermediates exist as diradicals, although a number of benzyne precursors have been investigated by electron paramagnetic resonance techniques. It seems reasonable that the formation of the 1,4-cycloadducts of benzene occurs by an essentially concerted, rather than a step-wise, process, particularly in view of the absence of 1,2-cycloadducts and hydrogen-abstraction products.
A number of observations prompted us to carry out an investigation of the reactions of tetrabromobenzylene and tetra-iobdobenzylene in solution. Pyrolysis of tetrachlorophthalic anhydride at a temperature of 800° and a pressure of 15 m.m. in a stream of nitrogen gave octachlorobiphenylene in 30% yield by dimerisation of tetrachlorobenzylene. A second product obtained in 34% yield was hexachlorobenzene. This presumably arose by the addition of elemental chlorine to tetrachlorobenzylene. Similarly when tetrafluorophthalic anhydride vapour was passed through a silica tube at 750° and a pressure of 0.6 m.m., octafluorobiphenylene was produced in 23% yield by the dimerisation of tetrafluorobenzylene. However tetrabromophthalic anhydride, in contrast to tetrafluorophthalic anhydride and tetrachlorophthalic anhydride, does not give the halogenated biphenylene on pyrolysis but gives only hexabromobenzene which is again presumably formed by the addition of elemental bromine to tetrabromobenzylene. In fact copious quantities of bromine are liberated during the pyrolysis of tetrabromophthalic anhydride. These results suggested that reactions of tetrabromobenzylene and also tetra-iobdobenzylene would be worthy of investigation in solution. The investigation of the tetrahalogenobenzynes has also been extended to tetrabromobenzylene and tetra-iobdobenzylene in order to rationalise certain data obtained in the reactions of tetrafluorobenzylene and tetrachlorobenzylene.

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DISCUSSION

The preparation of tetrabromobenzene by metallation of hexabromobenzene and subsequent decomposition of pentabromophenyl lithium was unsuccessful in small scale reactions due to the reluctance with which hexabromobenzene underwent halogen-metal exchange on treatment with an alkyl lithium reagent. Consequently, in view of the high yields of cycloadducts obtained in the reactions of tetrafluorobenzene and tetrachlorobenzene generated by aprotic diazotisation of tetrafluoroanthranilic acid and tetrachloroanthranilic acid, we decided to investigate the preparation of tetrabromoanthranilic acid and tetra-iodoanthranilic acid.

The published method for the preparation of tetrabromoanthranilic acid did not give the required product. Tetrachloroanthranilic acid has been prepared in greater than 80% yield from tetrachlorophthalic anhydride. Treatment of tetrachlorophthalic anhydride by ammonia followed by acidification gives tetrachlorophthalamic acid which is filtered off and converted to tetrachloroanthranilic acid by a Hofmann amide degradation using alkaline potassium hypochlorite or potassium hypobromite solutions. Attempts to utilise this procedure for the preparation of tetrabromoanthranilic acid from tetrabromophthalic anhydride were unsuccessful due to the failure of the tetrabromophthalamic acid to precipitate from aqueous solution on acidification. When tetrabromophthalic anhydride was treated with one equivalent of ammonia followed by alkaline potassium hypobromite, the only product isolated from the reaction was tetrabromophthalic acid. Tetrabromophthalic
anhydride can be readily converted to tetrabromophthalimide by
treatment with formamide in nitrobenzene\textsuperscript{74} and it was hoped that
this compound could be converted to tetrabromo-anthranilic acid
by a procedure analogous to that used for the conversion of
phthalimide to anthranilic acid.\textsuperscript{75} Tetrabromophthalimide was
heated under reflux with an excess of aqueous alkaline potassium
hypobromite solution. The solution, after heating for 3 hr., was
filtered to remove unreacted tetrabromophthalimide and acidified.
The yellow precipitate was recrystallised from ethanol-benzene
and appeared, from its melting point and infrared spectrum, to
be 2,3,4,5-tetrabromoaniline.\textsuperscript{76}

The preparation of tetra-iodoanthranilic acid from tetra-
iodophthalic anhydride is described in the literature\textsuperscript{40} and it
was hoped to utilise this procedure in the preparation of tetra-
bromoanthranilic acid. The sodium salt of tetrabromophthalamic
acid was prepared by treatment of tetrabromophthalic anhydride
with one equivalent of ammonia followed by one equivalent of
sodium hydroxide in dimethyl sulphoxide solution. The sodium
salt was then precipitated by the addition of a mixture of
ethanol and chloroform to the dimethyl sulphoxide solution.
Treatment of the sodium tetrabromophthalamate with alkaline
sodium hypobromite solution and final acidification of the
mixture gave a smooth conversion to tetrabromoanthranilic acid
in 78\% yield.

Tetrabromoanthranilic acid and tetra-iodoanthranilic
acid both gave the corresponding tetrahalogenobenzylene adducts
with furan (Table 3) using the aprotic diazotisation method.\textsuperscript{17,67}
TABLE 3

I

II

III

IV

V

VI

VII

VIII

IX

X
The products obtained were 5,6,7,8-tetrabromo-1,4-dihydro-1,4-epoxynaphthalene (I, X=Br, R=H) (29%) and 5,6,7,8-tetra-iodo-1,4-dihydro-1,4-epoxynaphthalene (I, X=I, R=H) (46.5%) which are analogous to the products obtained in the reactions of tetrafluorobenzyne and tetrachlorobenzyne with furan. The adducts of tetrabromobenzyne with furan and a number of other aromatic substrates have recently been prepared from pentabromo-phenyl lithium in yields ranging from 3% to 16%. When a solution of tetrabromoanthranilic acid in diethyl ether was added to an excess of benzene containing 3-methylbutyl nitrite at 50°C, three products were detected by gas liquid chromatography and also by thin layer chromatography. These compounds were separated by preparative chromatography on silica. One of the products was identified as 2,3,4,5-tetrabromophenetole (II, X=Br, R=C₆H₅) (7.5%) derived from the cleavage of diethyl ether by tetrabromobenzyne. This type of cleavage of simple aliphatic ethers by tetrachlorobenzyne has been previously reported in the literature. The yield of tetrabromophenetole was found to be dependent upon the ratio of diethyl ether to benzene used in the reaction and hence in subsequent reactions acetonitrile was used as the solvent for the tetrabromoanthranilic acid. The ether cleavage product has now been detected in the reaction of benzene with tetrachlorobenzyne in which diethyl ether was used as a solvent for the tetrachloroanthranilic acid. The second product, which was isolated in 27% yield, was shown to be tetrabromobenzobarrelene (III, X=Br, R=H, R₁=R²=R₃=H). This product arises by the 1,4-cycloaddition reaction of tetrabromobenzyne with benzene and is analogous to the products obtained in the reactions of the other tetrahalogeno-
benzyynes with benzene. The third compound was shown to be 2,3,4,5-tetrabromophenyl -(3'-methylbutyl) ether (II, X=Br, R=CH₂CH₂CH(CH₃)₂)(5%) which was initially assumed to be derived from the reaction of tetrabromobenzyne with the 3-methylbutan-1-ol, produced during the diazotisation of the tetrabromoanthranilic acid. This type of reaction was initially observed in the diazotisation of tetrachloroanthranilic acid by sodium nitrite in acetic or hydrochloric acids. 2,3,4,5-tetrachlorophenol, pentachlorobenzene, and 2,3,4,5-tetrachlorophenyl acetate were obtained by the addition of water, hydrochloric acid, and acetic acid respectively to the tetrachlorobenzyne. However, when a solution of tetrabromoanthranilic acid in diethyl ether was added to a stirred solution of 3-methylbutyl nitrite (1 equivalent) in diethyl ether, the ratio of the observed products (II, X=Br, R=C₅H₅) and (II, X=Br, R=CH₂CH₂CH(CH₃)₂) was 5:1 and in a similar experiment in which a five-fold excess of 3-methylbutyl nitrite was used, the ratio was 1.3:1. This result proves that the ratio of the two ethers is dependent upon the amount of 3-methylbutyl nitrite present and leads to the conclusion that the tetrahalogenobenzyynes can also cleave alkyl nitrites. The ether (II, X=Br, R=CH₂CH₂CH(CH₃)₂) was obtained in 43% yield when a solution of tetrabromoanthranilic acid in acetonitrile was added slowly to a stirred solution of 3-methylbutyl nitrite (5 mole) in acetonitrile. A fourth product, octabromoacridone (IV, X=Br), which undoubtedly arises from the reaction of tetrabromobenzyne with tetrabromoanthranilic acid, was also isolated in 8.5% yield from the reaction of tetrabromobenzyne.
with benzene in diethyl ether solution. When a solution of tetrabromoanthranilic acid in acetonitrile was added to benzene containing 3-methylbutyl nitrite at 50°, (IV, X=Br) (9.0%) together with (II, X=Br, R=CH₂CH₂CH(CH₃)₂) (4.6%) and (III, X=Br, R=R=R=H) (17.4%) were obtained. The reaction of benzene with tetrachlorobenzylene generated from tetrachloroanthranilic acid in the presence of diethyl ether gave 2,3,4,5-tetrachlorophenol (II, R=C₆H₅) (12.8%), tetrachlorobenzobarrelene (III, X=Cl, R=R=H) (50%), (II, X=Cl, R=CH₃CH₂CH(CH₃)₂) (8.6%) and (IV, X=Cl) (7.2%). The molar ratios of starting materials used in the latter experiment were identical to those used in the analogous reaction with tetrabromobenzylene. Consequently the fact that similar product ratios were observed in the two reactions indicates that tetrachlorobenzylene and tetrabromobenzylene have similar reactivities in this particular system.

While no attempt has been made to optimise the yields of the benzobarrelene derivatives subsequently described, they can undoubtedly be improved considerably. In the original reaction of tetrabromobenzylene with benzene, the yield of tetrabromobenzobarrelene was 27%. This yield was increased to 67% by running a solution of tetrabromoanthranilic acid in benzene/acetonitrile into benzene at 50° while concurrently adding one equivalent of 3-methylbutyl nitrite in benzene.

The reactions of the tetrahalogenobenzynes with monoalkylbenzenes result in the formation of both the possible 1,4-cycloadducts. However the ratio of the bridgehead substituted benzobarrelene (III, X=F, R=Br, R=H) to the vinyl-
substituted benzobarrelene (III, X = F, R¹ = Bu¹, R² = H) only approaches the statistical value in the reaction of tetrafluorobenzyne with t-butylbenzene, more of the adduct (III, X = F, R¹ = Alkyl, R² = H) is normally produced. Similar results were obtained in the reactions of tetrachlorobenzyne and tetrabromo-benzyne with mono-alkylbenzenes which suggests that the transition state leading to the formation of the bridgehead substituted and vinyl-substituted benzobarrelenes is product-like and that the greater than statistical formation of adducts (III, X = F, Cl, Br, I, R¹ = Alkyl, R² = H) is due to the increased thermodynamic stability of a trisubstituted double bond. In agreement with this explanation is the fact that in reactions of the tetra-halogenobenzynes with p-xylene only the vinyl-substituted benzobarrelenes (III, X = F, Cl, Br, I, R² = H, R¹ = CH₃) are obtained. Molecular orbital calculations for a number of alkyl-substituted benzenes have shown that in p-xylene the electron density is greatest at the unsubstituted ring carbon atoms which again may account for the absence of bridgehead substituted benzobarrelenes in the reactions of p-xylene with the tetra-halogenobenzynes.

Since the adducts (III, X = F, R = Bu¹, R¹ = R² = H) and (III, X = F, R¹ = Bu¹, R² = H) were obtained in an almost statistical ratio, one might conclude that there is no steric crowding in the transition state leading to the product (III, X = F, R = Bu¹, R¹ = R² = H). However there is a considerable steric effect in the product. The ¹H n.m.r. spectrum shows that there is a considerable barrier to rotation about the
bridgehead carbon to t-butyl-group bond. The presence of long-range \(^{19}\)F-\(^{1}\)H spin-spin coupling of proton-containing substituents to fluorine is extremely useful in structure determination and in the case of the compound \((\text{III}, X=F, R=\text{Bu}^t, R^1=R^2=R^3=\text{H})\), a six proton doublet \(\{J\}_{\text{H-F}}=4.5 \, \text{Hz}\) is observed downfield of a three proton singlet at 40\(^\circ\). The first conclusion which can be tentatively drawn from this evidence is that the transmission of the spin-spin information is occurring by a through-space mechanism. The second is that there is a barrier to rotation for the t-butyl group at room temperature. On raising the temperature in hexadeuteriodimethyl sulphoxide the doublet and singlet signals collapse at approximately 135\(^\circ\) and on raising the temperature, a doublet of integral area nine protons begins to appear. At a temperature of 200\(^\circ\) the doublet is reasonably resolved and shows a coupling constant \(\{J\}_{\text{H-F}}=2.9 \, \text{Hz}\) which is approximately two-thirds of the value obtained at 40\(^\circ\). If the spin-spin information was being transmitted by the normal through-bond mechanism the upfield three proton signal would be expected to occur as a doublet because these protons are the only ones which can assume the required planar zig-zag conformation. Preliminary results, using the change in chemical shift method, indicate that the energy barrier to rotation is of the order of 20 kcal. mole\(^{-1}\). As expected, the silicon compound \((\text{III}, X=F, R=\text{Si}(\text{CH}_3)_3, R^1=R^2=R^3=\text{H})\) shows a nine proton doublet for the methyl protons in its \(^1\)H n.m.r. spectrum. Evidently the increase in the carbon to silicon bond-length, compared to the analogous carbon to carbon bond length results in the reduction of the steric effect. In the analogous
adducts (III, X=Cl or Br, R=Bu, R'H=Br, R=R₂=R₃=H) the steric hindrance to rotation is so severe that collapse of the t-butyl resonances, a low-field six proton singlet and a higher-field three proton singlet does not occur even at 200°C. Evidently the steric interaction is even more severe in the reaction of tetra-iodo-benzyn with t-butylbenzene since only the adduct (III, X=I, R¹=Bu, R=R₂=R₃=H) was detected. These results suggest that the transition state which leads to the compounds (III, X=F, Cl, Br, I, R=Bu, R¹=R₂=R₃=H) is not symmetrical and completely product-like. It may well be that bond formation at the position para to the t-butyl group in the transition state is more advanced than bond formation at the carbon carrying the t-butyl group, as represented schematically in (V, X=Cl or Br, R=Bu). A model for the transition state of Diels-Alder reactions, in which one incipient bond is stronger or formed to a greater degree than the other, was first suggested by Woodward and Katz, and has been gaining support in recent years. This hypothesis has been invoked to explain the observed kinetics in the thermal cyclisation of hexa-1-cis-1,5-triene to cyclohexadiene.

