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STUDIES IN ARYNE CHEMISTRY

A Thesis

Submitted to

Loughborough University of Technology

by

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In Partial Fulfilment of the
Requirements for the Degree of

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SUMMARY

The principal methods for the generation of arynes and the types of reactions which they undergo are briefly reviewed.

Tetrachlorobenzynes has been generated from pentachlorophenyl magnesium chloride, pentachlorophenyl lithium, and tetrachloro-anthranilic acid. Reactions of tetrachlorobenzynes with benzene, substituted benzenes, naphthalene, anthracene, furan, tetraphenyl-cyclopentadienone, 1,3 - diphenyl-isobenzofuran, crotonaldehyde and acrolein are reported. Cycloadducts are obtained from these reactions in good yield. Certain reactions of tetrachloro-4-pyridyl lithium are reported.

The reactions of tetrachlorobenzynes and tetrafluorobenzynes with bicyclohepta - (2,2,1) - ene, bicyclohepta - (2,2,1)-dione, styrene, and α -methyl styrene are reported.

The cleavage of simple aliphatic ethers by tetrachlorobenzynes is reported, and the mechanism of the cleavage discussed. Cleavage of aliphatic ethers occurs by attack of the lone pair of electrons on the oxygen onto the arynes, accompanied by abstraction of a β -hydrogen from one of the alkyl groups, by the aryl residue.

All ^1H n.m.r. and i.r. spectral data for novel compounds prepared in the above reactions are reported.

ACKNOWLEDGEMENT

I would like to express my sincere thanks to Dr. H. Heaney for his friendly inspiration, help and enthusiasm throughout the course of this work.

I should also like to thank Miss Frances Jablonska for her tremendous effort and patience in typing this manuscript.

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CONTENTS

	<u>Page</u>
SUMMARY	ii
ACKNOWLEDGEMENT	iii
INTRODUCTION	1
<u>SECTION 1.</u> The Reactions of Highly Halogenated Arynes with Arenes.	
Introduction	10
Discussion	12
¹ H n.m.r. spectra	32
Experimental	33
<u>SECTION 2.</u> The Reactions of Tetrachloro and Tetrafluoro benzynes with Styrene and α - Methyl Styrene.	
Introduction.	56
Discussion	56
Experimental	63
<u>SECTION 3.</u> The Reactions of Tetrachloro and Tetrafluoro benzynes with Bicyclohepta (2,2,1) ene, and Bicyclohepta (2,2,1) diene.	
Introduction.	68
Discussion	69
Experimental	76

SECTION 4. The Reactions of Tetrachlorobenzene with

Aliphatic Ethers.

Introduction. 82

Discussion. 82

Experimental. 87

SECTION 5. The Reactions of Tetrachlorobenzene with

Acrolein and Crotonaldehyde.

Introduction. 91

Discussion. 92

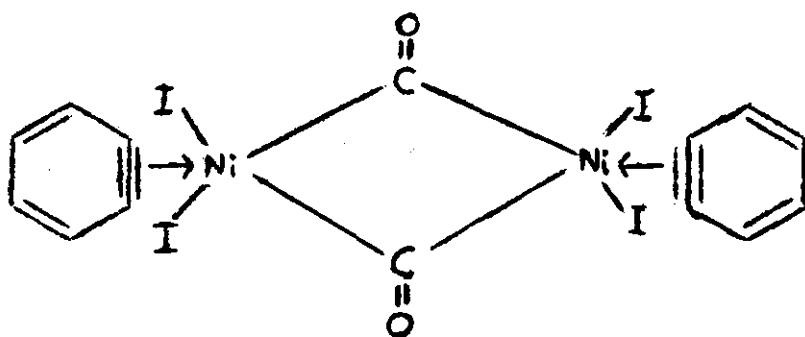
Experimental. 94

REFERENCES 96

INTRODUCTION

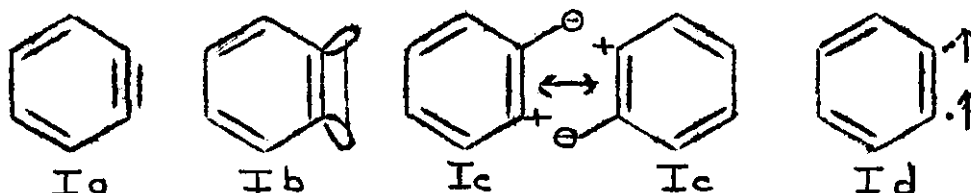
The strong nucleophile-initiated rearrangements of non-activated aryl halides have been known for almost seventy years.¹ It is only in the past fifteen years, however, that these reactions have been interpreted in terms of a benzyne mechanism, together with supporting evidence.^{2,3} Cine substitution reactions have often been regarded as indicative of a reaction involving these intermediates,⁴ particularly if electron withdrawing groups such as $-\text{NO}_2$ are absent. Recently, however, evidence for other mechanisms resulting in cine substitution has arisen.⁵

More recent evidence for the existence of aryne intermediates involves the detection of the appropriate peaks in the mass-spectra of known precursors,⁶ and the preparation of nickel carbonyl complexes of benzyne and tetrafluorobenzyne.⁷



The half-life of benzyne itself has been measured by flash photolysis⁸ of benzenediazonium-2-carboxylate, and time of flight mass spectrometry.⁹

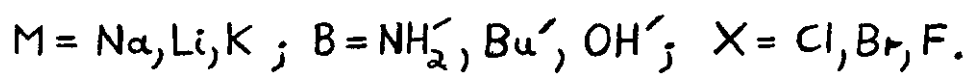
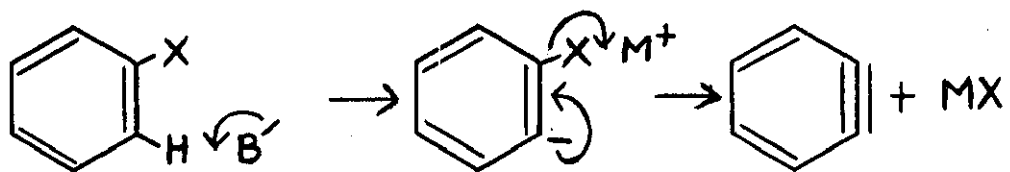
The actual structure of aryne intermediates has not yet been completely elucidated. The properties of the parent intermediate, called benzyne, 'dehydrobenzene' or o-phenylene, have led to a series of representative structures being used, all of which have advantages and disadvantages. The possibility that arynes from differing sources may have different structures cannot be overlooked. Hofmann's recent theoretical studies are of significance in this connection.¹⁰ Benzyne has been formulated in many ways, including those shown below.



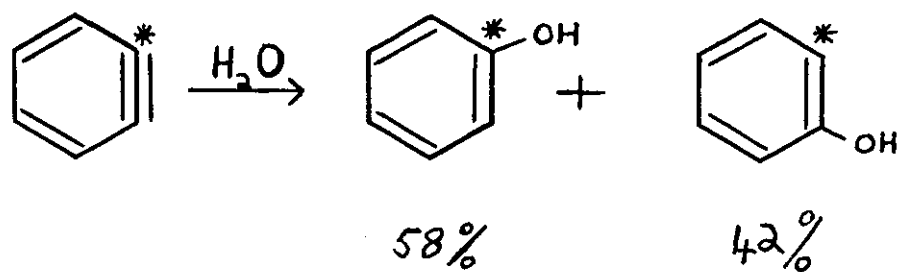
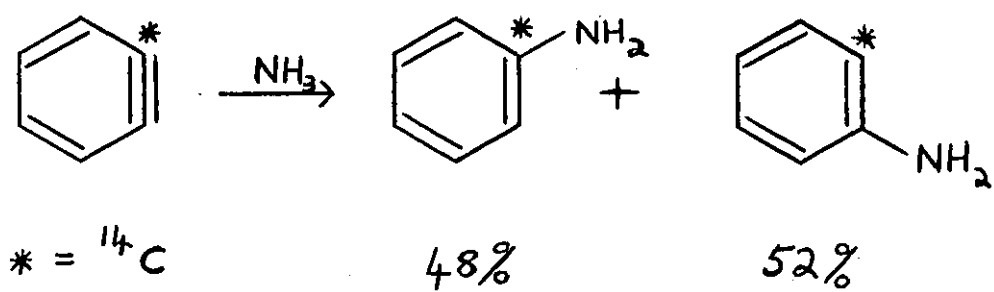
Ia is the commonly used formulation, since it accounts satisfactorily for many of the reactions which arynes undergo as dienophiles. It is generally agreed that the aromatic character of the cyclic system in arynes is undisturbed, and the two electrons of the 'third bond' are at right angles to the pi-cloud (Ib). The possibility of a singlet or a triplet

state diradical benzyne being generated by certain methods cannot be overruled. No evidence for such species has been found.¹¹ It is possible that a singlet species would revert to ground state benzyne, and that a similar process could occur with a triplet species, after intersystem crossing. Arynes will be denoted by the structure Ia throughout this thesis.

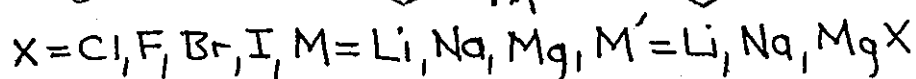
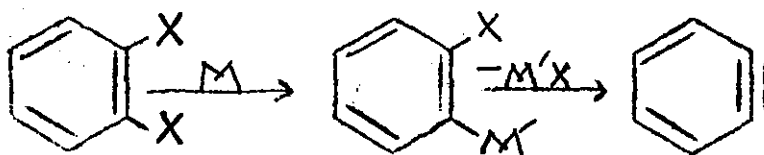
Arynes are generated by abstraction of atoms or groups from adjacent positions in the aromatic nucleus. The abstracted species are small thermodynamically stable molecules. Common examples are metal halides, and gases such as nitrogen and carbon dioxide. Strong nucleophiles such as *n*-butyl lithium and alkali-metal amides and hydroxides, all react with aryl halides to generate arynes, in which the eliminated species is formally hydrogen halide (see scheme 2a).¹² The reactions with alkali-metal amides and hydroxides generally lead to formation of amines and phenols respectively^{13,14} (see scheme 2b). Identical isomer ratios are obtained with different halogens, and it is difficult to rationalise the results except by invoking an aryne mechanism. *o*-Dihalogenoaromatic compounds can be reacted with metals such as magnesium, sodium, and lithium, or with organolithium reagents such as *n*-butyllithium, to give good yields of *o*-haloaryl metallic reagents. The aryne arises by elimination of metal halide from the initially formed *o*-haloaryl metallic compound.



Scheme 2a

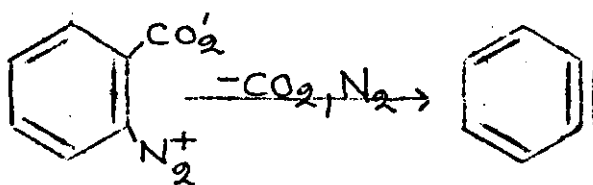


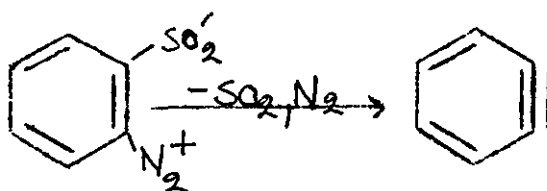
Scheme 2b



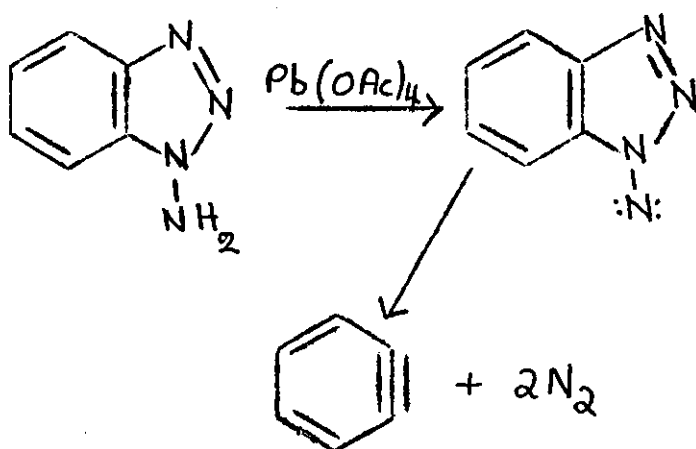
All *o*-haloaryl metallic compounds are labile, and give complex products on decomposition.¹⁵ For a given metal, the order of ease of metal halide elimination is $\text{F} > \text{Cl} = \text{Br}$,¹⁶ and for a given halogen, the order of ease of metal halide elimination is $\text{Na} > \text{Li} > \text{Mg} X$.¹⁷

Low temperature thermolysis of benzenediazonium-2-carboxylate results in the elimination of carbon dioxide and nitrogen, and generation of benzyne.¹⁸ Benzenediazonium-2-carboxylate can be formed and decomposed in situ by aprotic diazotisation of anthranilic acid.¹⁹ A less important, but similar method is the thermolysis of benzenediazonium-2-sulphinate.²⁰