Previous studies have shown that tetrafluorobenzyn reacts with anisole to give a mixture of two adducts. They are the bridgehead substituted benzobarrelene (III, X=F, R=OCH₂, R¹=R₂=R₃=H) and 5,6,7,8-tetrafluoro-1,4-etheno-2-tetralone (VI, X=F, R=H) in a ratio of 4:1. The latter product arises from the initially formed vinyl-substituted benzobarrelene (III, X=F, R¹=OCH₂, R=R²=R₃=H) which is an enol-ether and particularly susceptible to hydrolysis. The hydrolysis may be facilitated by participation of the disubstituted double bond of the non-
bridgehead isomer in the hydrolysis stage. The ratio of the
two compounds (III, X=Br, R=OCH₃, R¹=R²=R³=H) and the ketone
(VI, X=Br, R=H) isolated by preparative layer chromatography from
the reaction of tetrabromobenzynz with anisole was 3:1. This
value is widely different from that obtained previously from
the reaction of tetrachlorobenzynz with anisole when the pro-
ducts were separated by column chromatography and the ratio
of bridgehead substituted benzobarrelenes (III, X=Cl, R=OCH₃, R¹=R²
=R³=H) to ketone (VI, X=Cl, R=H) was approximately 100:1. This
latter reaction has been repeated and the products separated by
preparative layer chromatography on silica when the observed
ratio was 29:1. The discrepancy was undoubtedly due to our
failure to isolate some of the ketone (VI, X=Cl, R=H) in the
previous study. The product ratios observed in the reactions
of tetrahalogenobenzynes with anisole can be contrasted with the
ratios observed in the reactions of tetrahalogenobenzynes with
mono-alkylbenzenes. Whereas the ratio of bridgehead substituted
benzobarrelenes to vinyl-substituted benzobarrelenes approaches
the statistical value in most reactions of tetrahalogenobenzynes
with mono-alkylbenzenes, the ratios observed in reactions with
anisole show a predominance of the bridgehead substituted benzo-
barrelenes. This result suggests that the transition state
leading to the formation of 1,4-cycloadducts of tetrahalogeno-
benzenes with anisole is not necessarily symmetrical and that
substituents on an arene which can release electrons by a con-
jugative mechanism react with the tetrahalogenobenzynes to give
non-statistical mixtures of adducts. This result reflects the
known feature of electrophilic substitution of anisole which
occurs predominantly at the position para to the methoxyl.
group and also leads to the conclusion that the transition state leading to the adducts \((III, X=F, Cl, Br, R=OCH_2, R^1=R^2=R^3=H)\) does not involve an absolutely synchronous formation of the two new bonds as shown in \((V, X=F, Cl, Br, R=OCH_2)\). The difference in product ratios observed in the reactions of tetrachlorobenzynes with anisole can be explained if the ratio observed in the reaction of tetrachlorobenzyne with anisole (29:1) is considered to be 'normal'. The value observed in the reaction of tetrafluorobenzyne with anisole (4:1) can then be attributed to a lack of selectivity which tetrafluorobenzyne shows in a number of its cycloaddition reactions. The value observed in the reaction of tetrabromobenzyne with anisole (3:1) undoubtedly reflects an increase in the steric effect in the transition state leading to the bridgehead substituted benzobarrelene. It is of interest to note that the reaction of tetrabromobenzyne with \(\alpha\)-cresol methyl ether gave only the ketone \((VI, X=Br, R=CH_3)\) in 24% yield. The reaction of tetrafluorobenzyne with \(\alpha\)-cresol methyl ether produces a bridgehead substituted benzobarrelene in addition to the expected ketone \((VI, X=F, R=CH_2)\). The conclusion which must be drawn from these observations is that in the reactions of a \(para\)-substituted methoxybenzene with the tetrachlorobenzynes there is a considerable steric interaction in the transition state leading to the bridgehead substituted benzobarrelene which in the case of tetrabromobenzyne is sufficiently large so as to preclude the formation of this isomer.

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The reactions of certain alkylbenzenes with tetrabromo-
benzylene generated by aprotic diazotisation of tetrabromoanthra-
nilic acid produced a number of unexpected results. The
reaction of tetrabromobenzylene with benzene gave only the expected
benzobarrelene ($\text{III, } X=\text{Br}, \ R=\text{H}$). Analogous results
were obtained in the reactions of tetrabromobenzylene with p-
xylene ($\text{III, } X=\text{Br}, \ R=\text{H}$, $R^1=\text{CH}_3$) and mesitylene ($\text{III, } X=\text{Br},$
$R=\text{H}, \ R^1=\text{H}, \ R^2=\text{CH}_3$). However the reaction of tetrabromobenzylene
with toluene afforded three products of which two were found
to be the expected benzobarrelene derivatives ($\text{III, } X=\text{Br}, \ R=\text{CH}_3, \ R^1=\text{H}$) and ($\text{III, } X=\text{Br}, \ R^1=\text{CH}_3, \ R=\text{H}, \ R^2=\text{H}$). The ultra-
violet spectrum of the third compound, which was isolated in
2% yield, was characteristic of a naphthalene and the $^1H$ n.m.r.
spectrum indicated a $1,2,3,4$-tetrabromomethyl-naphthalene. In
order to gain further evidence of structure, $1,2,3,4$-tetra-
bromonaphthalene was prepared from the tetrabromobenzylene
adduct with furan ($\text{I, } X=\text{Br}, \ R=\text{H}$). The adduct was hydrogenated
in ethanol over a pre-reduced palladium on carbon catalyst
to give $5,6,7,8$-tetrabromo-1,4-dihydro-1,4-epoxy-tetralin
($\text{VII, } X=\text{Br}, \ R=\text{H}$) in 92% yield. Subsequent treatment of the
reduced adduct with constant boiling hydrobromic acid in
glacial acetic acid at 100° gave $1,2,3,4$-tetrabromonaphthalene
($\text{VIII, } R=\text{H}$) in 80% yield. Comparison of the ultraviolet
spectra of $1,2,3,4$-tetrabromonaphthalene and the novel product
isolated from the reaction of tetrabromobenzylene with toluene
showed that the two compounds were very similar. The
preparation of $1,2,3,4$-tetrabromo-5-methyl-naphthalene ($\text{VIII,}$
$R=\text{CH}_3, \ R=\text{H}$) from the adduct of tetrabromobenzylene with
2-methylfuran \((I, X=Br, R=CH_3)\) by a route analogous to that used for the preparation of \(1,2,3,4\)-tetrafluoronaphthalene confirmed that the novel product obtained from the reaction of tetrabromobenzyne with toluene was not \(1,2,3,4\)-tetrabromo-5-methylnaphthalene. The novel product was therefore \(1,2,3,4\)-tetrabromo-6-methylnaphthalene \((\text{VIII}, R^1=CH_3, R^2=H)\) which was confirmed by its preparation by an alternative route.

The reaction of tetrabromobenzyne with p-cresol methyl ether gave \(5,6,7,8\)-tetrabromo-1,4-dihydro-10-methyl-1,4-ethenotetralone-2 \((\text{VI}, X=Br, R=CH_3)\) in 24% yield which, like its fluorinated analogue, was found to lose ketene on photolysis and afforded the expected naphthalene derivative \((\text{VIII}, R^1=CH_3, R^2=H)\) in 50% yield. The reaction of tetrabromobenzyne with t-butylbenzene also gave \(1,2,3,4\)-tetrabromo-6-t-butylnaphthalene \((\text{VIII}, R^1=\text{Bu}^t, R=H)\) in 2.5% yield in addition to the two expected benzo-barrelene derivatives \((\text{III}, X=Br, R=\text{Bu}^t, R^1=R^2=\text{Bu}^t, R^3=H)\) and \((\text{III}, X=Br, R^1=\text{Bu}^t, R=R^2=R^3=H)\). The previously reported reactions of tetrafluorobenzyne with mono-alkylbenzenes gave only the isomeric benzoobarrelene derivatives. The reactions of tetrachlorobenzyne with mono-alkylbenzenes have not been previously reported but when tetrachloroanthranilic acid was diazotised in the presence of either toluene or t-butylbenzene only the two expected benzoobarrelene derivatives were formed. A number of observations are significant in a consideration of the mechanism by which naphthalene derivatives are formed. The non-bridgehead adducts do not disproportionate under the influence of tetrabromobenzyne. Tetrabromoanthranilic acid
was diazotised in benzene in the presence of the adduct (III, 
X=Br, R₁=CH₂, R₂=R³=H) but no naphthalene was detected by thin 
layer chromatography. However when the same adduct was stirred 
for 12 hr. with an excess of 3-methylbutyl nitrite in benzene, 
the naphthalene was produced in 6% yield. This reaction 
proceeds more rapidly in the presence of a trace of acetic 
acid. Analogous results have been observed in the conversion 
of the adduct (III, X=Br, R₁=R₂=R³=H) to the naphthalene 
(VIII, R₁=R₂=R³=H). In view of the successful conversion to 
naphthalenes of the non-bridgehead substituted benzobarrelenes 
from tetrabromobenzylene with toluene and t-butylbenzene, the 
disproportionation of bridgehead substituted isomers was 
studied using 3-methylbutyl nitrite in benzene containing 
acetic acid. These experiments did not afford the 1,2,3,4-
tetra-3-methylbutyl-5-alkynaphthalenes. The tetrabromobenzobarrelenes 
derived from benzene (III, X=Br, R=R₁=R₂=R³=H), p-xylene (III, 
X=Br, R=R₁=R₂=R³=H), and mesitylene (III, X=Br, R₁=H, 
R₂=R³=H) were also treated with an excess of 3-methyl 
butyl nitrite in benzene containing a trace of acetic acid. 
Thin layer chromatography on silica after 12 hr. showed only 
unconverted starting material present in the reaction 
mixture. It is evident from the present results that the 
presence of a disubstituted double bond and at least a tri-
substituted double bond are both required for the dispropor-
tionation reaction. A reaction of tetrabromobenzylene with 
α-xylene was therefore carried out. The two expected benzo-
barrelenes (III, X=Br, R=R₁=CH₂, R₂=R³=H) and (III, X=Br, R=R³=H, 
R₂=H).
were isolated in 23 and 34.4% yields respectively together with 5,6-dimethyl-1,2,3,4-tetrabromonaphthalene (VIII, X=Br, R=CH$_3$, R'=CH$_3$) (0.5%) and 6,7-dimethyl-1,2,3,4-tetra-bromonaphthalene (VIII, X=Br, R=H, R'=CH$_3$) (0.7%). The ratio of the two naphthalenes is, within experimental error, identical to the ratio of the two benzobarrelene derivatives. The two benzobarrelenes were subsequently converted into the expected naphthalene derivatives by treatment with an excess of 3-methyl butyl nitrite in benzene containing a trace of acetic acid. The mechanism of the disporportionation reaction is not clear but it may involve the formation of a carbonium ion (Scheme 8) which results from a reaction of the substituted benzobarrelene with the nitrosonium ion. Presumably the nitrosonium ion can only attack a disubstituted double bond and that transannular electron release by a trisubstituted (or a tetrasubstituted) double bond is also necessary. Proton abstraction and loss of nitrosoacetylene would account for the observed product (Scheme 8). In order to attempt to test this hypothesis, a reaction was carried out between tetrabromobenzyne and nitroso benzene. It was hoped that 1,4-cycloaddition of the tetrabromobenzyne across the aromatic ring of nitroso benzene would occur to give a mixture of the isomeric 1,2,3,4-tetrabromo-nitroso benzobarrelenes. Subsequent loss of nitrosoacetylene from the non-bridgehead substituted benzobarrelene by the mechanism postulated in Scheme 8 might have been expected to give 1,2,3,4-tetrabromonaphthalene (VIII, R=R'=H). This product was not observed in the reaction mixture. Evidently
Scheme 8.
the failure to observe 1,4-cycloaddition across the aromatic ring in nitrosobenzene can be explained by the presence of the nitroso-group. Benzyne, generated from benzothiadiazole-1,1-dioxide, reacts with nitrosobenzene to give a carbazole derivative which is a 2:1 adduct of benzyne and nitrosobenzene. The mechanism proposed for this reaction involves an initial attack of the lone pair of electrons on nitrogen on the benzyne. Presumably the reaction of tetrabromobenzyne with nitrosobenzene would be more likely to favour 1,4-cycloaddition across the aromatic ring if the nitrosobenzene contained an electron releasing group, for example p-nitrosotoluene. The reactions in which naphthalenes are produced from benzobarrelene derivatives are complicated as is evidenced by the low yields of naphthalene derivatives obtained when the adducts (III, X=Br, R=CH₃, R²=R³=H) and (III, X=Br, R¹=Bu⁺, R²=R³=H) were treated with an excess of 3-methylbutyl nitrite in benzene containing acetic acid. After isolation of the naphthalene derivatives from the above reactions by preparative layer chromatography on silica using light petroleum as solvent, the base-line was scraped from the p.l.c. plate. The silica was washed with chloroform and the washings were re-chromatographed in a chloroform-benzene solvent when a multiplicity of products was observed. These products could presumably arise by a series of rearrangements of the carbonium ion shown in Scheme 8. Similar types of Wagner-Meerwein rearrangements have been observed in the acetolyses of benzobicyclo [2.2.2] octen-2-yl and octa-5,7-dien-2-yl brosylates and more
recently in the reaction of tetrafluorobenzobarrelene with t- 
butyl hypochlorite in acetic acid solution.91

The yields of 1,4-cycloadducts obtained in the reactions 
of tetrahalogenobenzenes with arenes increase with increasing 
nucleophilicity of the arene. This has been demonstrated in 
reactions in which tetrafluorobenzene66 and tetrachlorobenzene67 
were allowed to compete for an excess of equimolar amounts of 
benzene and p-xylene. The competition data obtained in these 
experiments showed that the ratio of the benzene and p-xylene 
adducts was 1:6.5 in the case of tetrafluorobenzene and 1:19.5 
with tetrachlorobenzene. The data obtained in these reactions 
cannot be rationalised in terms of the simple inductive effect 
of the halogens as reflected by their electronegativity values,92 
although the inductive effect of substituents is normally 
thought to be of prime importance in affecting aryne reactions, 
since the two electrons of the "third-bond" are orthogonal to 
the aromatic pi-electron system.1 Similar experiments have 
been carried out in which tetrabromobenzene and tetra-iodobenzene 
have been allowed to compete for an excess of equimolar amounts 
of benzene and p-xylene. The benzobarrelene derivatives were 
separated by preparative layer chromatography and the ratios 
obtained were 1:18.5 for tetrabromobenzene and 1:19.5 for 
tetra-iodobenzene. These results, taken into consideration 
with the results obtained in the analogous reactions of tetra-
fluorobenzene and tetrachlorobenzene, indicate that tetrafluoro-
benzene shows anomalous behaviour. However in order to rule 
out any discrepancies which may have arisen due to the
different techniques used in isolation of the products, the data obtained from reactions in which tetrafluorobenzyne and tetrachlorobenzyne were allowed to compete for an excess of equimolar amounts of benzene and p-xylene have been checked by gas chromatography with accurate integration of peak areas and also by isolation using preparative layer chromatography. No difference was observed from the previously published values. Estimates for the heats of formation of the isomeric dichlorobenzyynes and for tetrachlorobenzyne have recently been made from mass spectrometric studies. They indicate a low stability for tetrachlorobenzyne. The competition data described above may indicate that tetrafluorobenzyne is so destabilised by the inductive effect of the four fluorine atoms that it has lost a considerable amount of the selectivity which aryynes normally show.

The reaction of benzyne with bicyclohepta[2.2.1] diene was reported by Simmons to give exclusively a (2+2)\pi cycloadduct (IX,X=H) having exo geometry. The structure was assigned on the basis of the \textsuperscript{1}H n.m.r. spectrum and by comparison with an authentic sample of the endo-adduct prepared by trapping benzocyclobutadiene as the Diels-Alder adduct with cyclopenta diene. The reactions of the tetrahalogenobenzyynes with bicyclohepta[2.2.1] diene were investigated primarily to establish whether a (2+2+2)\pi cycloadduct was formed. It was also of interest to compare the ratios of the (2+2)\pi to (2+2+2)\pi cycloadducts obtained in the reactions with the competition data obtained in the reactions of the tetrahalo-
genobenzynes with an excess of equimolar mixtures of benzene and p-xylene. When tetrafluorobenzyne was generated in the presence of an excess of bicyclohepta [2.2.1] diene, two products were observed. These compounds were shown to be (IX, X=F) and (X, X=F) in a ratio of 6:1 and 4:1 when the tetrafluorobenzyne was generated from pentafluorophenyl lithium in diethyl ether and cyclohexane respectively. The structure of the compound (IX, X=F) follows from the fact that hydrogenation in the presence of palladium on carbon gave a compound which was identical in every respect to the (2+2)W cycloadduct obtained in the reaction of tetrafluorobenzyne with bicyclohepta [2.2.1] diene. That exo addition had occurred was established by the fact that the resonance due to the protons at positions 5- and 8- appear as a sharp singlet in the $^1$H n.m.r. spectrum. Only in the exo-adduct are the bond angles such that no spin-spin coupling is expected. The structure of the compound (X, X=F) follows from elemental analysis and molecular weight determination which showed it to be isomeric with the compound (IX, X=F). The $^1$H n.m.r. spectrum showed the absence of olefinic protons and the presence of five types of protons in the expected ratios. The reaction of tetrachlorobenzyne, generated from pentachlorophenyl lithium and from tetrachloroanthranilic acid, gave the analogous adducts (IX, X=Cl) and (X, X=Cl) with bicyclohepta[2.2.1] diene in the ratio of 2.2:1 and 1.85:1 respectively. Tetrabromobenzyne, generated by aprotic diazotisation of tetrabromoanthranilic acid gave (IX, X=Br) and (X, X=Br) in the ratio of 3:1. The products
from the reaction of tetrabromobenzene with bicyclohepta
\([2,2,1]\) diene were isolated by preparative layer chromatography
on silver nitrate-impregnated silica whereas the products from
the tetrachlorobenzene reaction were isolated by column
chromatography. The reaction of tetrachlorobenzene with
bicyclohepta \([2,2,1]\) diene was therefore repeated and the
products were separated by preparative layer chromatography.
No difference was observed from the previously reported value\(^9\)." 
Reactions of other arynes with bicyclohepta \([2,2,1]\) diene have
been reported subsequently. The ratio of the analogous adducts
obtained in a reaction with 4,5-dimethoxybenzyne was 3:1\(^9\),\(^5\) and
with benzyne and a series of 4-substituted benzyynes was 2.8:1.\(^9\),\(^6\)
Thus tetrafluorobenzene displays a lack of selectivity in its
reaction with bicyclohepta \([2,2,1]\) diene which may be related
to the lower stability suggested previously. The data for
reactions with equimolar mixtures of benzene and \(p\)-xylene
discussed earlier were found to be 1:6.75 for tetrafluorobenzene
and approximately 1:20 for the other tetrahalogenobenzynes.