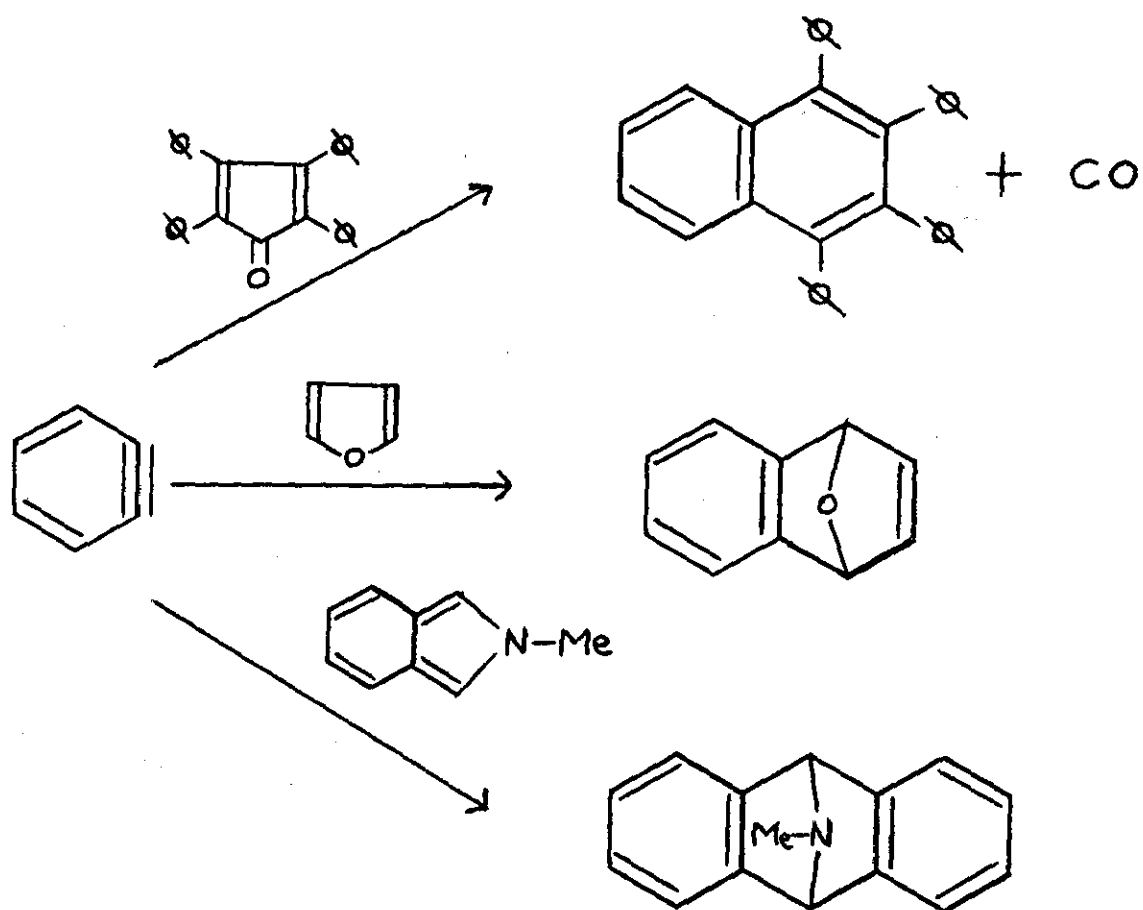
An oxidative method of generating arynes, involves treatment of 1 - aminobenzotriazole with lead tetraacetate. The reaction is thought to proceed via a nitrene intermediate.²¹



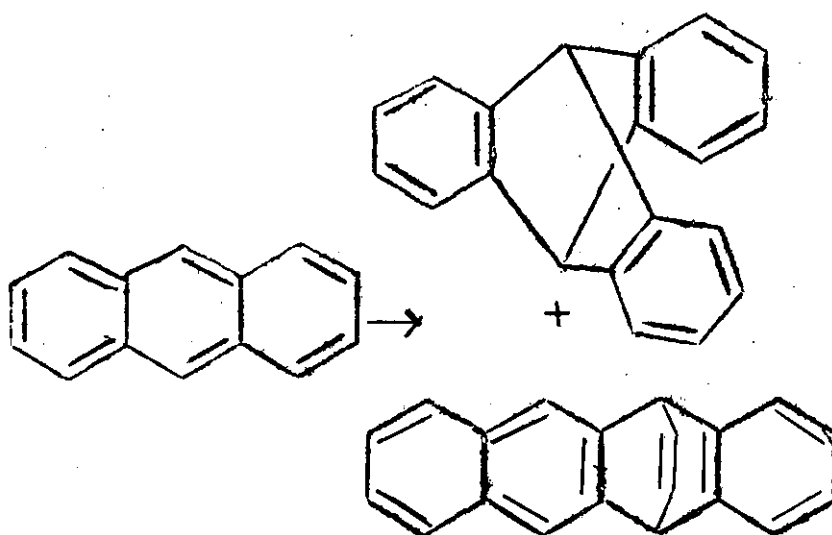
Other less important methods of generating arynes include irradiation of 1, 2, 3, - benzothiadiazole - 1, 1 - dioxide,²² and high temperature pyrolysis of ^hphthalic anhydride.⁶ Arynes generated by the latter method are formed and react in the vapour phase, and some arynes show different properties to arynes generated by other methods. The kinetics of dimerisation of benzyne generated by flash photolysis of phthalic anhydride have recently been reported.²³

In all their reactions, arynes behave as strong electrophiles. Their reactions as dienophiles have been widely reported. With furan,²⁴ tetraphenylcyclopentadienone,²⁵ and N-methylisoindole,²⁵ 1,4 addition compounds have been obtained in good yields (see scheme³).

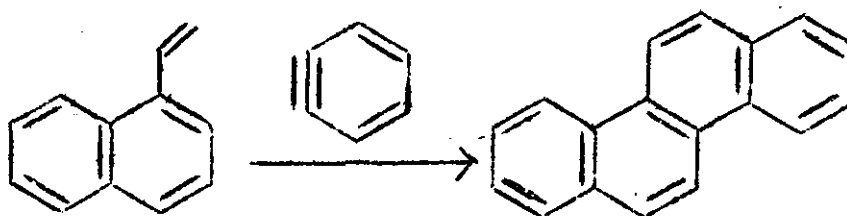
In the reactions of benzyne with anthracene and substituted anthracenes, two Diel's Alder type addition compounds are obtained; the highly stable hydrocarbon triptycene, formed by 9, 10 addition across the anthracene,²⁶ and small amounts of the 1,4 addition product.²⁷



Scheme 3

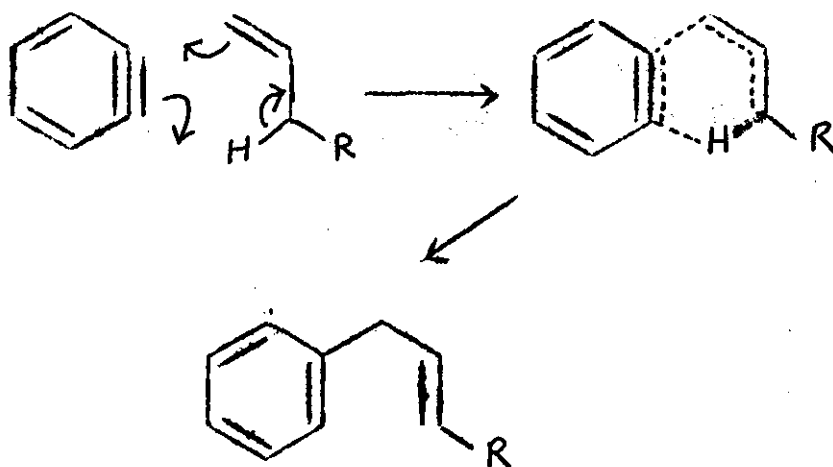


With vinyl naphthalene, benzyne reacts to give chrysene.²⁸



In the absence of trapping agents, benzyne dimerizes to give biphenylene, if generated from 1 - aminobenzotriazole²¹ or benzenediazonium-2-carboxylate.¹⁸ When generated from organolithium compounds or Grignard reagents, in the absence of trapping agents, benzyne reacts with its organometallic precursor or with other organometallic reagents.²⁹ The use of this type of reaction as a method of preparing triphenylene and substituted triphenylenes has been reported.³⁰

With simple olefines having allylic hydrogens, benzyne undergoes a so called insertion reaction,³¹ probably involving a six-centred transition state.



Many other reactions of arynes are known, all of which involve either insertion or addition of the type shown above. 1, 2-Cycloaddition reactions are relatively rare, but have been reported with enamines,³² and with bicyclohepta - (2, 2, 1) - one and bicyclohepta - (2, 2, 1) - diene.³¹

SECTION 1.

The Reactions of Highly Halogenated Arynes with Arenes.

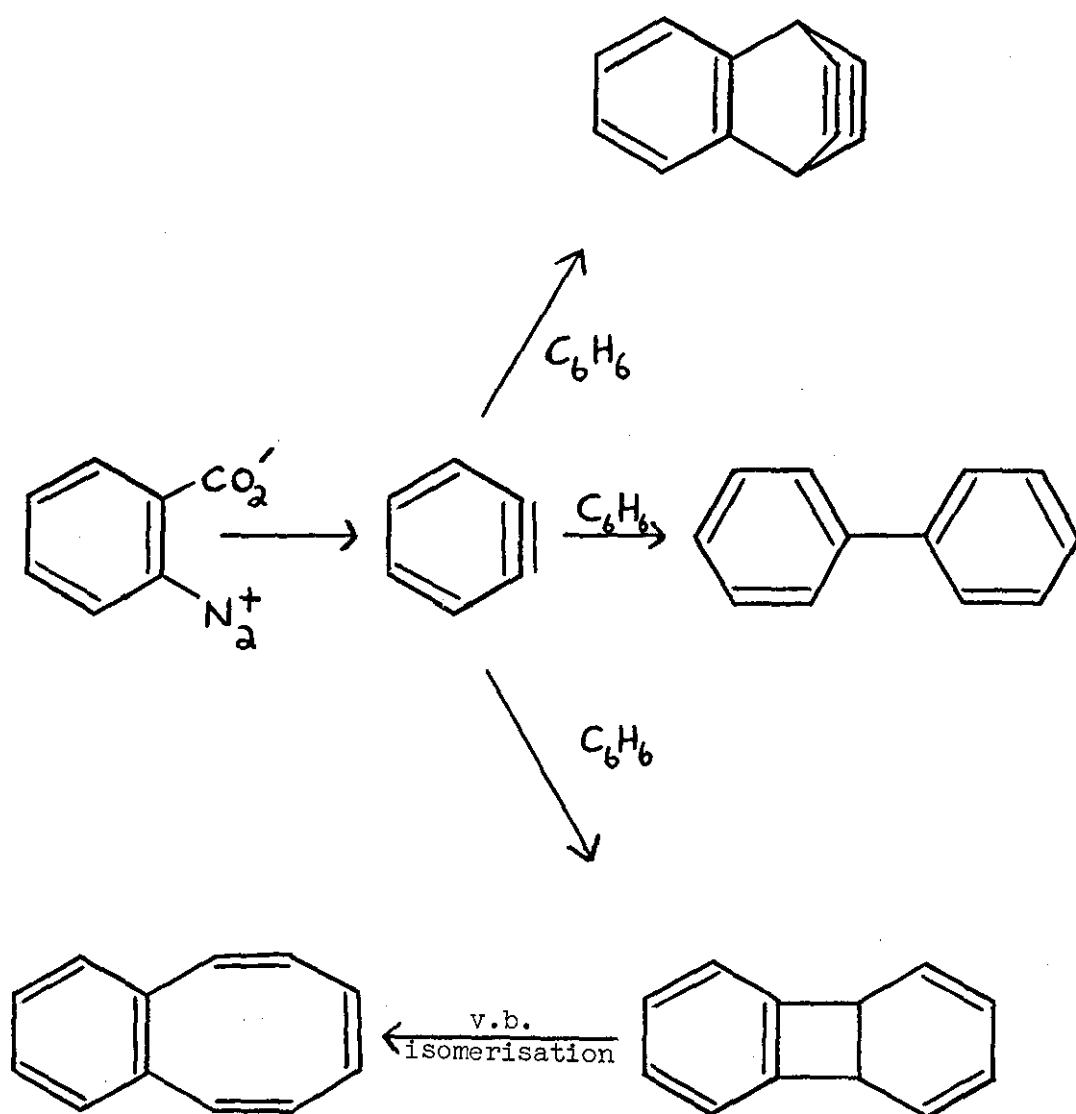
INTRODUCTION

The first reported reaction of an aryne with a simple aromatic compound was by Miller and Stiles,³³ who generated benzyne via benzenediazonium-2-carboxylate, in the presence of benzene, and isolated three products in low yield, namely the 1, 2 and 1, 4 addition products (8% and 2% yields respectively), and the insertion product, biphenyl (6%) (see scheme 1).

We postulated three reasons for expecting high yields of addition products between highly halogenated arynes and aromatic hydro-carbons.

It was known that aromatic hydrocarbons form charge transfer complexes with highly fluorinated aromatic compounds.^{34, 35}

We have similar evidence from ¹H.m.r. spectra which suggests that charge transfer complexes are formed between highly chlorinated aromatic compounds and aromatic hydrocarbons. The aromatic protons in 1,2,4,5 tetrachlorobenzene show up as a singlet at τ 2.76 when the ¹H nuclear magnetic resonance spectrum is recorded in carbon tetrachloride. In hexadeuterobenzene however, the singlet is observed at τ 3.40. The upfield shift of 0.64 p.p.m. is attributed to charge transfer complex formation. The highly electrophilic nature of benzyne intermediates,



Scheme 1

suggested that a charge transfer complex could be formed between a highly halogenated aryne precursor and an aromatic hydrocarbon, leading to enhanced reactivity between the hydrocarbon and the aryne.

The known higher stabilities of pentafluorophenyl³⁶ and pentachlorophenyl³⁷ Grignard reagents and pentafluorophenyl lithium,³⁸ as compared to o-fluorophenyl Grignard reagents and lithiocompounds, suggested a higher activation energy for the formation of tetrafluoro and tetrachlorobenzynes which might result in a considerable increase in reactivity. It follows that pentachlorophenyl lithium would also be expected to be more stable than o-chlorophenyl lithium.

Finally, the inductive effect of the halogens would increase the electrophilic character of the aryne, and so change its reactivity towards aromatic compounds.

We proposed to investigate methods of generating highly halogenated arynes and their reactions with arenes. Vorozhtsov et al.³⁹ reported that 3,4,5,6 - tetrafluorobiphenyl is formed in the reaction of tetrafluorobenzene with benzene, but the spectral data quoted do not fit this compound.