The mechanisms of formation of the adducts \((\text{IX}, X=H, 
F, Cl, Br)\) and \((\text{X}, X=H, F, Cl, Br)\) are not certain. The isolation
of the \((2+2)\Pi\) cycloadduct in the reaction of benzyne with
bicyclohepta \([2,2,1]\) diene and the absence of carbonium ion
rearrangement products led to the suggestion that a concerted
cycloaddition was involved.\(^2\)\(^5\) However the \((2+2)\Pi\) cycloadduct
cannot be formed by a concerted reaction under orbital symmetry
control.\(^1\)\(^0\),\(^1\)\(^1\) Cycloaddition reactions of chlorosulphonyl
isocyanate with olefins have been shown to be stereospecific

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in a number of cases,\textsuperscript{97} including bicyclohepta $[2.2.1]$ diene when no rearrangement products were observed. A pseudo-concerted reaction,\textsuperscript{98} could involve a 1,4-dipolar species which, if it collapsed to product sufficiently rapidly would not result in carbonium ion rearrangement products being observed. Evidence for the participation of a 1,4-dipolar species can be tentatively drawn from the difference in the ratios of $(JX,X=F)$ and $(X,X=F)$ when tetrafluorobenzyne was generated in the presence of an excess of bicyclohepta $[2.2.1]$ diene in cyclohexane and in diethyl ether. A 1,4-dipolar species would be more easily stabilised in the more polar solvent, diethyl ether and consequently an increase in the ratio of the $(2+2)\Sigma$ to $(2+2+2)\Sigma$ cycloadduct might be expected. An increase in the ratio from 4:1 to 6:1 was observed. That rapid collapse occurs in aryne $(2+2)\Sigma$ cycloadditions has been shown by the stereoselectivity of reactions involving vinyl ethers,\textsuperscript{99} vinyl esters,\textsuperscript{99} and 1,2-dichloroethylene.\textsuperscript{8} Evidently these reactions are 'near concerted'. Thus although no rearrangement products were observed in the reactions of tetrahalogenobenzynes with bicyclohepta $[2.2.1]$ diene this does not infer that a concerted cycloaddition is necessarily involved in the formation of the adduct $(IX,X=H,F,Cl,Br)$. The formation of the adduct $(X,X=H,F,Cl,Br)$ can occur by an orbital symmetry allowed concerted mechanism.\textsuperscript{10,11} On the basis that the transition state for a concerted addition is of lower energy than the transition state involved in a two-step mechanism, it is most likely that the reaction leading to the formation of the $(2+2+2)\Sigma$ cycloadduct does involve a concerted cycloaddition.
EXPERIMENTAL

All General Methods are as reported in Section 1 (Experimental). Reactions involving the formation of adducts between tetrahalogenobenzenes from the appropriate tetrahalogenoanthranilic acids and liquids were carried out using the liquid as solvent. It was necessary, in most cases to use a small volume of acetonitrile to attain complete dissolution of the tetrahalogenoanthranilic acids. All liquid co-reactants described were dried by storage over sodium wire and were freshly distilled as required.

The observed molecular weights of adducts derived from tetrachlorobenzyne and tetrabromobenzyne, as determined by mass spectroscopy, refer to the major molecular ions in the isotopic cluster.

Preparation of Tetra bromoanthranilic acid

Method (1) Tetram bromophthalic anhydride (23.2 g., 0.05 mole) was added to ammonia solution (20 ml., 20%), and stirred until the solution became clear. The clear solution was poured into excess of dilute sulphuric acid but the tetrabromophthalamic acid did not precipitate as expected. The solution was therefore cooled to 5° and an alkaline solution of sodium hypochlorite (4.0 g., 0.1 mole of sodium hydroxide and 0.05 molar equivalents of sodium hypochlorite) was added. The solution was then heated at 70-80° for 3 hr. Addition of excess of hydrochloric acid to the mixture precipitated a pale yellow crystalline solid which, after recrystallisation from aqueous ethanol, was found to be...
Tetrabromophthalic acid, m.p. 265° (lit. 266°), (90% yield), νmax 3500-2800 (OH), 1735 (C=O) cm⁻¹.

**Method (2)**

Tetrabromophthalimide (2.0 g., 0.004 mole) prepared by the method of Pratt and Young,74 was heated under reflux with a solution of potassium hydroxide (3.6 g., 0.064 mole), bromine (2.8 g., 0.016 mole) in water (40 ml.) for 3 hr. Addition of excess of hydrochloric acid to the alkaline solution precipitated a light brown solid which was extracted into ether. Removal of the ether and recrystallisation of the residue from ethanol-benzene (1:4) gave 2,3,4,5-tetraphromaniline, m.p. 120° (lit. 122°), (53% yield), νmax 3480, 3380 (OH) cm⁻¹.

**Method (3)**

Aqueous ammonia (8.1 ml., d 0.880) was added to a stirred solution of tetrabromophthalic anhydride (17.8 g., 0.038 mole) in dimethyl sulphoxide (50 ml.). Stirring was continued for a further 10 min. then sodium hydroxide (1.5 g., 0.038 mole) in water (2 ml.) was added. After a further 30 min., a mixture of ethanol (36 ml.) and chloroform (80 ml.) was added dropwise to the solution with the resultant precipitation of the sodium salt of tetrabromophthalamic acid. The sodium salt, after air drying on a Buchner filter, was treated with sodium hypobromite solution (0.1 mole) in iced water (50 ml.). The resultant solution was stirred for 75 min. at ambient temperature, more sodium hydroxide (1.5 g., 0.038 mole) was added and the temperature raised to 75° for a further 75 min. The clear solution was then poured into excess of aqueous hydrochloric acid and the precipitated solid filtered off. Recrystallisation from aqueous ethanol gave tetrabromo-
anthranilic acid, m.p. 205° (lit. 39 m.p. 204-5°), (78% yield), ν max 3480, 3380 (NH₂), 1700 (C=O) cm⁻¹.

Tetraiodoanthranilic acid was prepared from tetraiodophthalic anhydride by an identical procedure.

Tetrachloroanthranilic acid was prepared by a modification of the method of Orndorff and Nichols. 38

Reaction of Tetraiodobenzayne with Benzene

(1) Using diethyl ether as solvent - Tetraiodoanthranilic acid (4.54 g., 0.01 mole) in dry diethyl ether (50 ml.) was added dropwise to a stirred solution of 3-methylbutyl nitrite (3 ml.) in dry benzene (100 ml.) maintained at 50°. Heating was continued for 0.5 hr. after complete addition of the tetraiodoanthranilic acid. The crystalline yellow precipitate was filtered off and recrystallised from chloroform to give octa bromoacridone (IV,X=Br) (8.6%), m.p. > 350°. (Found C, 19.5; H, 0.20; N, 1.80. C₁₃H₁₂Br₈N₀ requires C, 18.90; H, 0.15; N, 1.70%). ν max 3340 (NH), 1660 (C=O) cm⁻¹.

The benzene, 3-methylbutyl alcohol and diethyl ether were distilled off from the filtered solution and the residual oil was examined by analytical thin layer chromatography which showed the presence of three products. Separation by preparative layer chromatography gave:

(a) 2,3,4,5-tetra bromophenyl-(3'-methylbutyl) ether (II,X=Br, R=CH₂CH₂CH(CH₃)₂) (5.2%) m.p. 40° (from ethanol). (Found C, 27.60; H, 2.60. C₁₁H₁₂Br₄O requires C, 27.50; H, 2.50%, ν 2.90 (s, 1H), 5.8-6.2 (m, 2H), 8.0-8.4 (m, 3H), 8.8-9.1 (d, 6H). ν max 3080, 2960, 2880, 1560, 1470, 1420, 1390, 1335, 1270,
1240, 1165, 1140, 1065, 1020, 990, 920, 910, 835, 770, 680 cm\(^{-1}\).

(b) 2,3,4,5-tetrabromophenyl ethyl ether (II, \(X=\text{Br}, \ R=\text{C}_2\text{H}_5\))

(7.4\%) m.p. 96\(^0\) (from ethanol). (Found C, 22.00; H, 1.50. \(\text{C}_8\text{H}_6\text{Br}_4\text{O}\) requires C, 21.95; H, 1.40\%).

\(\gamma\) 3.1 (s, 1H), 5.7-6.1 (q, 2H), 8.4-8.6 (t, 3H).

\(\nu_{\text{max}}\) 3100, 3080, 2995, 2950, 2900, 2880, 1610, 1565, 1525, 1425, 1400, 1335, 1310, 1270, 1240, 1170, 1155, 1110, 1060, 1040, 960, 855, 850, 825, 770, 680 cm\(^{-1}\).

(c) 5,6,7,8-tetrabromo-1,4-dihydro-1,4-ethenonaphthalene

(III, \(X=\text{Br}, \ R=\text{H}, \ R'=\text{H}, \ R''=\text{H}\))(27\%), m.p. 165\(^0\) (from ethanol) (lit.\(^{77}\) m.p. 160-1\(^0\)). (Found C, 30.75; H, 1.20\%; M \([\text{mass spectroscopy}]\) 470. Calculated for \(\text{C}_{12}\text{H}_6\text{Br}_4\text{O}\) C, 30.70; H, 1.30\%; M 470).

\(\gamma\) 2.98-3.2 (m, 4H), 4.4-4.65 (m, 2H).

\(\nu_{\text{max}}\) 3020, 2950, 2860, 1625, 1580, 1400, 1345, 1240, 1210, 1120, 750, 680 cm\(^{-1}\).

(2) Using acetonitrile as solvent - Tetrabromoanthranilic acid (2.27 g., 0.005 mole) in dry benzene (100 ml.) and acetonitrile (45 ml.) was added slowly to a stirred solution of 3-methylbutyl nitrite (1.5 ml.) in dry benzene (100 ml.) at 50\(^0\). Heating was continued for 0.5 hr. after complete addition. The crystalline yellow precipitate was filtered off and re-crystallised from chloroform to give (IV, \(X=\text{Br}\))(9.0\%). The benzene, 3-methylbutyl alcohol and acetonitrile were distilled off from the filtered solution and the residual oil was examined by analytical thin layer chromatography which showed the presence
of two products. Separation by preparative layer chromatography gave \((II, X=Br, R=CH_2CH_2CH(CH_3)_2)(4.6%)\) and \((III, X=Br, R=R^1=R^2=R^3=H)(17.4%)\).

The above reaction has been optimised by the concurrent addition of tetrabromoanthranilic acid \((1.14 \text{ g.}, 0.0025 \text{ mole})\) in benzene \((30 \text{ ml.})\) and acetonitrile \((30 \text{ ml.})\) together with 3-methylbutyl nitrite \((0.34 \text{ ml.}, 0.0025 \text{ mole})\) in benzene \((60 \text{ ml.})\) to benzene \((100 \text{ ml.})\) stirred at 50\(^\circ\). In this experiment the formation of \((II, X=Br, R=CH_2CH_2CH(CH_3)_2\) was eliminated and the yield of the benzene adduct \((III, X=Br, R=R^1=R^2=R^3=H)\) was increased to 67%. Other experiments describing the reaction of tetrabromobenzyn in this thesis have not been optimised.

**Reaction of Tetrachlorobenzyn with Benzene**

Tetrachloroanthranilic acid \((2.75 \text{ g.}, 0.01 \text{ mole})\) in dry diethyl ether \((50 \text{ ml.})\) was added dropwise to a stirred solution of 3-methylbutyl nitrite \((3 \text{ ml.})\) in dry benzene \((100 \text{ ml.})\) maintained at 50\(^\circ\). Heating was continued for 0.5 hr. after complete addition of the tetrachloroanthranilic acid. The crystalline yellow precipitate was filtered off and re-crystallised from chloroform to give \((IV, X=Cl)(7.2\%)\).

Removal of benzene, 3-methylbutyl alcohol and diethyl ether gave a viscous oil which was examined by analytical thin layer chromatography and shown to contain three products. Separation by preparative layer chromatography gave \((II, X=Cl, R=CH_2CH_2CH(CH_3)_2)(8.6\%), (II, X=Cl, R=C_2H_5)(12.8\%)\) and \((III, X=Cl, R=R^1=R^2=R^3=H)(30\%).\)
Reaction of Tetrabromobenzyn with Diethyl ether

Tetrabromoanthranilic acid (1.14 g., 0.0025 mole) in dry diethyl ether (50 ml.) was added dropwise to a stirred, refluxing solution of 3-methylbutyl nitrite (0.34 ml., 0.0025 mole) in dry ether (100 ml.). Heating was continued for 0.5 hr. after complete addition. Removal of (IV, X=Br) by filtration and evaporation of the solvent gave a viscous oil which was shown by gas liquid chromatography to contain two products. Separation by preparative layer chromatography gave (II, X=Br, R=CH₂CH₂CH(CH₃)₂) (7%) and (II, X=Br, R=C₂H₅) (36%).

The reaction was repeated in the presence of a five-fold excess of 3-methylbutyl nitrite (1.17 ml., 0.0125 mole) when, after removal of (IV, X=Br), the products observed were (II, X=Br, R=CH₂CH₂CH(CH₃)₂) (24%) and (II, X=Br, R=C₂H₅) (32%).

Reaction of Tetrabromobenzyn with 3-Methylbutyl nitrite.

Tetrabromoanthranilic acid (2.27 g., 0.005 mole) in acetonitrile (50 ml.) was added slowly to a stirred solution of 3-methylbutyl nitrite (3.4 ml., 0.025 mole) in acetonitrile (100 ml.) maintained at 50°. Stirring was continued for 0.5 hr. after complete addition. Removal of 3-methylbutyl alcohol and acetonitrile gave a brown oil which was shown by gas liquid chromatography to contain one major component. Purification by elution from a neutral alumina column in light petroleum gave (II, X=Br, R=CH₂CH₂CH(CH₃)₂) (42.9%).
Reaction of Tetraiodobenzene with Benzene

Aprotic diazotisation of tetraiodoanthranilic acid by 3-methylbutyl nitrite in benzene/acetonitrile gave, after removal of solvents and purification by preparative layer chromatography, 5,6,7,8-tetraido-1,4-dihydro-1,4-ethenonaphthalene (III, X=I, R=H) (25%), m.p. 200°C (from ethanol-chloroform). (Found C, 22.00; H, 1.00. \( C_{12}H_6I_4 \) requires C, 21.90; H, 0.90%).

\( ^\gamma 3.01-3.22 \text{ (m, 4H), } 4.4-4.7 \text{ (m, 2H)}. \)

\( \nu_{max} \) 3080, 3020, 2940, 1625, 1590, 1400, 1325, 1230, 1200, 1100, 980, 845, 690 cm\(^{-1}\).

Reaction of Tetrabromobenzene with Furan

Purification of the crude product by preparative layer chromatography gave 5,6,7,8-tetrabromo-1,4-dihydro-1,4-epoxynaphthalene (I, X=Br, R=H) (29%) m.p. 167°C (from ethanol) (lit. 155-6°C). (Found C, 26.10; H, 0.95%; M \([\text{mass spectroscopy}]\) 460. Calculated for \( C_{10}H_4Br_4O \), C, 26.10; H, 0.90%; M 460).

\( ^\gamma 2.8-2.9 \text{ (m, 2H), } 4.1-4.2 \text{ (m, 2H)}. \)

\( \nu_{max} \) 3040, 2940, 1600, 1550, 1340, 1330, 1285, 1200, 1100, 1010, 900, 870, 815, 730, 700 cm\(^{-1}\).

The adduct (I, X=Br, R=H) (100 mg.) in ethanol (35 ml.) was hydrogenated at atmospheric pressure in the presence of pre-reduced palladium on carbon (20 mg., 10%) to give, after removal of solvent and catalyst, 5,6,7,8-tetrabromo-1,4-dihydro-1,4-epoxy tetralin (VII, X=Br, R=H) (92%) m.p. 187°C (from ethanol). (Found C, 26.10; H, 1.25. \( C_{10}H_6Br_4O \) requires C, 26.00; H, 1.30%).
\[ T \text{ 4.3-4.6} \text{ (m, 2H)}, 7.9-8.8 \text{ (m, 4H).} \]

\[ \nu_{\text{max}} \text{ 3020, 2970, 2920, 2880, 1465, 1450, 1360, 1340, 1305, 1285, 1255, 1220, 1175, 1135, 1115, 1030, 995, 945, 900, 870, 825, 800, 740 \text{ cm}^{-1}. \]

The hydrogenated adduct (VII, \( X=Br, R=H \))(92 mg.) was heated at 100\(^\circ\) for 6 hr. with constant boiling hydrobromic acid (5 ml.) and glacial acetic acid (5 ml.). The resultant solution was poured into water (20 ml.) and the precipitate formed was extracted into ether. The extract was washed with sodium bicarbonate solution (50 ml., 10\%) and dried over anhydrous magnesium sulphate. Removal of the ether gave 1,2,3,4-tetra bromonaphthalene (VIII, \( R=^1R=^2R=H \))(80\%) m.p. 196\(^\circ\) (from ethanol) (lit. 19.00 m.p. 196\(^\circ\)).

\( \nu \text{ 1.6-1.9 (m, 2H), 2.3-2.5 (m, 2H).} \)

\( \lambda_{\text{max}} \text{ (ethanol) 292 (log}^{10} 2.91), 303 (3.66), 314'(3.72), 332 (2.90) \text{ n.m.} \)

**Reaction of Tetraiodobenzylene with Furan**

Removal of solvents and excess of furan left a viscous yellow oil which was purified by preparative layer chromatography to give 5,6,7,8-tetraiodo-1,4-dihydro-1,4-epoxynaphthalene (I, \( X=I, R=H \))(46.5\%) m.p. 172\(^\circ\) (from ethanol-chloroform). (Found C, 18.95; H, 0.75. \( C_{10}H_{14}I_4 \) requires C, 18.55; H, 0.60\%).

\( \nu \text{ 2.8-2.87 (m, 2H), 4.25-4.35 (m, 2H).} \)

\( \nu_{\text{max}} \text{ 3020, 2940, 1550, 1400, 1280, 1240, 1200, 1090, 1000, 890, 865, 720 \text{ cm}^{-1}.} \)
Reaction of Tetrabromobenzene with p-Xylene.

The crude product, after removal of solvents and excess of p-xylene, was dissolved in a small volume of benzene and eluted from a neutral alumina chromatography column in light petroleum to give 5,6,7,8-tetramethyl-1,4-dihydro-2,10-dimethyl-1,4-ethenonaphthalene (III, X=Br, R=H, R'=H, R''=CH₃) (23.8%) m.p. 167° (from ethanol). (Found C, 33.70; H, 2.00%; M [mass spectroscopy] 498. C₁₄H₁₀Br₄ requires C, 33.75; H, 2.00%; M 498).

ν₃ 3.6-3.8 (m, 2H), 4.95-5.15 (dxd, 2H), 8.1 (d, 6H).

ν max 3060, 3020, 2990, 2940, 2860, 1640, 1580, 1450, 1355, 1340, 1250, 1215, 1200, 1110, 1050, 880, 785, 725 cm⁻¹.

Reaction of Tetraiodobenzene with p-Xylene

Removal of solvents and excess of p-xylene gave a partially crystalline oil which was separated from a small quantity of octabromoacridone (IV, X=Br) by preparative layer chromatography to give 5,6,7,8-tetraiodo-1,4-dihydro-2,10-dimethyl-1,4-ethenonaphthalene (III, X=I, R=H, R'=H, R''=CH₃) (31%) m.p. 176° (from ethanol-chloroform). (Found C, 24.65; H, 1.55. C₁₄H₁₀I₄ requires C, 24.50; H, 1.50%).

ν₃ 3.66-3.88 (m, 2H), 5.05-5.2 (dxd, 2H), 8.1 (d, 6H).

ν max 3060, 3010, 2980, 2930, 2910, 2850, 1640, 1580, 1450, 1350, 1300, 1240, 1215, 1190, 1140, 1000, 1025, 870, 840, 780 cm⁻¹.

Reaction of Tetrachlorobenzene with Toluene

Examination of the crude product, obtained after removal of excess of toluene, by analytical thin layer chromatography
on silica showed only one component to be present. However examination on a silver nitrate-impregnated silica plate with light-petroleum-benzene (50:50) as a solvent system showed two components. Separation was achieved by preparative layer chromatography on silver nitrate-impregnated silica plates and gave:

(a) \(5,6,7,8\)-tetrachloro-1,4-dihydro-1-methyl-1,4-ethenonaphthalene (III, \(X=Cl, R=CH_2, R^1=R^2=R^3=H\)) (4\%), m.p. 132°
(from ethanol). (Found C, 51.05; H, 2.75%; M \([\text{mass spectroscopy}]\) 306. \(C_{13}H_8Cl_4\) requires C, 51.0; H, 2.65%; M 306).
\(\nu\) 3.0-3.55 (m, 4H), 4.5-4.75 (m, 1H), 7.75 (s, 3H).
V \(_{\text{max}}\) 3060, 3020, 2940, 2900, 1630, 1590, 1465, 1390, 1370, 1350, 1335, 1235, 1135, 1120, 1090, 950, 900, 870, 830, 730, 720 cm\(^{-1}\).

(b) \(5,6,7,8\)-tetrachloro-1,4-dihydro-2-methyl-1,4-ethenonaphthalene (III, \(X=Cl, R=CH_2, R^1=R^2=R^3=H\)) (12.7\%), m.p. 102°
(from ethanol). (Found C, 51.15; H, 2.55%; M \([\text{mass spectroscopy}]\) 306. \(C_{13}H_8Cl_4\) requires C, 51.0; H, 2.65%; M 306).
\(\nu\) 3.0-3.03 (t, 2H), 3.55-3.8 (m, 1H), 4.65-5.0 (m, 2H), 8.1 (d, 3H). V \(_{\text{max}}\) 3080, 3020, 2980, 2920, 2870, 1660, 1600, 1445, 1370, 1320, 1245, 1220, 1210, 1135, 1035, 920, 825, 805, 760, 720, 690 cm\(^{-1}\).

Reaction of Tetrabromobenzylene with Toluene

Separation of the isomeric products was achieved by preparative layer chromatography on silver nitrate-impregnated silica as described for the chlorine analogue above to give:
(a) 5,6,7,8-tetrabromo-1,4-dihydro-1-methyl-1,4-ethenonaphthalene (III, X=Br, R=R'=CH₂, R¹=R²=R³=H) (5.2%), m.p. 147°C (from ethanol). (Found C,32.25; H,1.65%; M [mass spectroscopy] 484. C₁₃H₈Br₄ requires C,32.25; H,1.65%; M 484).

νᵐₓ 2.95-3.52 (m, 4H), 4.45-4.67 (m, 1H), 7.78 (s, 3H).

(b) 5,6,7,8-tetrabromo-1,4-dihydro-2-methyl-1,4-ethenonaphthalene (III, X=Br, R¹=Cl), R²=H (17.9%), m.p. 145°C (from ethanol). (Found C,32.85; H,1.80%; M [mass spectroscopy] 484. C₁₃H₈Br₄ requires C,32.25; H,1.65%; M 484).

νᵐₓ 3.0-3.2 (t, 2H), 3.55-3.8 (m, 1H), 4.6-4.95 (m, 2H), 8.1 (d, 3H).

(c) 1,2,3,4-tetrabromo-6-methylnaphthalene (VIII, R=R²=H, R¹=CH₂, R¹=H) (2.1%), m.p. 121°C (from ethanol). (Found C,29.0; H,1.35%; M [mass spectroscopy] 458. C₁₁H₆Br₄ requires C,28.85; H,1.30%; M 458).

νᵐₓ 1.7-2.0 and 2.36-2.6 (m, 3H), 7.48 (s, 3H).

λᵐₓ (ethanol) 280 (3.84), 290 (3.88), 302 (3.86), 314 (3.75), 340 (2.90) n.m.

Reaction of Tetrachlorobenzene with t-Butylbenzene.

Removal of solvents and excess of t-butylbenzene gave a yellow oil which was examined by thin layer chromatography.
and found to contain two components. Separation by preparative layer chromatography gave:

(a) 5,6,7,8-tetrachloro-1,4-dihydro-1-t-butyl-1,4-ethenonaphthalene (III, $X=Cl$, $R=\text{Bu}^t$, $R^1=R^2=R^3=H$) (9.3%), m.p. 159° (from ethanol). (Found C, 55.35; H, 4.00%; M [mass spectroscopy] 348. $C_{16}H_{14}Cl_4$ requires C, 55.20; H, 4.00%; M 348).

$\delta$ 2.7-3.27 (m, 4H), 4.31-4.6 (m, 1H), 8.2 (s, 6H), 8.8 (s, 3H).

$\nu_{\text{max}}$ 3100, 3080, 2990, 2980, 2960, 2900, 1640, 1600, 1560, 1520, 1470, 1410, 1385, 1380, 1365, 1345, 1325, 1270, 1260, 1240, 1220, 1200, 1175, 1140, 1105, 1065, 960, 930, 910, 870, 850, 800, 735, 700, 680 cm$^{-1}$.

(b) 5,6,7,8-tetrachloro-1,4-dihydro-2-t-butyl-1,4-ethenonaphthalene (III, $X=Cl$, $R=\text{Bu}^t$, $R=R^1=H$, $R^2=R^3=H$) (33.9%), m.p. 108° (from ethanol). (Found C, 55.20; H, 4.10%; M [mass spectroscopy] 348. $C_{16}H_{14}Cl_4$ requires C, 55.20; H, 4.00%; M 348).

$\delta$ 2.95-3.2 (t, 2H), 3.5-3.75 (m, 1H), 4.6-4.9 (m, 2H), 8.0 (s, 9H).

$\nu_{\text{max}}$ 3080, 3030, 2980, 2950, 2920, 2880, 1640, 1600, 1550, 1480, 1465, 1400, 1370, 1320, 1290, 1255, 1240, 1220, 1215, 1140, 1105, 1065, 950, 920, 840, 830, 790, 740, 715, 690, 665, 650 cm$^{-1}$.

Reaction of Tetrabromobenzynne with t-Butylbenzene

The crude product, after removal of solvents and excess of t-butylbenzene, was partially purified by elution from a short alumina chromatography column in light petroleum-benzene (70: 30). Thin layer chromatography on silica showed the presence
of three components in the eluate. Preparative layer chromatography on silica using light petroleum as the solvent gave:

(a) 5,6,7,8-tetrabromo-1,4-dihydro-1-t-butyl-1,4-ethenonaphthalene (III,\(X=\text{Br}, R=\text{Bu}^t, R^1=R^2=R^3=\text{H}\)) (2.7%), m.p. 170° (from ethanol). (Found C, 36.35; H, 2.75%; M [mass spectroscopy] 526. \(C_{16}H_{14}Br_4\) requires C, 36.55; H, 2.70%; M 526).  

\[\gamma' 2.71-3.30 \text{ (m, } 4\text{H}), 4.33-4.61 \text{ (m, } 1\text{H}), 8.2 \text{ (s, } 6\text{H}), 8.8 \text{ (s, } 3\text{H)}. \]

\[\nu_{\text{max}} 3090, 3020, 2980, 2950, 2920, 2890, 1640, 1600, 1530, 1465, 1410, 1380, 1340, 1330, 1300, 1230, 1190, 1150, 1130, 1080, 1040, 950, 890, 775, 705, 690 680 \text{ cm}^{-1}. \]

(b) 5,6,7,8-tetrabromo-1,4-dihydro-2-t-butyl-1,4-ethenonaphthalene (III,\(X=\text{Br}, R_1=\text{Bu}^t, R=R^2=\text{H}\)) (16.5%) m.p. 165° (from ethanol). (Found C, 36.55; H, 2.75%; M [mass spectroscopy] 526. \(C_{16}H_{14}Br_4\) requires C, 36.55; H, 2.70%; M 526).  

\[\gamma' 3.0-3.2 \text{ (t, } 2\text{H}), 3.6-3.8 \text{ (m, } 1\text{H}), 4.45-4.8 \text{ (m, } 2\text{H}), 9.0 \text{ (s, } 9\text{H)}. \]

\[\nu_{\text{max}} 3090, 3070, 3020, 2970, 2940, 2910, 2880, 1640, 1600, 1525, 1480, 1465, 1400, 1370, 1350, 1315, 1250, 1230, 1220, 1210, 1120, 1100, 1060, 1030, 965, 945, 930, 920, 880, 835, 825, 780, 755, 725, 690, 680 \text{ cm}^{-1}. \]

(c) 1,2,3,4-tetrabromo-6-t-butylnaphthalene (VIII,\(R=R^2=\text{H}, R^1=\text{Bu}^t\)) (2.5%) m.p. 168° (from ethanol). (Found C, 33.50; H, 2.40%; M [mass spectroscopy] 500. \(C_{14}H_{12}Br_4\) requires C, 33.60; H, 2.40%; M 500).  

\[\gamma' 1.75-2.0 \text{ and } 2.3-2.45 \text{ (m, } 3\text{H}), 8.6 \text{ (s, } 9\text{H)}. \]

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Reaction of Tetraiodobenzyn with t-Butylbenzene

The crude product, after removal of excess of t-butylbenzene and solvent was examined by thin layer chromatography which showed only one component to be present. Chromatography on silver nitrate-impregnated silica also showed one component and so the crude material was purified by elution from a neutral alumina column in light petroleum-benzene (50:50). Removal of the solvent gave 5,6,7,8-tetraiodo-1,4-dihydro-2-t-butyl-1,4-etheno-
naphthalene \((\text{III, } X = \text{I, } R^1 = \text{Bu}, \text{ } R^2 = \text{R}^3 = \text{H})(22.5\%), \text{ m.p. } 149^\circ \text{ (from ethanol-chloroform). (Found C, 26.60; H, 2.05. } C_{16}H_{14}I_4 \text{ requires C, 26.90; H, 1.95%).}

\(\delta 3.0-3.2 \text{ (t, 2H), } 3.6-3.77 \text{ (m, 1H), } 4.5-4.8 \text{ (m, 2H), } 8.97 \text{ (s, 9H).}

\(\nu_{\max} 3090, 3070, 3030, 2970, 2940, 2910, 2870, 1640, 1600, 1525, 1490, 1470, 1390, 1370, 1355, 1340, 1250, 1235, 1210, 1195, 1120, 1100, 1060, 1030, 945, 930, 920, 880, 835, 820, 785, 760, 730, 690, 680, 640 \text{ cm}^{-1}.