Reactions of tetrafluorobenzene⁴⁰ have been investigated in these laboratories concurrently with the work reported in this thesis, and therefore we have concentrated our activities on

the chemistry of tetrachlorobenzene. It was also proposed to extend this work to include trichloropyridines and tetrabromobenzene.³⁸

DISCUSSION

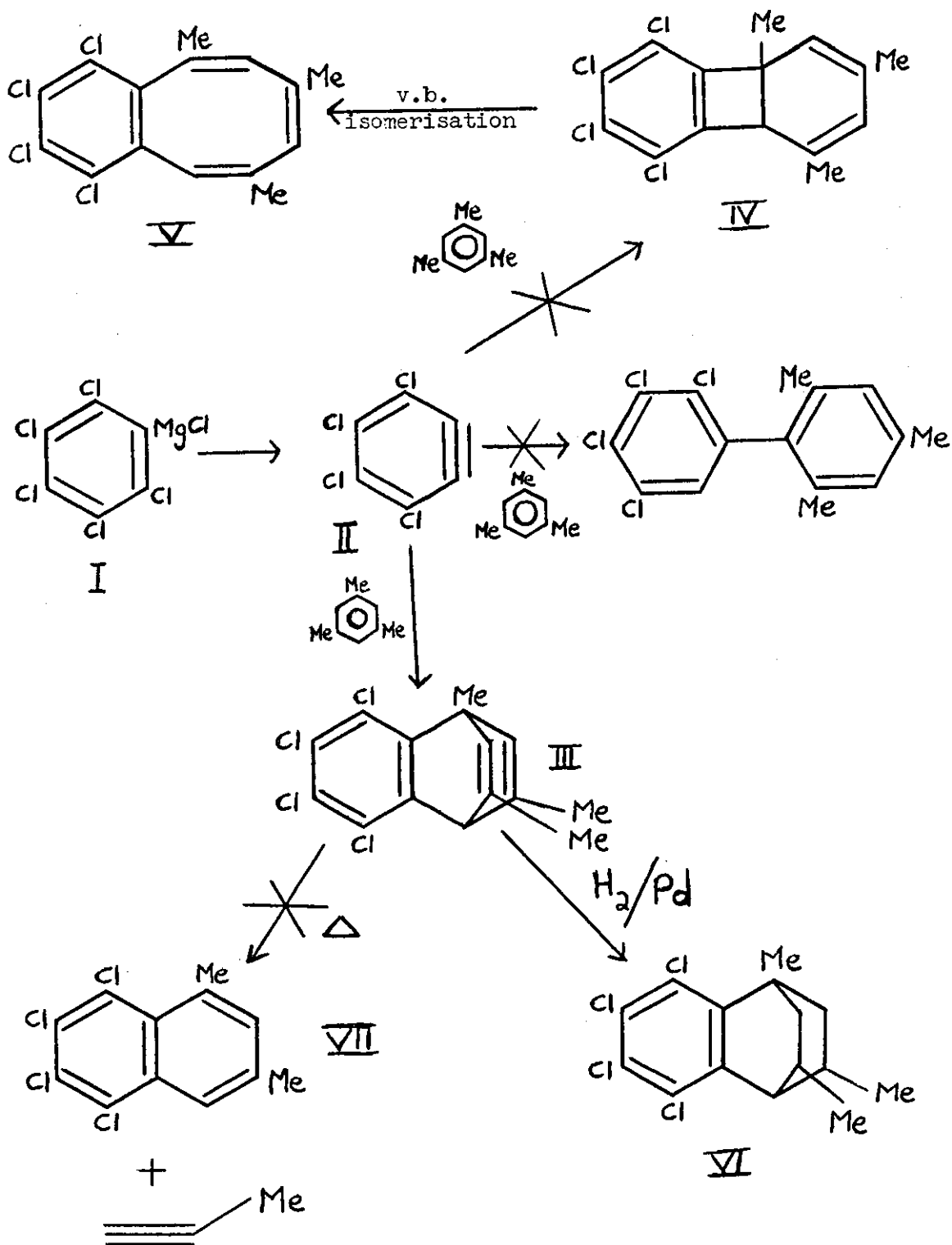
Three easily prepared precursors suggested themselves as being suitable for the preparation of tetrachlorobenzene.

Pentachlorophenyl magnesium chloride had been prepared previously in good yield from hexachlorobenzene and magnesium by entrainment with 1, 2 - dibromoethane in benzene/ether solution.³⁷ Preparation of pentachlorophenyl magnesium chloride by this procedure, followed by carboxylation gave pentachlorobenzoic acid in 55% yield. Generation of tetrachlorobenzene was attempted by replacing the ether in a solution of the Grignard reagent with benzene, and heating the mixture under reflux for twelve hours. After hydrolysis and work up, only pentachlorobenzene and unreacted hexachlorobenzene were obtained. From this result, it was obvious that pentachlorophenyl magnesium chloride was more stable than either pentafluorophenyl magnesium chloride or bromide, both of which decomposed in refluxing benzene to give the aryne.⁴⁰

Consequently, in a further reaction, pentachlorophenyl magnesium chloride was prepared in ether/mesitylene solution, the ether replaced by mesitylene, and the mixture heated under reflux

at this considerably higher temperature. After hydrolysis and work up, the mixture was fractionally distilled to give unreacted hexachlorobenzene and an adduct. This was shown to be the 1, 4 addition compound of tetrachlorobenzene and mesitylene namely 1, 4 - dihydro - 5, 6, 7, 8, - tetrachloro - 1, 4 - othenonaphthalene, (III). The structure was assigned on the basis of elemental analysis, ^1H n.m.r., and infrared and ultraviolet spectra. A benzocyclooctatriene structure, (V) which could arise by valence bond isomerisation of a 1, 2 adduct (see scheme 2) was excluded, because the compound absorbed two moles of hydrogen when reduced in the presence of a palladium/carbon catalyst. The 1, 2 adduct, (IV) is excluded on the basis of the u.v. spectrum showing no absorption above 220 m μ , while the possibility of the compound having a biphenyl structure is excluded by all the spectral data and the reduction.

The reduction product, (VI) was a crystalline compound which melted over a temperature range. Gas chromatographic analysis showed the presence of three components and it was assumed therefore to be a mixture of the three possible isomers, namely the ones with the non-bridgehead methyl groups both endo, both exo, and one exo and one endo. High temperature pyrolysis of the adduct in an evacuated sealed tube resulted in carbonation. Unlike the analogous tetrafluorinated adduct,⁴⁰ the dimethyl naphthalene, (VII) obtained by loss of methyl acetylene from the adduct, was not observed. It is suggested that loss of acetylene



Scheme 2

from these adducts only takes place in the vapour state, and the chlorinated mesitylene adduct, (III) carbonised before vapourisation could occur.

When refluxed in p-xylene, pentachlorophenyl magnesium chloride decomposed, and separation of the products by column chromatography, gave hexachlorobenzene, and the expected 1, 4 adduct of tetrachlorobenzene and p-xylene, (VIII). In theory two isomeric adducts could be formed from this reaction, but in practice, only the adduct which contained no bridgehead methyl groups, was obtained. This result is analagous to that obtained in the reaction between tetrafluorobenzene and p-xylene.⁴⁰ The reasons for this are not clear, despite the fact that a comprehensive study of the reactions of tetrafluorobenzene and alkyl substituted benzenes has been carried out.⁴¹

These reactions showed that tetrachlorobenzene could be generated in good yield from pentachlorophenyl magnesium chloride, which was considerably more stable than pentafluorophenyl magnesium chloride. However, this method of generating tetrachlorobenzene left much to be desired since preparation of the Grignard reagent took a long time (at least 48 hrs.), and the high stability of the Grignard reagent meant that reactions in the presence of low boiling compounds would be extremely difficult to achieve.

The preparation of pentachlorophenyl lithium from pentachlorobenzene and n-butyl lithium offered a convenient method of obtaining a tetrachlorobenzene precursor. At about the time that this work was initiated, the metallation of pentachlorobenzene in tetrahydrofuran was reported.⁴² We independently confirmed this result both by carboxylation and bromination of the pentachlorophenyl lithium. Bromination afforded pentachlorobromobenzene in 80% yield.