Reaction of Tetrabromobenzyn with Isopropylbenzene

The crude product was shown by thin layer chromatography to contain two components. Preparative layer chromatography on silica gave:

(a) 5,6,7,8-tetrabromo-1,4-dihydro-1-isopropyl-1,4-etheno-
naphthalene \((\text{III, } X = \text{Br, } R = \text{Pr}^1, \text{ } R^1 = \text{R}^2 = \text{R}^3 = \text{H})(6.0\%), \text{ m.p. } 124^\circ \text{.}"

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(from ethanol). (Found C, 35.20; H, 2.50%; M \[mass spectroscopy\] 512. C\textsubscript{15}H\textsubscript{12}Br\textsubscript{4} requires C, 35.15; H, 2.35%; M 512).

\[\nu_{\text{max}}\text{ 3080, 2980, 2950, 2880, 1640, 1600, 1540, 1465, 1400, 1340, 1335, 1325, 1310, 1255, 1225, 1200, 1150, 1130, 1090, 1045, 1005, 970, 945, 920, 900, 870, 835, 785, 710, 685, 640 \text{ cm}^{-1}.\]

(b) 5,6,7,8-tetrabromo-1,4-dihydro-2-isopropyl-1,4-ethenonaphthalene (II, X = Br, R\textsuperscript{1} = Br\textsuperscript{1}, R\textsuperscript{2} = R\textsuperscript{3} = H) \(\text{(22.5\%)}\), m.p. 109\degree C (from ethanol). (Found C, 35.30; H, 2.25%; M \[mass spectroscopy\] 512. C\textsubscript{15}H\textsubscript{12}Br\textsubscript{4} requires C, 35.15; H, 2.35%; M 512).

\[\nu_{\text{max}}\text{ 3080, 3030, 2970, 2940, 2880, 1650, 1600, 1530, 1470, 1455, 1390, 1370, 1350, 1280, 1250, 1240, 1215, 1200, 1170, 1120, 1100, 1055, 1030, 945, 920, 890, 875, 860, 830, 790, 760, 690, 680, 640 \text{ cm}^{-1}.\]

### Reaction of Tetrabromobenzene with o-Xylene

Examination of the reaction mixture by thin layer chromatography on silica showed the presence of three components which were separated by preparative layer chromatography on silver nitrate-impregnated silica. A re-examination of the component of highest \(R_f\) value showed that it contained two compounds which were separated by preparative layer chromatography on silver nitrate-impregnated silica using 40-60\degree C.
petroleum ether-benzene (85:15) as a solvent system. The four compounds were found to be:

(a) 5,6,7,8-tetrabromo-1,4-dihydro-1,2-dimethyl-1,4-ethenonaphthalene (III, X=Br, R=R'=CH3, R''=H) (23.1%), m.p. 123\(^\circ\)C (from ethanol). (Found C,33.60; H,2.05%; M [mass spectroscopy] 498. C\(_{14}H_{10}Br_4\) requires C,33.75; H,2.00%; M 498).

\(\nu\) 2.95-3.2 (m, 1H), 3.4-3.65 (m, 2H), 4.4-4.8 (m, 1H), 7.8 (s, 3H), 8.15 (d, 3H).

\(\nu\)\(_{\text{max}}\) 3060, 3030, 2980, 2950, 2920, 1660, 1610, 1560, 1500, 1470, 1445, 1400, 1340, 1330, 1320, 1280, 1230, 1200, 1170, 1150, 1100, 1050, 970, 940, 920, 870, 850, 820, 800, 770, 695, 670 cm\(^{-1}\).

(b) 5,6,7,8-tetrabromo-1,4-dihydro-2,3-dimethyl-1,4-ethenonaphthalene (III, X=Br, R=R'=H, R''=CH3) (34.4%), m.p. 161\(^\circ\)C (from ethanol). (Found C,33.80; H,2.05%; M [mass spectroscopy] 498. C\(_{14}H_{10}Br_4\) requires C,33.75; H,2.00%; M 498).

\(\nu\) 3.05-3.25 (m, 2H), 4.8-5.0 (m, 2H), 8.2 (s, 6H).

\(\nu\)\(_{\text{max}}\) 3080, 3010, 2980, 2940, 2920, 2860, 1650, 1600, 1440, 1400, 1350, 1340, 1315, 1280, 1250, 1230, 1200, 1130, 1100, 970, 950, 910, 875, 820, 780, 760, 745, 690, 665 cm\(^{-1}\).

(c) 1,2,3,4-tetrabromo-5,6-dimethylnaphthalene (VIII, R=R'=CH3, R''=H) (0.5%), m.p. 193\(^\circ\)C (from ethanol). (Found C,30.60; H,1.50%; M [mass spectroscopy] 472. C\(_{12}H_{8}Br_4\) requires C,30.50; H,1.70%; M 472).

\(\nu\) 1.63-1.85 (m, 1H), 2.4-2.6 (m, 1H), 7.3 (s, 3H), 8.1 (s, 3H).
\[ \lambda_{\text{max}} \text{ (ethanol)} \] 280 (log, 3.86), 293 (3.89), 306 (3.85), 315 (3.79), 340 (3.74) n.m.

(d) \[ 1,2,3,4\text{-tetrabromo-6,7-dimethylnaphthalene} \ (\text{VIII}, \text{R}=\text{H}, \text{R}_1=\text{R}_2=\text{CH}_3) (7.0\%), \text{ m.p. } 184^\circ \text{C} \text{ (from ethanol).} \] (Found C,30.30; H,1.80%; M [mass spectroscopy] 472. \text{C}_{12}\text{H}_8\text{Br}_4 \text{ requires C,30.50; H,1.70%; M 472}).

\[ \tau^2 \text{.05 (s, 2H), 7.55 (s, 6H).} \]
\[ \lambda_{\text{max}} \text{ (ethanol)} \] 282 (3.81), 295 (3.84), 304 (3.83), 313 (3.78), 345 (3.15) n.m.

**Reaction of Tetrabromobenzene with Mesitylene**

The crude product was shown to contain one component by thin layer chromatography on silver nitrate-impregnated silica. Elution from a neutral alumina chromatography column in light petroleum-benzene (80:20) gave, after removal of solvent, 5,6,7,8-tetrabromo-1,4-dihydro-1,3,10-trimethyl-1,4-ethenonaphthalene (III, X=Br, R_1=H, R_2=R_3=CH_3) (40.6%) m.p. 124°C (from ethanol) (lit.\[77 \] m.p. 124.5°). (Found C,35.25; H,2.15%; M [mass spectroscopy] 512. Calculated for \text{C}_{15}\text{H}_{12}\text{Br}_4, C,35.15; H,2.35%; M 512).

\[ \tau^4 \text{.0-4.2 (q, 2H), 5.24 (t, 1H), 7.9 (s, 3H), 8.09 (d, 6H).} \]
\[ \nu_{\text{max}} \] 3050, 3010, 2980, 2950, 2920, 2900, 2860, 1675, 1635, 1580, 1550, 1510, 1465, 1445, 1430, 1395, 1385, 1355, 1340, 1330, 1285, 1275, 1250, 1210, 1150, 1130, 1110, 1060, 1045, 1020, 940, 885, 825, 810, 795, 750, 735, 660 cm\(^{-1}\).
Reaction of Tetrabromobenzylene with Anisole

The reaction mixture was washed with 2N hydrochloric acid solution before removal of solvents and excess of anisole. The viscous yellow oil remaining was examined by thin layer chromatography on silica and shown to contain two components. Preparative layer chromatography on silica using benzene as a solvent system gave:-

(a) 5,6,7,8-tetrabromo-1,4-dihydro-1-methoxy-1,4-etheno-naphthalene (III, X=Br, R=OCH₃, R¹=R²=R³=H) (14.8%), m.p. 127° (from ethanol). (Found C,31.40; H,1.75%; M [mass spectroscopy] 500. C₁₃H₈Br₄O requires C,31.20; H,1.60%; M 500).

ν₂.8-3.27 (m, 4H), 4.45-4.75 (m, 1H), 6.28 (s, 3H).

max 3000, 2960, 2940, 2840, 1635, 1590, 1540, 1470, 1455, 1445, 1410, 1365, 1340, 1315, 1290, 1275, 1255, 1225, 1185, 1155, 1135, 1105, 1080, 1050, 1025, 980, 940, 900, 835, 795, 710, 675 cm⁻¹.

(b) 5,6,7,8-tetrabromo-1,4-dihydro-1,4-etheno-2-tetralone (VI, X=Br, R=H) (5%), m.p. 227° (from ethanol-chloroform).

(Found C, 29.60; H,1.30. C₁₂H₆Br₄O requires C,29.65; H,1.25%).

ν 3.1-3.4 (m, 2H), 4.9-5.3 (m, 2H), 7.88-8.0 (m, 2H).

max 2960, 2930, 1740 (C=O), 1410, 1360, 1310, 1265, 1130, 1080, 1005, 985, 970, 900, 795, 765, 695, 650 cm⁻¹.

Reaction of Tetrachlorobenzylene with Anisole

Tetrachlorobenzylene (0.01 mole) was generated from tetrachloroanthranilic acid in the presence of excess of anisole.

Removal of excess of anisole, after washing with 2N hydrochloric
acid left a viscous oil which was shown by thin layer chromatography to be a mixture of two major components. Separation by preparative layer chromatography on silica gave (III, X=Cl, R=OCH$_3$, R$_1$=H, R$_2$=H) (57.5%) m.p. 122$^\circ$ (from ethanol) (lit.$^6$ m.p. 122$^\circ$) and (VI, X=Cl, R=H) (1.9%) m.p. 151$^\circ$ (from ethanol) (lit.$^6$ m.p. 150$^\circ$).

**Preparation of p-Cresol methyl ether**

Dimethyl sulphate (48 ml.) was added dropwise to a stirred solution of p-cresol (54 g., 0.5 mole) in sodium hydroxide solution (200 ml., 8.5%) maintained at 10$^\circ$. The solution was heated under reflux for 2 hr. to complete the methylation then cooled to ambient temperature. The crude product, which separated as a yellow oil, was washed with sulphuric acid (250 ml., 10%), water (250 ml.) and dried over anhydrous magnesium sulphate. Distillation gave p-cresol methyl ether (55.8 g., 90%) b.p. 170-6$^\circ$ (lit.$^{10}$ b.p. 157$^\circ$). The distilled product showed no phenol absorption in the infrared spectrum.

**Reaction of Tetrabromobenzyn with p-Cresol methyl ether**

Removal of solvent and excess of p-cresol methyl ether after washing with 2N hydrochloric acid gave a viscous oil which was shown by thin layer chromatography on silica to contain one major component. Preparative layer chromatography on silica using benzene as a solvent system gave 5,6,7,8-tetrabromo-1,4-dihydro-10-methyl-1,4-etheno-2-tetralone (VI, X=Br, R=CH$_3$) (24%), m.p. 200$^\circ$ (from ethanol). (Found C, 31.10; H, 1.60.)
The adduct (VI, X=Br, R=CH$_3$) (150 mg.) was photolyzed in dry diethyl ether (50 ml.) for 1 hr. using a medium pressure mercury source. The reaction was followed by thin layer chromatography and samples were taken at 10 min. intervals until the starting material had completely disappeared. The ether was removed by distillation and the brown residue was purified by preparative layer chromatography on silica. The crystalline material obtained (66 mg., 50%) was shown by $^1$H n.m.r., ultraviolet, and infrared spectroscopy to be identical to naphthalene (VIII, R=R$^2$=H, R$^1$=CH$_3$).

**Reaction of Tetrabromobenzene with 2-Methylfuran**

The crude product, after removal of solvent and excess of 2-methylfuran was examined by thin layer chromatography on silica and found to contain one major component. Elution from neutral alumina in light petroleum-benzene (80:20) gave 5,6,7,8-tetra-bromo-1,4-dihydro-1-methyl-1,4-epoxynaphthalene (I, X=Br, R=CH$_3$) (53.8%), m.p. 113° (from ethanol). (Found C, 27.90; H, 1.36.

**C$_{13}$H$_8$Br$_4$O** requires C, 31.20; H, 1.60%).

$^\ast$ 3.67-3.95 (m, 1H), 5.05-5.15 (d, 1H), 5.4-5.6 (q, 1H), 7.75-8.1 (m, 5H).

$\nu_{max}$ 3060, 3000, 2920, 2860, 1735 (C=O), 1445, 1430, 1410, 1360, 1350, 1315, 1300, 1270, 1260, 1230, 1140, 1125, 1090, 1030, 990, 955, 920, 880, 830, 785, 735, 725, 660 cm$^{-1}$.

The adduct (VI, X=Br, R=CH$_3$) (150 mg.) was photolyzed in dry diethyl ether (50 ml.) for 1 hr. using a medium pressure mercury source. The reaction was followed by thin layer chromatography and samples were taken at 10 min. intervals until the starting material had completely disappeared. The ether was removed by distillation and the brown residue was purified by preparative layer chromatography on silica. The crystalline material obtained (66 mg., 50%) was shown by $^1$H n.m.r., ultraviolet, and infrared spectroscopy to be identical to naphthalene (VIII, R=R$^2$=H, R$^1$=CH$_3$).

**Reaction of Tetrabromobenzene with 2-Methylfuran**

The crude product, after removal of solvent and excess of 2-methylfuran was examined by thin layer chromatography on silica and found to contain one major component. Elution from neutral alumina in light petroleum-benzene (80:20) gave 5,6,7,8-tetra-

**C$_{13}$H$_8$Br$_4$O** requires C, 31.20; H, 1.60%).

$^\ast$ 3.67-3.95 (m, 1H), 5.05-5.15 (d, 1H), 5.4-5.6 (q, 1H), 7.75-8.1 (m, 5H).

$\nu_{max}$ 3060, 3000, 2920, 2860, 1735 (C=O), 1445, 1430, 1410, 1360, 1350, 1315, 1300, 1270, 1260, 1230, 1140, 1125, 1090, 1030, 990, 955, 920, 880, 830, 785, 735, 725, 660 cm$^{-1}$.
Adduct (I, X=Br, R=CH$_3$) (1.0 g.) was hydrogenated in ethanol (70 ml.) in the presence of a pre-reduced palladium on carbon catalyst (50 mg., 10%) to give, after the removal of catalyst and solvent, 5,6,7,8-tetrabromo-1,4-dihydro-1-methyl-1,4-epoxytetralin (VII, X=Br, R=CH$_3$) (820 mg., 82%) m.p. 122° (from ethanol). (Found C, 27.9%; H, 1.75. C$_{11}$H$_8$Br$_4$ requires C, 27.75; H, 1.70%).

$\nu$ 4.6-4.8 (m, 1H), 7.8-8.8 (m, 4H), 8.11 (s, 3H).

$\nu_{max}$ 3010, 2990, 2970, 2950, 2880, 1585, 1535, 1460, 1450, 1400, 1345, 1290, 1260, 1245, 1210, 1185, 1175, 1165, 1120, 1095, 1070, 1010, 1000, 970, 910, 890, 880, 850, 830, 815, 810, 750, 665, 655 cm$^{-1}$.

The hydrogenated adduct (VII, X=Br, R=CH$_3$) (82 mg.) was then converted, by treatment with constant boiling hydrobromic acid and acetic acid at 100°, to 1,2,3,4-tetrabromo-5-methylnaphthalene (VIII, R=CH$_3$, $R^1=R^2=H$) (77 mg., 80%), m.p. 198° (from ethanol). (Found C, 28.90; H, 1.30%; M [mass spectroscopy] 458. C$_{11}$H$_6$Br$_4$ requires C, 28.85; H, 1.30%; M 458).

$\nu$ 1.6-1.9 (m, 1H), 2.5-2.8 (m, 2H), 7.0 (s, 3H).

$\lambda_{max}$ (ethanol) 285 (3.92), 298 (3.94), 310 (3.85), 320 (3.77), 327 (3.70) n.m.
Formation of 1,2,3,4-tetrabromo-6-methylnaphthalene (VIII, R=R'=H, R''=CH₃) from (III, X=Br, R'=CH₃, R''=H)

The adduct (III, X=Br, R'=CH₃, R''=H) (100 mg.) was added to a stirred solution of 3-methylbutyl nitrite (0.5 ml.) in benzene (25 ml.) containing glacial acetic acid (0.1 ml.) heated at 50°. Heating was continued for 6 hr. when thin layer chromatography on silica showed that the starting material had disappeared and that a product of greater Rₚ value than the starting material had been formed. Preparative layer chromatography on silica gave (VIII, R=R'=H, R''=CH₃) (6.3%).

In analogous experiments the adducts (III, X=Br, R'=Bu⁺, R''=H), (III, X=Br, R=R'=CH₃, R''=H), and (III, X=Br, R=R'=H, R''=CH₃) were converted into the naphthalenes (VIII, R=R'=H, R''=Bu⁺), (VIII, R=R'=CH₃, R''=H) and (VIII, R=R', R''=CH₃) in 10.5, 12.5 and 15.7% yields respectively.

The adducts (III, X=Br, R=R'=H, R''=CH₃), (III, X=Br, R=R'=H, R=R'=CH₃), and (III, X=Br, R=R'=H, R=alkyl) did not form naphthalene derivatives when treated with 3-methylbutyl nitrite and acetic acid in benzene.

Reaction of Tetrabromobenzene with Benzene and p-Xylene.

A solution of tetrabromanthranilic acid (1.14 g., 0.0025 mole) in benzene (39 g., 0.5 mole) and p-xylene (53 g., 0.5 mole) was added dropwise to a stirred solution of 3-methylbutyl nitrite (0.34 ml., 0.0025 mole) in benzene (39 g., 0.5 mole) and p-xylene (53 g., 0.5 mole) maintained at 50°. The mixture was heated at 50° for ½ hr. and the solvents removed by distillation.
residue when examined by thin layer chromatography on silver nitrate-impregnated silica showed two components. Separation by preparative layer chromatography gave the benzene adduct (III, X=Br, \( R=R_1=R_2=R_3=H \)) and the p-xylene adduct (III, X=Br, \( R=R_1=R_2=H, R_1^1=R_3^3=CH_3 \)) in a ratio of 1:18.5.

A similar experiment in which tetraiodobenzyne was generated in the presence of equimolar quantities of benzene and p-xylene gave the benzene adduct (III, X=I, \( R=R_1=R_2=R_3=H \)) and the p-xylene adduct (III, X=I, \( R=R_2=H, R_1^1=R_3^3=CH_3 \)), in a ratio of 1:19.4.

Reaction of Tetrafluorobenzyne with Benzene and p-Xylene

n-Butyl lithium (2 ml., 0.005 mole) was added slowly to a stirred solution of bromopentafluorobenzene (1.24 g., 0.005 mole) in benzene (39 g., 0.5 mole) and p-xylene (53 g., 0.5 mole) maintained at -10° in a nitrogen atmosphere. Stirring was continued for 0.5 hr. at -10° before the temperature was allowed to rise to ambient. The mixture was washed with water and the solvents were removed by distillation. The crude product was extracted into ether and the solution filtered through a cone of anhydrous magnesium sulphate. The ether solution was examined by gas liquid chromatography which showed two major components. The relative peak areas were determined by an integration counter and the two components were found, by comparison with standards, to be the benzene adduct (III, X=F, \( R=R_1=R_2=R_3=H \)) and the p-xylene adduct (III, X=F, \( R=R_2=H, R_1^1=R_3^3=CH_3 \)) in a ratio of 1:7.0.

The two components present in the reaction mixture were separated by preparative layer chromatography on silica when
the ratio was found to be 1:6.8.

Reaction of Tetrabromobenzynes with Bicyclohepta (2,2,1) diene.

A solution of tetrabromoanthranilic acid (2.27 g., 0.05 mole) in acetonitrile (50 ml.) was added slowly to a stirred solution of 3-methylbutyl nitrite (0.68 ml., 0.05 mole) in bicyclohepta (2,2,1) diene (200 ml.) maintained at 50°. Heating was continued for 0.5 hr. after complete addition. Removal of acetonitrile and excess of bicyclohepta (2,2,1) diene gave a viscous yellow oil which was shown by thin layer chromatography on silica to contain two components. Preparative layer chromatography on silver nitrate-impregnated silica gave:

(a) 1,2,3,4-tetrabromobenzonortricyclole (X, X=Br)(9.8%), m.p. 218° (from ethanol-chloroform). (Found C,32.40; H,1.80%; M [mass spectroscopy] 484. C₁₃H₈Br₄ requires C,32.25; H,1.65%; M 484).

7.6 (m, 2H), 7.6 (m, 1H), 8.05 (t, 1H), 8.3 (m, 2H), 8.6 (d, 2H).

vₘₐₓ 3010, 2990, 2960, 2940, 2860, 1450, 1380, 1350, 1280, 1270, 1260, 1240, 1220, 1210, 1185, 1135, 1060, 1000, 980, 940, 920, 890, 820, 800, 780, 720, 700, 665 cm⁻¹.

(b) exo-3,4-tetrabromobenzotricyclo (4,2,1,0²,5) nona-3,7-diene (IX, X=Br)(32.2%), m.p. 135° (from ethanol-chloroform). (Found C,32.20; H,1.70%; M [mass spectroscopy] 484. C₁₃H₈Br₄ requires C,32.25; H,1.65%; M 484).
\( \tau 3.65 \text{ (t, 2H)}, 6.9 \text{ (s, 2H)}, 7.05 \text{ (m, 2H)}, 8.5-8.7 \text{ (d, 1H)}, 9.07-9.25 \text{ (d, 1H)}. \)

\[ \nu \text{max} \]

\( 3070, 2980, 2890, 1570, 1460, 1400, 1365, 1335, 1325, 1290, 1255, 1190, 1160, 1115, 1105, 1085, 960, 925, 910, 900, 810, 770, 745, 690, 670 \text{ cm}^{-1}. \)

**Reaction of Tetrachlorobenzyne with Bicyclohepta (2,2,1) diene**

Generation of tetrachlorobenzyne from tetrachloroanthranilic acid in the presence of excess of bicyclohepta (2,2,1) diene gave \((X,X=\text{Cl})\) and \((IX,X=\text{Cl})\) in a ratio of 1:2.5 when the products were separated by preparative layer chromatography on silver nitrate-impregnated silica.
SECTION 3

The Reactions of Tetrahalogenobenzynes

with Biphenylene.
INTRODUCTION

The original paper describing the synthesis of biphenylene (I, Table 4) contained convincing evidence of structure obtained by classical methods. Further proof of structure was obtained from electron diffraction studies of the vapour phase and by X-ray analysis of the crystalline material. These studies led to the conclusion that biphenylene has the structure of a dibenzocyclobutadiene. They also showed that the central bonds are significantly longer than the bonds which make up the six-membered rings. A more refined X-ray analysis has established the complete planarity of the biphenylene molecule and the exact bond distances and angles between all of the carbon atoms. The results obtained also indicate that biphenylene is closer structurally to a tetramethylene-cyclobutane than to a tetramethylcyclobutadiene. That there is a considerable degree of resonance interaction between the two benzenoid rings, despite the unusual length of the central bonds, has been adduced from the ultraviolet spectrum of biphenylene and by the directing influence which mono-substituted biphenylenes exert on the position of entry of a second substituent into the other benzene ring.

Biphenylene undergoes electrophilic substitution exclusively at the 2-position but has not previously been found to undergo cycloaddition reactions of the Diels-Alder type. Benzene solutions of biphenylene give a yellow colour indicative of charge-transfer complex formation when treated with maleic
anhydride but collapse to a cycloadduct is not observed even when the components are heated at $140^\circ$ in the absence of a solvent. The peculiar stability of the charge-transfer complex formed between tetracyanoethylene and biphenylene has been ascribed to cross-ring electronic interactions in biphenylene and to the geometry of the complex. The biphenylene-tetracyanoethylene complex is reported to have the tetracyanoethylene lying in a plane parallel to that of the biphenylene and symmetrically placed over the potential cyclobutadiene ring. The concept of stabilisation of a cyclobutadiene system through complex formation has been suggested in the past, although significant stabilisation in such a loosely bound state as that in a charge-transfer complex might not be expected.

The reaction of biphenylene with aryne intermediates has not been previously reported to give cycloaddition products although triphenylene was isolated in low yields together with biphenylene after the flash photolysis of benzenediazonium-2-carboxylate. This suggested that the triphenylene could have arisen by a Diels-Alder type reaction between biphenylene and benzyne. A similar mechanism has been postulated to account for the formation of dodecahydrotriphenylene in reactions involving cyclo-hexyne. The possibility that the triphenylene derivatives, observed in reactions involving arynes generated from organo-metallic precursors, arose by a Diels-Alder type reaction between benzyne and biphenylene has been discounted. When benzyne was generated from o-fluorophenylmagnesium bromide in
tetrahydrofuran in the presence of biphenylene, no increase in the normal yield of triphenylene was observed and the biphenylene was completely recovered.\textsuperscript{30} The mechanism of triphenylene formation in reactions involving organometallic compounds has been shown to involve a step-wise series of reactions of organometallic compounds with aryne intermediates. The lead tetraacetate oxidation of 1-aminobenzotriazole in benzene solution gives rise to biphenylene and a trace amount of triphenylene.\textsuperscript{64} The possibility that benzyne, generated in this way, undergoes a cycloaddition reaction with biphenylene to form the observed triphenylene has also been investigated and ruled out.\textsuperscript{112} The failure to observe cycloadducts in the reactions of biphenylene with benzyne generated from a number of precursors and the high yields of cycloadducts obtained in the reactions of tetrahalogenobenzynes with a number of aromatic compounds,\textsuperscript{66,67} led us to an investigation of the reactions of the tetrahalogenobenzynes with biphenylene.

DISCUSSION

The reactions of the tetrahalogenobenzynes with naphthalene derivatives lead exclusively to cycloaddition at the 1,4-positions. However although molecular orbital calculations show the highest sum of the free valence index values for the 1,4-positions in the hypothetical cycloaddition of maleic anhydride to biphenylene, the calculated product stabilities indicate that 2,4a-cycloaddition
should be favoured.\textsuperscript{113} When tetrachlorobenzyne was generated by aprotic diazotisation of tetrachloroanthranilic acid in the presence of biphenylene (2 mole), the major product was isolated by preparative layer chromatography (6.1\%) and was found to be 1,2,3,4-tetrachloro-5,10b-dihydro-5,10b-ethenobenz[a]biphenylene (II, \(X=\text{Cl}\))(Table 4.), which is the 2,4a-cycloadduct derived from tetrachlorobenzyne and biphenylene. Similarly when tetrafluorobenzyne was generated from pentafluorophenyl lithium in light petroleum in the presence of biphenylene (2 mole), the crude reaction mixture showed one major product which was isolated by preparative layer chromatography and shown to be 1,2,3,4-tetrafluoro-5,10b-dihydro-5,10b-ethenobenz[a]biphenylene (II, \(X=\text{F}\)) in 10.5\% yield. This is the analogous 2,4a-cycloadduct of tetrafluorobenzyne and biphenylene. The molecular formulae for the 1:1 adducts of tetrachlorobenzyne and tetrafluorobenzyne with biphenylene were established by elemental analysis and mass spectrometry. That 2,4a-cycloaddition of the tetrahalogenobenzenes to biphenylene had occurred was evident from spectroscopic data. The ultraviolet spectra of the adducts (II, \(X=\text{Cl}\) or \(\text{F}\)) were compared with the spectra for benzo\textsubscript{cyclobutene}\textsuperscript{114} and 1,2-dimethylenebenzocyclobutene\textsuperscript{115} and indicated the presence of the methylenebenzo\textsubscript{cyclobutene} chromophore. The \(^1\text{H}\) n.m.r. spectrum of the adduct (II, \(X=\text{Cl}\)) showed resonances at 2.06-2.95\(\text{\tau}\), integral area four protons, which can be assigned to the four protons on the benzene ring, a multiplet at 3.1\(\text{\tau}\), integral area two protons,
TABLE 4

I

II

III

IV

V

VI
which can be assigned to the two protons a and b of the etheno bridge, a doublet at 3.55 T, integral area one proton, which can be assigned to proton c, and a multiplet at 4.6 T, integral area one proton, which can be assigned to the bridgehead proton x. The $^1H$ n.m.r. spectrum of the fluorinated analogue (II, X=F) was very similar. The mass spectrum of the chlorinated adduct (II, X=Cl) showed the expected isotopic cluster for the presence of four chlorine atoms, and the major cleavage of the molecular ion occurred by the loss of chlorine and hydrogen chloride. The mass spectrum of the fluorinated adduct (II, X=F) showed that the major cleavage of the molecular ion occurred by loss of hydrogen fluoride. The hydrogenation of adduct (II, X=Cl) in ethanol with hydrogen in the presence of palladium on carbon resulted in the uptake of five moles of hydrogen with the formation of the reduced adduct, 1,2,3,4-tetrachloro-5,6,6a,6b,7,8,9,10,10a,10b-decahydro-5,10b-ethano-benzo[a]biphénylene (III). No definite break was observed after the uptake of two moles of hydrogen which was expected by analogy with the results obtained in the hydrogenation of the cycloadducts derived from the tetrahalogenobenzynes with benzene and alkylbenzenes.66,67 When the hydrogenation was interrupted after the uptake of a volume of hydrogen corresponding to two moles, the reaction mixture was shown, by thin layer chromatography, to consist of a complex mixture of compounds containing both the starting material (II, X=Cl) and the "fully hydrogenated" product (III). The complex mixture
of products observed after the uptake of two moles of hydrogen presumably consists of the partially hydrogenated intermediates. This result is in accord with the rapid reduction of benzocyclobutene which readily absorbs three moles of hydrogen to give bicyclo[4.2.0]octane in the presence of a palladium catalyst.116

The possibility of obtaining a 2:1 adduct of tetrachlorobenzene or tetrafluorobenzene with biphenylene by reactions of the mono-adducts (II, X=Cl or F) with the appropriate tetrahalogenobenzene has been investigated. The addition of a second molecule of the tetrahalogenobenzene could theoretically result in the formation of six possible isomeric 2:1 adducts. Cycloaddition across the 7,10-positions of the mono-adduct would give a mixture of two adducts with structures based upon dibenzo[4,9]biphenylene in which the etheno-bridges could be on the same side or opposite sides of the plane of the molecule. Similarly cycloadditions across the 6b,9- or 8,10a-positions would each give a mixture of two cycloadducts with structures based upon dibenzo[4,9]biphenylene and dibenzo[4,9]biphenylene respectively. The reactions of the mono-adducts (II, X=Cl or F) with tetrachlorobenzene or tetrafluorobenzene constitute a 1,4-cycloaddition to a benzocyclobutene system and so in order to gain further information about the preferred position of attack of the aryne, a reaction was carried out between tetrachlorobenzene and benzocyclobutene. Tetrachlorobenzene was generated by the aprotic diazotisation of tetrachloroanthranilic acid in the presence of a ten-fold
excess of benzocyclobutene. Excess of benzocyclobutene, together with solvent, was removed by distillation. Examination of the residue by thin layer chromatography on silica and on silica impregnated with 10% silver nitrate showed only one product which was isolated by preparative layer chromatography in 30.5% yield and found to be 5,6,7,8-tetrachloro-1,4-dihydro-1,2-ethano-1,4-ethanonaphthalene (IV). That cycloaddition of the aryne across the 2a,5-positions of benzocyclobutene had occurred was evident from the $^1$H n.m.r. spectrum of the product which shows multiplets at 3.3 and 3.8 of integral areas two protons and one proton which can be assigned to the olefinic protons in the 9,10- and 3-positions respectively. Multiplets at 4.63 and 6.0 of integral areas one proton and three protons can be assigned to the four methylene protons of the ethano-bridge. Models show that in adduct (IV) the spatial arrangement of the atoms is such that one of the methylene protons of the ethano-bridge lies very close to the chlorinated benzene ring and is strongly deshielded which accounts for the marked downfield shift in the $^1$H n.m.r. spectrum. It seems unlikely, on the basis of this result, that cycloaddition of an aryne across the 7,10-positions of the mono-adducts (II, X=Cl or F) would occur and thus only four isomeric 2:1 cycloadducts might be anticipated. The adduct (II, X=Cl) was treated with tetrachlorobenzylene (7 moles), generated from tetrachloroanthranilic acid in acetonitrile at 50° and the reaction mixture was examined.
by thin layer chromatography, after filtration from octa-
chloroacridone. The only component present was found to be
the unreacted adduct (II, X=Cl) which was subsequently
recovered quantitatively from the reaction mixture. Similarly
when tetrafluorobenzene (7 moles) was generated from penta-
fluorophenyl lithium in the presence of the adduct (II, X=F),
the starting material was again recovered quantitatively from
the reaction mixture. The only evidence which has been obtained
for the formation of a 2:1 adduct was in the initial reaction
of tetrafluorobenzene with biphenylene when a reactant ratio
of 1:1 was used. The mono-adduct (II, X=F) was formed in
12.4% yield together with a trace amount of a second product
whose mass spectrum indicated that it was a 2:1 adduct of
tetrafluorobenzene and biphenylene. This product has not been
observed in subsequent reactions of tetrafluorobenzene with
biphenylene even when a 2:1 ratio of tetrafluorobenzene to
biphenylene was employed.