Since tetrahydrofuran has been reported to cleave in the presence of organo-lithium reagents at elevated temperatures,⁴³ this solvent was considered to be unsatisfactory for aryl reactions in which the organolithium compound could well require heating before decomposition occurred. Consequently, the metallation of pentachlorobenzene with n-butyl lithium was attempted in diethyl ether solution, but carboxylation and bromination of the reaction mixtures obtained gave poor yields of pentachlorobenzoic acid (5%) and pentachlorobromobenzene (12%), and other products were obtained but they were not investigated further.

Halogen-metal interconversion using pentachlorobromobenzene and n-butyl lithium in diethyl ether solution was then achieved at -75°C. After carboxylation of the organolithium reagent, pentachlorobenzoic acid was obtained in high yield.

Benzene was added to a solution of pentachlorophenyl lithium in ether, and the mixture was allowed to warm to room temperature. Hydrolysis of the mixture after 2 hrs. at room temperature, followed by vacuum distillation of the product gave two compounds, pentachlorobenzene and a new crystalline solid. Elemental analysis, ^1H n.m.r., u.v., and i.r. spectra showed the compound to be the 1, 4 adduct of tetrachlorobenzynes and benzene, (X) formed in 37% yield. The pentachlorobenzene was assumed to have arisen from hydrolysis of undecomposed organolithium reagent. The yield of (X) was increased to 62.5% when after adding benzene, ether was removed by distillation until a reflux temperature of 50°C was reached, and then maintained for 2hrs. before hydrolysis. This indicated that pentachlorophenyl lithium is, as expected, more stable than pentafluorophenyl lithium,³⁸ since elimination of metal fluorides from orthohaloorganometallic compounds is easier than elimination of metal chlorides.⁴⁴ Hydrogenation of the adduct (X) using palladium/carbon, yielded the corresponding tetrahydro-compound, (XI) as in the reduction of the mesitylene and p-xylene adducts, (III) and (VIII). Unlike the reduced mesitylene and p-xylene adducts, (XI) was not an isomeric mixture and melted sharply. Pyrolysis of (X) in a sealed, evacuated tube at 375°C ,

yielded 1, 2, 3, 4 - tetrachloronaphthalene, (XII) through loss of acetylene. Unlike the pyrolysis of the mesitylene adduct, (III) only partial carbonisation occurred, presumably because of the higher volatility of the benzene adduct.

During the course of this work, Rausch et al.⁴⁵ reported that good yields of pentachlorophenyl lithium could be obtained by metallation of hexachlorobenzene with *n*-butyl lithium in both diethyl ether and tetrahydrofuran. This result was confirmed, and it was decided to use hexachlorobenzene as the precursor for pentachlorophenyl lithium in all subsequent reactions, since it was cheaper than pentachlorobenzene, and unlike pentachlorobromobenzene, was immediately available.

Preparation and decomposition of pentachlorophenyl lithium from this precursor, in the presence of *p*-xylene, mesitylene, durene, hexamethylbenzene, anthracene, naphthalene and anisole yielded 1, 4 addition products in good yield (see scheme 3).

In the reactions with *p*-xylene and durene, only the non-bridge head substituted adduct was formed in each case. The absence of the bridge head substituted adducts might suggest that the transition state for the formation of such adducts involved serious steric strain. However, an adduct, (XV) was obtained in reasonable yield from hexamethylbenzene.

The overall yields of adducts varied from compound to compound, but in general, they increased with increasing electron density in the aromatic ring. This was shown more clearly in a reaction in which tetrachlorobenzene competed for equimolar amounts of benzene and p-xylene. The ratio of benzene adduct to p-xylene adduct produced in the reaction was 1:24. This compares with the competition of tetrafluorobenzene for benzene and p-xylene which resulted in a ratio of benzene to p-xylene adduct of 1:6.7. This suggests that tetrachlorobenzene differs in electrophilicity from tetrafluorobenzene. The more electrophilic benzyne is clearly less selective.

The reaction of tetrachlorobenzene with anthracene was of interest in view of the high reactivity towards 1, 4 addition. Addition at the 1, 4 positions of anthracene as well as the more reactive 9, 10 position was predicted. This reasoning was confirmed, and the 1, 4 adduct (XXII) was isolated in 1.7% yield from the mother liquors obtained after recrystallising the 9, 10 adduct, (XXI) namely 1, 2, 3, 4 - tetrachlorotriptycene (54%). Similar results have been reported by Klandermann using benzyne generated from benzenediazonium-2-carboxylate with a variety of substituted anthracenes.²⁷

The reaction of tetrachlorobenzene with anisole gave two adducts, (XVI), 62%, and in very low yield, (XVII), 0.8%. The latter resulted from cleavage of the non-bridge head substituted adduct, which has

an enol - ether structure. The two adducts could be easily separated, by either column chromatography on alumina or by means of the Girard reagent 'P'.

An attempt was made to trap tetrachlorobenzynes, generated by this method, with furan. However, the only product isolated from the final mixture was pentachlorobenzene and an unidentified mixture of compounds containing aliphatic residues. This result was not surprising, since it is well known that furan is metallated at temperatures below that at which tetrachlorobenzynes would have been formed.⁴⁶ Pentafluorophenyl lithium however, is reported to give a 1, 4 adduct of tetrafluorobenzynes with furan,⁴⁷ but the lithio compound decomposes at about 0°C, compared with pentachlorophenyl lithium which does not decompose significantly below 20°C.

Tetrachlorobenzynes were successfully trapped with 1, 3 - diphenylisobenzofuran to give the expected adduct, (XXIII) in 66% yield.

This method of generating tetrachlorobenzynes was on the whole satisfactory. The only serious limitation was that compounds containing groups reactive towards the organolithium precursor could not be studied.

The mechanism of the reaction, leading to formation of these 1, 4 adducts, is at present uncertain, although some relevant points can be made. No positive evidence has been forthcoming to support

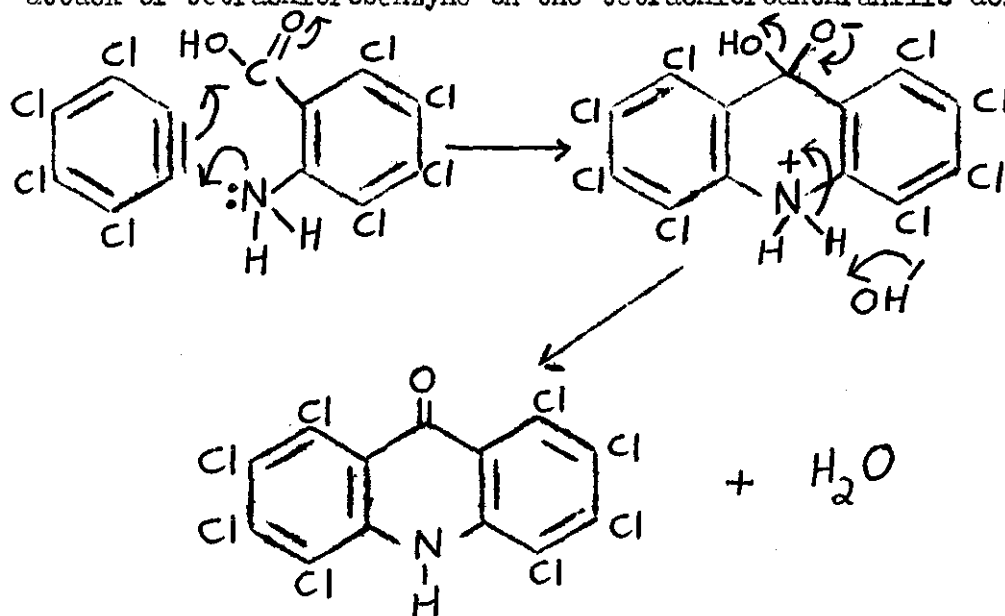
the idea that arynes exist as diradicals, despite the fact that a number of their precursors have been investigated by electron paramagnetic resonance techniques.¹¹ The formation of 1, 4 adducts by an ionic mechanism could occur by a concerted or by a stepwise mechanism by the Woodward - Hoffmann rules.⁴⁸ In view of the fact that no 1, 2 adducts or hydrogen abstraction products were isolated in the above reactions of tetrachlorobenzynes with aromatic hydrocarbons, a concerted mechanism would seem to be more likely.

The 1, 4 adducts of durene, naphthalene, and anisole were all reduced to the corresponding fully saturated compounds by hydrogen in the presence of palladium/carbon catalyst. The hexamethylbenzene adduct could not be reduced even in the presence of a platinum oxide catalyst. This is surprising, since the corresponding tetrafluorobenzynes/hexamethylbenzene 1,4 adduct was reduced easily in the presence of palladium on carbon.

While this work was being undertaken, the diazotisation of tetrachloro anthranilic acid in acetic or hydrochloric acids with sodium nitrite was reported.⁴⁹ The disadvantage of using an aqueous or other protogenic medium for diazotising anthranilic acids to give arynes, is that the aryne will preferentially react with the highly nucleophilic components present in the solution. For example, Howo,⁴⁹ obtained 2, 3, 4, 5 - tetrachlorophenol, pentachlorobenzene, and 2, 3, 4, 5 - tetrachlorophenyl acetate as major

products. It was suggested that these arose by addition of water, hydrochloric acid, and acetic acid respectively, to the tetrachlorobenzene. A more promising method for generating tetrachlorobenzene from tetrachloroanthranilic acid was aprotic diazotisation with an alkyl nitrite. This method has been reported to give good yields of benzene from anthranilic acid.¹⁹

Accordingly, a solution of tetrachloroanthranilic acid in ether was added to excess iso-amyl nitrite in a large volume of benzene, at 45°C. The 1, 4 addition product of tetrachlorobenzene and benzene, (X) was isolated in 55% yield, together with octachloroacridone in 7% yield. This latter product probably arises from attack of tetrachlorobenzene on the tetrachloroanthranilic acid.

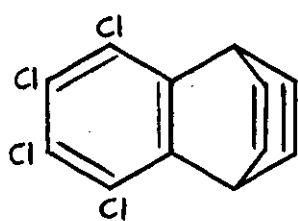


In similar reactions with p-xylene and anisole, identical 1, 4 adducts to those obtained from the pentachlorophenyllithium precursor were produced in comparable yields.

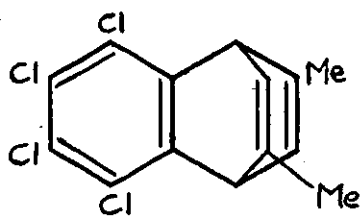
A competition reaction between tetrachlorobenzyn, generated from the anthranilic acid, and p-xylene and benzene, gave a ratio of benzene to p-xylene adduct of 1:19.5, compared to the ratio of 1:24 obtained when the aryne was generated from the lithio-compound. The difference between these ratios is probably accounted for by slight differences in the reaction conditions. Since the relative rate data are of the same order of magnitude, it was concluded that tetrachlorobenzyn generated from tetrachloroanthranilic acid is identical in properties to that generated from the lithio-compound.

1, 4 Addition products of tetrachlorobenzyn with furan, (XXIV) and tetraphenylcyclopentadienone, (XXV) were obtained in good yield, when tetrachloroanthranilic acid was diazotised under identical conditions to those outlined above, in the presence of furan and tetraphenylcyclopentadienone respectively. These two compounds have been widely used as aryne trapping agents (see introduction).

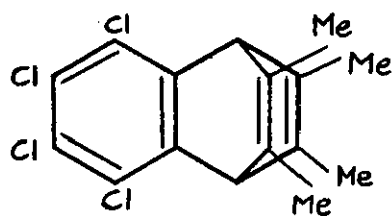
The above results demonstrate that tetrachlorobenzyn can be generated in good yield by aprotic diazotisation of tetrachloroanthranilic acid. This method of producing the aryne was simpler to achieve practically, than either of the two organometallic routes previously investigated.



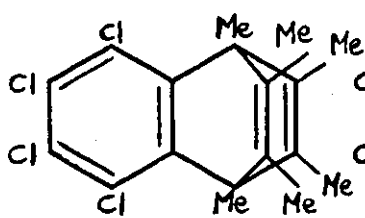
X



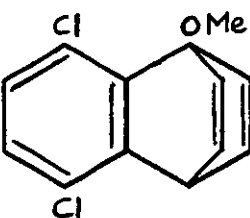
VIII



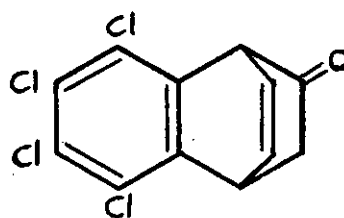
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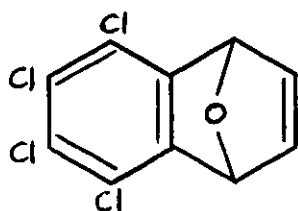
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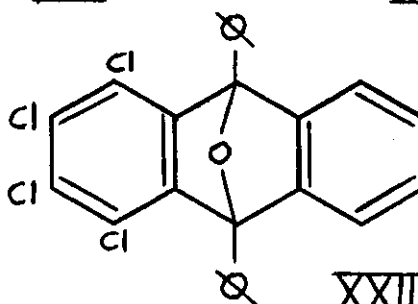
XVI