In view of the good yields of naphthalene derivatives obtained in the pyrolyses of the adducts obtained from tetra-
fluorobenzene with benzene and alkylbenzenes, it was of interest
to us to investigate the pyrolysis of the adduct (II, X=F).
Aromatisation by loss of acetylene from the adduct might
reasonably be expected to give 1,2,3,4-tetrafluorobenzo[biphenylene. The adduct (II, X=F) was pyrolysed at 330° by
the procedure described for the pyrolysis of tetrafluoro-
benzobarrelene and thin layer chromatography on silica
showed the presence of one major component in the pyrolysate. The product was isolated as a yellow oil by preparative layer chromatography on silica and purified by precipitation from benzene solution as a trinitrofluorenone complex which was subsequently recrystallised from methanol-benzene. The unknown compound was regenerated from its trinitrofluorenone complex by elution from a short neutral alumina column in benzene and sublimed to give a yellow crystalline material whose ultraviolet spectrum showed a marked similarity to that of benzo[a]biphenylene but whose molecular formula, as determined by accurate mass measurement on the molecular ion, was found to be C_{42}H_{16}F_{12}. Thus the compound obtained is evidently not 1,2,3,4-tetrafluorobenzo[a]biphenylene. The failure of the adduct (II, X=F) to undergo aromatisation by thermal loss of acetylene can perhaps be understood in the light of the observed mass spectral data for the adducts (II, X=Cl or F). The major fragmentation of the molecular ion does not occur by loss of acetylene but by loss of hydrogen halide whereas in the mass spectra of the tetrafluorobenzobarrelen derivatives, the major fragmentation of the molecular ion always occurs by loss of acetylene. The observation of naphthalene derivatives, in addition to the expected isomeric benzobarrelenes, in the reactions of certain alkylbenzenes with tetrabromobenzyne generated by aprotic diazotisation of tetrabromoanthranilic acid prompted an investigation of the reaction of tetrabromobenzyne with
biphenylene. The reaction of tetrabromobenzyne with o-xylene gave a mixture of the two naphthalenes derived from the bridgehead and non-bridgehead substituted benzobarrelenes and in view of the results obtained in the reactions of biphenylene with tetrafluorobenzyne and tetrachlorobenzyne, it was hoped that the reaction of biphenylene with tetrabromobenzyne would produce 1,2,3,4-tetrabromobenz[a]biphenylene in addition to the expected 2,4a-cycloadduct. Tetrabromobenzyne was generated by the aprotic diazotisation of tetrabromoanthranilic acid in acetonitrile in the presence of biphenylene (3 mole) and the crude reaction mixture was examined by thin layer chromatography which showed unchanged biphenylene together with one other component. The product was separated from biphenylene by preparative layer chromatography on silica and was found, on the evidence of its $^1$H n.m.r. spectrum, mass spectrum, and elemental analysis, to be 1,2,3,4-tetrabromo-5,10b-dihydro-5,10b-ethenobenz[a]biphenylene (II, X=Br) in 4.9% yield. No evidence was obtained which suggested the possible formation of 1,2,3,4-tetrabromobenz[a]biphenylene.

The reaction of biphenylene with tetrachlorobenzyne gave, in addition to the 2,4a-cycloadduct (II, X=Cl) (Table 4.), a second product in 0.5% yield, which was shown by elemental analysis and accurate mass measurement on the molecular ion to be isomeric with the adduct (II, X=Cl). An analogous product was obtained in 3.6% yield in the reaction of biphenylene with tetrafluorobenzyne. The ultraviolet spectrum
of the product derived from the reaction of biphenylene with tetrachlorobenzyne was very similar to that of the product derived from the corresponding reaction with tetrafluorobenzyne and showed a characteristic naphthalene chromophore. That the unknown compounds contained an ethynyl group was indicated by their infrared spectra which both showed strong absorptions at 3300 cm\(^{-1}\) and weak absorptions at 2110 cm\(^{-1}\). The \(^1\)H n.m.r. spectrum of the unknown product from biphenylene and tetrachlorobenzyne, determined at 60 MHz, showed a doublet of integral area one proton centred at 1.6 \(\tau\), a triplet of integral area one proton centred at 2.4 \(\tau\), a multiplet of integral area five protons centred at 2.65 \(\tau\), and a singlet at 7.3 \(\tau\), of integral area one proton. The 60 MHz \(^1\)H n.m.r. spectrum of the fluorinated analogue was very similar and showed a one-proton doublet centred at 1.95 \(\tau\), a one-proton triplet centred at 2.45 \(\tau\), a five-proton multiplet centred at 2.75 \(\tau\), and a one-proton singlet at 7.3 \(\tau\). The resonance at 7.3 \(\tau\) in the \(^1\)H n.m.r. spectra of both compounds provides further support for the presence of an ethynyl group in the molecules. The fluorinated compound was hydrogenated in ethanol over a pre-reduced palladium on carbon catalyst. An examination of the 60 MHz \(^1\)H n.m.r. spectrum of the reduction product showed that the low-field region of the spectrum was identical to that observed in the parent compound but that the singlet at 7.3 \(\tau\) had been replaced by a broadened quartet centred at 7.68 \(\tau\) and a triplet centred at 9.0 \(\tau\) which are characteristic of
an ethyl group. The $^1$H n.m.r. spectrum of the reduced compound obtained at 100 MHz showed that the methylene of the ethyl group did not, in fact, appear as a quartet but as a well defined quartet of doublets. That the doublets in the methylene region of the n.m.r. spectrum were caused by long-range $^{19}$F - $^1$H spin-spin coupling was established by comparison with the spectrum of 1,2,3,4-tetrafluoro-5-ethynaphthalene which shows an identical spin-spin pattern for the methylene of the ethyl group. On the basis of this evidence, the compound obtained by the reduction of the unknown fluorinated compound would appear to be a 1,2,3,4-tetrafluoro-5-ethynaphthalene derived from a 1,2,3,4-tetrafluoro-5-ethynyl-naphthalene. It is of interest to note that the chemical shifts of the ethyl group in the reduced fluorinated compound and in 1,2,3,4-tetrafluoro-5-ethynaphthalene are markedly different. In the reduced fluorinated compound, the methylene group is centred at 7.68τ and the methyl group at 9.0τ, whereas in 1,2,3,4-tetrafluoro-5-ethynaphthalene, the methylene group is centred at 6.9τ and the methyl at 8.7τ which indicates that in the reduced fluorinated compound, the ethyl group is experiencing a considerable shielding effect which can be explained by the presence of an adjacent phenyl group whose steric requirement is such that it lies at an angle approaching ninety degrees to the plane of the naphthalene ring. Evidence for the non-coplanarity of the phenyl group was obtained from the ultra-
violet spectrum of the reduced fluorinated compound which was very similar to that of 1,2,3,4-tetrafluoroanaphthalene. This implies that in the reduced fluorinated compound the phenyl group is not fully conjugated with the naphthalene residue. The 100 MHz $^1$H n.m.r. spectrum of the reduced fluorinated compound revealed, on scale expansion of the low-field region of the spectrum, that the triplet centred at $2.45\tau$ in the 60 MHz spectrum is, in fact, a partially resolved doublet of doublets. That this doublet of doublets is associated with the doublet ($|\mu|=4.2$ Hz) centred at $1.95\tau$ is evident from the fact that irradiation at the centre of the doublet caused the doublet of doublets centred at $2.45\tau$ to collapse to a doublet and irradiation at the centre of the doublet of doublets caused the doublet centred at $1.95\tau$ to collapse to a broadened singlet. This latter information, taken into consideration with other evidence indicates that the naphthalene residue of the reduced fluorinated compound contains adjacent aromatic protons and leads to the conclusion that the compound is most probably 1,2,3,4-tetrafluoro-5-ethyl-6-phenylanaphthalene (VI) (Table 4.), derived from 1,2,3,4-tetrafluoro-5-ethynyl-6-phenylanaphthalene ($V, X=F$)(Table 4). By analogy, the unknown compound from the reaction of biphenylene with tetrachlorobenzylene is 1,2,3,4-tetrachloro-5-ethynyl-6-phenylanaphthalene ($V, X=Cl$). Two explanations for the spin-spin splitting observed for the adjacent protons on the naphthalene ring offered themselves as feasible. The first was that proton
H_A (Scheme 9) resonates as a doublet of doublets as a result of spin-spin coupling to proton H_B, with additional long-range $^{19}$F - $^1$H spin-spin coupling to fluorine F_x, and that proton H_B resonates as a doublet as a result of spin-spin coupling to proton H_A. This explanation has been ruled out on the basis of a number of observations. The $^1$H n.m.r. spectrum of 1,2,3,4-tetrafluoro-6,7-dimethylnaphthalene, obtained by the pyrolysis of 5,6,7,8-tetrafluoro-1,4-dihydro-2,3,9,10-tetramethyl-1,4-ethenonaphthalene at 400°C, shows only a broadened singlet for the aromatic protons which means that the long-range spin-spin coupling of proton H_A to fluorine F_x cannot reasonably be as large as 3.5 Hz which would be necessary to justify the above explanation. In addition to this proton H_B would need to experience a strong deshielding influence such that the normal resonance positions for the $\alpha$- and $\beta$-protons in a naphthalene are reversed. In fact proton H_B might be anticipated to experience a shielding effect caused by an adjacent phenyl group lying out of plane. Finally the above reasoning cannot be invoked to explain the identical spin-spin splitting observed for the adjacent protons on the naphthalene ring in compound (V, X=Cl). A more reasonable explanation for the observed $^1$H n.m.r. spectral data is that the spin-spin coupling of proton H_A to proton H_B causes proton H_A to resonate as a doublet ($|J|_{H_A-H_B} = 4.2$ Hz) and that proton H_B is further long-range coupled ($|J| = 3.5$ Hz) to protons on the adjacent phenyl ring and hence resonates as
Scheme 9.
a doublet of doublets. Evidence for the long-range coupling of proton $H_B$ to protons on the phenyl ring was obtained in the previously described spin-decoupling experiment. When the centre of the doublet of doublets centred at $2.45 \tau$ was irradiated, the resonance pattern of the five-proton aromatic multiplet centred at $2.75 \tau$ changed considerably. The origin of the compounds $(V, X=F$ or $Cl)$ was investigated and a number of observations were of interest. The two compounds $(V, X=F)$ and $(V, X=Cl)$ were produced in experiments in which the tetrahalogenobenzynes were generated from pentafluorophenyl lithium and tetrachloroanthranilic acid respectively which proves that the product $(V)$ is not a function of the method of generation of the aryne. The possibility that the products $(V, X=F$ or $Cl)$ arose from the initially formed $2,4a$ cycloadducts $(II, X=F$ or $Cl)$ was considered and discounted by carrying out two experiments in which the appropriate tetrahalogenobenzyne was generated in the presence of the corresponding $2,4a$-cycloadduct. The products $(V, X=Cl$ or $F)$ were not detected in either experiment which leads to the suggestion that these compounds are possibly derived from the $1,4$-cycloadduct shown in Scheme 9. The isolated benzocyclobutadiene system generated in the $1,4$-cycloadduct does not result in dimerisation as might have been expected, and the inherent instability of the $1,2$-double bond in the benzocyclobutadiene may well be the driving force towards aromaticity. The evidence presented for the structure of the unknown compounds
obtained in the reactions of biphenylene with tetrachloro-
and tetrafluorobenzyne suggests that they are 1,2,3,4-tetra-
halogeno-5-ethynyl-6-phenynaphthalenes but a synthesis by
an unambiguous route is necessary in order to obtain absolute
proof of structure.
EXPERIMENTAL

All General Methods are as reported in Sections 1 and 2 (Experimental).

Preparation of Biphenylene

A solution of anthranilic acid (34.2 g., 0.25 mole) in tetrahydrofuran (250 ml) containing trichloroacetic acid (0.3 g.) was stirred magnetically in a 600 ml plastic beaker and cooled to 5° in an ice-bath. 3-Methylbutyl nitrite (55 ml, 0.41 mole) was added over a period of 2 min. and the reaction mixture was stirred for a further 1.5 hr. at 18-25° after which time a buff-coloured precipitate of benzenediazonium-2-carboxylate was observed. The mixture was cooled to 10° and the mother liquors were removed by decantation after settling of the product. The zwitter-ion was purified by washing with two 50 ml portions of cold tetrahydrofuran and two 50 ml portions of 1,2-dichloroethane, with decantation after each washing. The solvent-wet benzenediazonium-2-carboxylate was slurried with 1,2-dichloroethane (150 ml) and added in small portions to a 2 l beaker containing 1,2-dichloroethane (1.25 l), which was stirred magnetically and heated to gentle reflux on a magnetic stirrer - hot plate. Vigorous frothing occurred when the benzenediazonium-2-carboxylate was added and ceased a few minutes after completion of the addition when the solution assumed a clear red-brown colour which indicated the end of the reaction. The 1,2-dichloroethane was removed by distillation until
approximately 75 ml of residue remained in the flask. The reaction was then repeated on the same molar scale. The final residues were combined, diluted with ethylene glycol (600 ml), and the product distilled from a flask fitted with an air condenser. The fraction b.p. 150-200° was collected and the distillate cooled to 10° when the crude biphenylene precipitated and was filtered off. Washing with water (3 x 50 ml) and a final recrystallisation from ethanol gave biphenylene (6.1 g., 8.8% based on anthranilic acid), m.p. 112° (lit. 109-112°).

Reaction of Tetrachlorobenzylene with Biphenylene. (Reactant ratio 1:2).

A solution of tetrachloroanthranilic acid (1.38 g., 0.005 mole) in acetonitrile (60 ml) was added dropwise to a stirred solution of biphenylene (1.5 g., 0.01 mole) in acetonitrile (60 ml) containing 3-methylbutyl nitrite (0.68 ml., 0.005 mole) heated at 50°. Stirring was continued for ½ hr. after complete addition of the tetrachloroanthranilic acid. Filtration of the solution from a small quantity of octachloroacidone and removal of acetonitrile together with 3 methylbutan-1-ol by distillation left a semicrystalline solid. Thin layer chromatography showed the presence of three components which were separated by preparative layer chromatography on silica and were found, in order of decreasing Rf value, to be (a) recovered biphenylene,

(b) 1,2,3,4-tetrachloro-5,10b-dihydro-5,10b-ethenobenz[a]biphenylene (II, X=Cl)(6.1%), m.p. 116° (from ethanol).
(Found C, 59.25; H, 2.20%; M \text{mass spectroscopy} 366.

C\textsubscript{18}H\textsubscript{8}Cl\textsubscript{4} requires C, 59.10; H, 2.20%; M 366).

\textit{T} 2.06-2.95 (m, 4H), 3.1 (m, 2H), 3.55 (d [\text{J} = 5.8 \text{ Hz}], 1H)
and 4.6 (m, 1H).

\lambda_{\text{max}} \text{ (hexane)} 230 (\log{\varepsilon} 4.42), 248 (4.15), 270 (3.80),
281 (3.76), 294 (3.78), 300 (3.77) and 308 (3.85) n.m.

Hydrogenation of adduct (II, X=Cl) (50 mg.) in ethanol
(100 ml) over a pre-reduced palladium on carbon catalyst (10
mg., 10%) gave, after removal of catalyst and solvent, 1,2,3,4-
tetrachloro-5,6,6a,6b,7,8,9,10,10a,10b-decahydro-5,10b-ethano-
benzo[a]biphenylene. (III) (72%), m.p. 98\degree (from ethanol).
M/e 374.0139. C\textsubscript{18}H\textsubscript{18}Cl\textsubscript{35} requires 374.0163.

\textit{T} 6.2-6.45 (m, 1H), 7.1-9.6 (m, 17H).

\nu_{\text{max}} 2980, 2930, 2870, 1450, 1365, 1340, 1330, 1315, 1300,
1270, 1205, 1165, 1140, 1070, 1020, 920, 870, 815, 750, 675, 660
\text{cm}^{-1}.

(c) A third product was isolated (0.5\%) whose low resolution
mass spectrum indicated that it was isomeric with the adduct
(II, X=Cl) but whose structure was not further investigated at
this stage.

The reaction between tetrachlorobenzynne and biphenylene
was repeated on twice the molar scale described above and the
crude reaction mixture was separated, by elution from neutral
alumina in light petroleum, into (a) recovered biphenylene,
(b) 1,2,3,4-tetrachloro-5,10b-dihydro-5,10b-ethenobenzo[a
biphenylene (II, X=Cl) (5.4\%).
(c) 1,2,3,4-tetrachloro-5-ethynyl-6-phenynaphthalene (V),
(X=Cl) (0.4%), m.p. 99° (from ethanol). (Found C, 58.40;
H, 2.35%; M [mass spectroscopy] 366. $C_{18}H_8Cl_4$ requires
C, 59.10; H, 2.20; M 366. M/e 363.9381. $C_{18}H_8Cl_4$ requires
363.9380.

$\lambda_{max}$ (ethanol) 294 ($\log_{10}$ 3.55), 305 (3.64), 316 (3.60) n.m.
$\nu_{max}$ 3300 (H-C::;C ), 3070, 2930, 2860, 2110 (C=), 1600,
1545, 1480, 1465, 1445, 1400, 1360, 1315, 1280, 1190, 1180,
1145, 1105, 1075, 1045, 1010, 950, 915, 895, 870, 825, 810,
765; 755, 710, 695, 670 cm$^{-1}$.

Reaction of Tetrachlorobenzene with Biphenylene (Reactant
ratio 2:1).

A solution of tetrachloroanthranilic acid (2.75 g., 0.01
mole) in acetonitrile (60 ml) was added slowly to a stirred
solution of biphenylene (0.75 g., 0.005 mole) and 3-methylbutyl
nitrite (1.35 ml, 0.01 mole) in acetonitrile (60 ml) heated at
50°. Heating was continued for $\frac{1}{2}$ hr. after complete addition.
Filtration from a small quantity of octachloroacridone and
removal of solvent again left a semi-crystalline solid which
was separated by preparative layer chromatography into (a)
unreacted biphenylene, (b) adduct (II, X=Cl) (5%) and (c)
compound (V, X=Cl) (0.5%).

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Reaction of Tetrafluorobenzene with Biphenylene (Reactant ratio 1:1).

n-Butyl lithium in hexane solution (2 ml., 0.005 mole) was added to a stirred solution of bromopentafluorobenzene (1.235 g., 0.005 mole) in dry light petroleum (100 ml) at -60° in an atmosphere of nitrogen. After complete addition, the mixture was stirred for 1 hr. at -60° then the temperature was allowed to rise to -30° when a solution of biphenylene (0.75 g., 0.005 mole) in dry light petroleum was added at a slow drop rate. The solution was stirred for ½ hr. at -30° before being allowed to rise to ambient temperature. Examination of the reaction mixture by thin layer chromatography on silica showed the presence of three components which were shown, in order of decreasing Rf values, to be (a) recovered biphenylene, (b), 1,2,3,4-tetrafluoro-5,10b-dihydro-5,10b-ethenobenzene [a] biphenylene (II, X=F) (12.4%), colourless oil. M/e 300.0559. C_{18}H_{8}F_{4} requires 300.0562. 

\[ \begin{align*}
\text{IR} & 2.2-3.0 (m, 4H), 3.18 (m, 2H), 3.61 (d [\text{J} = 5.7 \text{ Hz}]) 1H), \\
& \text{and} 4.8 (m, 1H).
\end{align*} \]

\[ \lambda_{\text{max}} \text{ (hexane)} = 238 (\log_{10} 3.95), 247 (3.79), 268 (3.65), 279 (3.67), 285 (3.60), 292 (3.67), 298 (3.64), 305 (3.71) \text{n.m.} \]

(c) A trace amount (0.25%) of a second product whose low resolution mass spectrum indicated that it was a 2:1 adduct derived from tetrafluorobenzene and biphenylene. This product was not observed in subsequent reactions between tetrafluorobenzene and biphenylene.

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Reaction of Tetrafluorobenzyne with Biphenylene (Reactant ratio 1:2).

When tetrafluorobenzyne was generated as above in the presence of biphenylene (2 mole), the crude reaction mixture was shown, by thin layer chromatography, to contain three components which were again separated by preparative layer chromatography to give (a) recovered biphenylene, (b) 1,2,3,4-tetrafluoro-5,10b-dihydro-5,10b-ethenobenz[a]biphenylene (II, X=F) (10.5%), (c) 1,2,3,4-tetrafluoro-5-ethyl-6-phenylnaphthalene (V, X=F) (3.6%), colourless oil. M/e 300.0567. C_{18}H_{8}F_{4} requires 300.0562.

T 1.95 (d [ \text{J} = 4.2 \text{ Hz}, \text{1H}], 2.45 (t, \text{1H}), 2.75 (m, \text{5H}), 7.3 (s, \text{1H}).

\lambda_{\text{max}} \text{ (ethanol) 285 (log} 10 \text{E 3.75), 292 (3.73), 306 (3.50), 320 (2.97) n.m.}

\nu_{\text{max}} 3300 (\text{H-C} \equiv \text{C}), 3070, 2930, 2110 (\text{C} \equiv \text{C}, 1670, 1610, 1525, 1500, 1470, 1450, 1410, 1370, 1300, 1270, 1130, 1120, 1100, 1080, 1065, 1045, 1030, 990, 965, 880, 805, 760, 700, 650 \text{ cm}^{-1}.

Hydrogenation of compound (V, X=F) (100 mg.) in ethanol (100 ml) over a pre-reduced palladium on carbon catalyst (15 mg., 10%) gave, after removal of catalyst and solvent, 1,2,3,4-tetrafluoro-5-ethyl-6-phenylnaphthalene (VI) (80%), m.p. 92° (from ethanol). (Found C, 70.30; H, 4.00%; M \text{ [mass spectroscopy]304. } C_{18}H_{12}F_{4} \text{ requires C, 71.05; H, 4.00%; M 304.})

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**T** 1.95 (d $[\text{H} = 4.2 \text{ Hz}]$, 1H), 2.45 (t, 1H), 2.75 (m, 5H), 7.68 (qxp $[J_{\text{H-H}} = 4.0 \text{ Hz}, J_{\text{H-F}} = 2.0 \text{ Hz}]$, 2H), 9.0 (t $[J_1 = 4.0 \text{ Hz}]$, 3H).

$\lambda_{\text{max}}$ (ethanol) 275 (log$\varepsilon$ 3.75), 284 (3.87), 290 (3.83), 306 (3.37), 322 (3.05) n.m.

Reaction of Tetrafluorobenzylene with Biphenylene (Reactant ratio 2:1).

An attempt to produce a 2:1 adduct of tetrafluorobenzylene and biphenylene by increasing the ratio of tetrafluorobenzylene to biphenylene to 2:1 was unsuccessful. Removal of solvents and separation of the crude reaction mixture by preparative layer chromatography gave (a) unreacted biphenylene, (b) adduct (II, $X=F$)(9.3%), and (c) compound (V, $X=F$)(1.1%).

Reaction of Tetrabromobenzylene with Biphenylene

A solution of tetrabromoanthranilic acid (2.28 g., 0.005 mole) in acetonitrile (50 ml) was added concurrently with a solution of 3-methylbutyl nitrite (0.68 ml, 0.005 mole) in acetonitrile (50 ml) to a solution of biphenylene (2.5 g., 0.017 mole) in acetonitrile (50 ml), stirred and heated at $50^\circ$. Heating was continued for 0.5 hr. after complete addition. Examination of the reaction mixture by thin layer chromatography showed the presence of biphenylene and one

** Determined at 100 MHz by P.C.M.U.
reaction product. Separation by preparative layer chromatography on silica gave (a) recovered biphenylene,

(b) 1,2,3,4-tetrabromo-5,10b-dihydro-5,10b-ethenobenza[a]
biphenylene (II, X=Br) (4.9%), m.p. 122° (from ethanol).
(Found C, 39.75; H, 1.60%; M [mass spectroscopy] 544. \( \text{C}_{18} \text{H}_{8} \text{Br}_4 \) requires C, 39.75; H, 1.50%; M 544).
\( \tilde{\nu} \) 1.93-2.93 (m, 4H), 3.15 (m, 2H), 3.58 (d \( [\text{J} = 6.0 \text{ Hz}] \), 1H) and 4.78 (m, 1H).
\( \lambda_{\text{max}} \) (ethanol) 235 (log \( \varepsilon \) 3.88), 245 (3.75), 269 (3.63), 276 (3.65), 283 (3.64), 294 (3.60), 302 (3.68) n.m.

**Reaction of Tetrachlorobenzene with Adduct (II, X=Cl).**

A solution of tetrachloroanthranilic acid (1.38 g., 0.005 mole) in acetonitrile (50 ml) was added dropwise with stirring to a solution of the adduct (II, X=Cl) (0.25 g., 0.0058 mole) in acetonitrile (50 ml) containing 3-methylbutyl nitrite (0.68 ml, 0.005 mole) and heated at 50°. Heating was continued for 0.5 hr. after complete addition of the tetrachloroanthranilic acid. Examination of the reaction mixture by thin layer chromatography after filtration from octachloroacridone and comparison with an authentic sample showed only unreacted (II, X=Cl) present in the reaction mixture.

**Reaction of Tetrafluorobenzene with Adduct (II, X=F).**

n-Butyl lithium in hexane solution (2 ml, 0.005 mole) was added to a stirred solution of bromopentafluorobenzene (1.235 g., 0.005 mole) in dry light petroleum (100 ml) at -60° in an
atmosphere of nitrogen. The mixture was stirred at \(-60^\circ\) for 1 hr. after complete addition then the temperature was allowed to rise to \(-30^\circ\) when a solution of adduct \((\text{II, } X=F)(0.25 \text{ g., 0.00058 mole})\) in dry light petroleum (50 ml) was added drop-wise to the solution of pentafluorophenyl lithium. The temperature of the solution was maintained at \(-30^\circ\) for 0.5 hr. before being allowed to rise to ambient temperature. Examination of the reaction mixture by thin layer chromatography showed only one major component which was shown to be \((\text{II, } X=F)\) by comparison with an authentic sample. A number of minor components were observed in the reaction mixture whose \(R_f\) values were greater than that of the starting material. Comparison with standard samples by gas liquid chromatography indicated that these compounds were polyfluorobiphenylds.

**Pyrolysis of Adduct (II, X=F)**

The adduct \((\text{II, } X=F)\) was placed into two Pyrex tubes in 50 mg. quantities and evacuated (0.3 m.m.) and flushed with dry oxygen-free nitrogen. The tubes were re-evacuated, sealed, and heated for 12 hr. at 330\(^\circ\). The cold tubes were opened and the product dissolved in chloroform. Thin layer chromatography on silica indicated one major product which was isolated by preparative layer chromatography on silica to give a yellow oil (42 mg.) after removal of solvent. The yellow oil was dissolved in benzene (2.5 ml) and the benzene solution was treated with a solution of 2,4,7-trinitrofluoren-
9-one (48 mg.) in benzene (2.5 ml). The yellow solution was evaporated down to a total volume of 3 ml, cooled to 10° in an ice-bath and methanol (5 ml) added. The precipitated 2,4,7-trinitrofluoren-9-one complex (62 mg.) (m.p. 182°), after recrystallisation from methanol-benzene, was redissolved in benzene and eluted from a short neutral alumina column in benzene. Removal of the benzene left a yellow oil (32 mg.) which was purified by sublimation (100°, 0.2 m.m.) and gave a yellow crystalline material (9 mg.), m.p. 95°. M/e 748,1074. C₄₂H₁₁₁₆F₁₂ requires 748.1050.

\[ \lambda_{\text{max}} \text{ (ethanol)} = 255 \text{ (log} \, \text{ 4.13)}, 285 \text{ (3.95)}, 295 \text{ (3.91)}, 325 \text{ (3.61)}, 339 \text{ (3.59)}, 386 \text{ (3.69)}, 407 \text{ (3.97)}, 430 \text{ (4.05)} \text{ n.m.} \]

**Reaction of Tetrachlorobenzene with Benzocyclobutene.**

A solution of tetrachloroanthranilic acid (2.75 g., 0.01 mole) in acetonitrile (40 ml) was added dropwise with stirring to a solution of benzocyclobutene (10.4 g., 0.1 mole) and 3-methylbutyl nitrite (1.35 ml, 0.01 mole) in acetonitrile (40 ml) at 50°. Heating was continued for 0.5 hr. after complete addition of the tetrachloroanthranilic acid. Filtration from a small quantity of octachloroacridone and removal of acetonitrile, 3-methylbutan-1-ol, and excess of benzocyclobutene by distillation, left a viscous yellow oil.

Dissolution of the oil in chloroform and examination by thin layer chromatography on silica showed one major component present in the reaction mixture. A further examination by
thin layer chromatography on silver nitrate-impregnated silica also showed one component and so the product was isolated by preparative layer chromatography on silica which gave 5,6,7,8-tetrachloro-1,4-dihydro-1,2-ethano-1,4-ethenonaphthalene (IV) (30.5%), m.p. 116° (from ethanol). (Found C, 52.90; H, 2.60%; M \[mass spectroscopy\] 318. C\textsubscript{14}H\textsubscript{8}Cl\textsubscript{4} requires C, 52.90; H, 2.55%; M 318.)

\[\begin{align*} &3.1-3.5 \text{ (m, 2H), 3.7-3.9 \text{ (m, 1H), 4.5-4.75 \text{ (m, 1H), 5.8-6.4 \text{ (m, 1H), 6.88-7.4 \text{ (m, 3H).}}}
\end{align*}\]

\[\begin{align*} &\text{\( \nu \) max 3070, 3050, 3030, 2960, 2930, 1575, 1415, 1375, 1360, 1345, 1305, 1285, 1250, 1240, 1230, 1215, 1195, 1180, 1165, 1105, 1080, 1060, 1040, 990, 940, 930, 900, 830, 780, 730, 705, 675 \text{ cm}^{-1}.}
\end{align*}\]

**Preparation of 1,2,3,4-Tetrafluoro-6,7-dimethylnaphthalene.**

A recrystallised sample of 5,6,7,8-tetrafluoro-1,4-dihydro-2,3,9,10-tetramethyl-1,4-ethenonaphthalene (500 mg.) was pyrolysed for 12 hr. in an evacuated Pyrex tube. The residue was extracted into chloroform and thin layer chromatography showed one major product in the pyrolysate. The crude product was purified by elution from neutral alumina in light petroleum which gave 1,2,3,4-tetrafluoro-6,7-dimethylnaphthalene (62%), m.p. 61° (from ethanol - light petroleum) (lit.\textsuperscript{66} m.p. 62.5°).
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