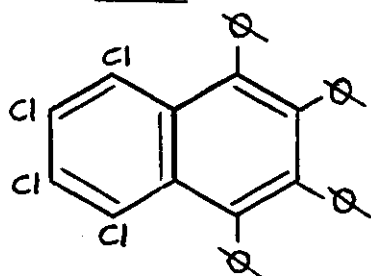
XVII



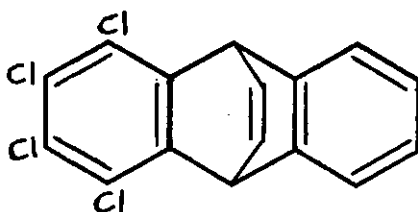
XXIV



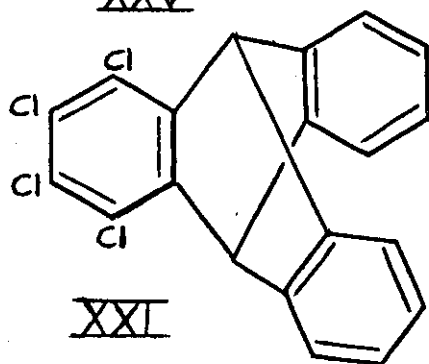
XXIII



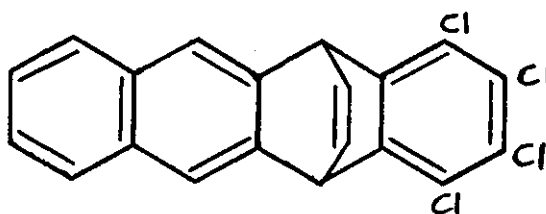
XXV



XIX



XXI

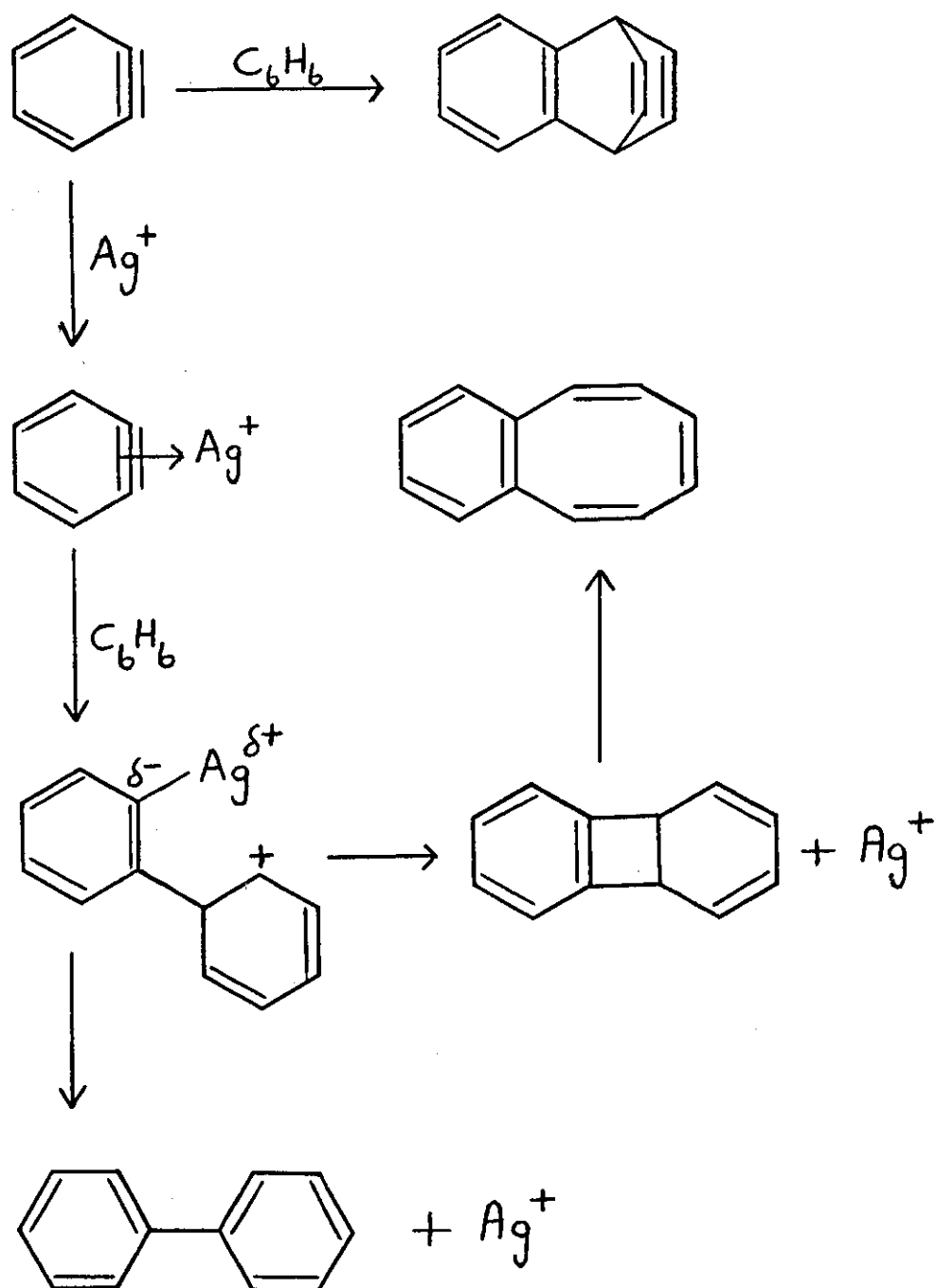


XXII

After these results had been obtained, Friedman⁵⁰ reported that the widely quoted work of Miller and Stiles,³³ was somewhat misleading, since they had silver ion contaminant inadvertently present in their starting material. Friedman postulated the initial formation of a silver ion/benzynes complex which he states would be more electrophilic than the benzyne itself. This complex can break down to form biphenyl or the 1, 2 adduct, which itself valence bond isomerizes to benzocyclooctatetraene (see scheme 4). In the absence of silver ion, Friedman obtained the 1, 4 adduct as major product.

Since neither we, nor Brower,⁴¹ had obtained evidence of tetrachlorobenzynes and tetrafluorobenzynes undergoing 1, 2 addition with arenes, it was decided to investigate the effect of silver ion on the reactions of tetrachloro and tetrafluorobenzynes with arenes.

Pentafluorophenyl lithium was prepared in benzene solutions containing traces of silver oxide, bromide, and nitrate. After decomposition to the aryne, the products were analysed by G.L.C., and found to contain only the 1, 4 adduct of tetrafluorobenzynes and benzene. The mixtures were compared with G.L.C. standards of the 1, 4 adduct, the benzocyclooctatetraene, and 2, 3, 4, 5 - tetrafluorobiphenyl, kindly provided by J.P.N. Brower.



Scheme 4

Pentachlorophenyl lithium was decomposed under similar conditions to those outlined above. G.L.C. examination of the products showed the presence of the 1, 4 tetrachlorobenzene/benzene adduct, (X) only. When tetrachlorobenzene was prepared from tetrachloroanthranilic acid in the presence of benzene containing traces of silver oxide, bromide and nitrate, the only product found was again the 1, 4 adduct.

On the basis of these results, we suggest that tetrahalogenobenzenes do not form the necessary silver complexes for 1, 2 additions to occur. This can be explained by the fact that benzene itself is more electron rich than tetrahalogenobenzenes, and can therefore more readily donate electrons to the silver ion to form a complex.

No reports of the preparation of either pentabromophenyl lithium or pentabromophenyl magnesium bromide have appeared in the literature. We decided to investigate the possibility of preparing pentabromophenyl lithium from the readily available hexabromobenzene, in order to obtain a tetrabromobenzene precursor. The reactions of tetrabromobenzene in solution are of interest in view of Cava's results on the pyrolysis of tetrabromophthalic anhydride.⁵¹

He obtained only hexabromobenzene as product, whereas tetrachlorophthalic anhydride gives octachlorobiphenylene on pyrolysis.^{51, 52} Since aryl bromides are known to react more readily with both magnesium and alkyl lithium compounds, no difficulty was envisaged.

Accordingly, hexabromobenzene was treated with n-butyl lithium under similar conditions to those used in metallating hexachlorobenzene. Carboxylation of the mixture followed by hydrolysis, yielded a negligible amount of acidic material, the hexabromobenzene being recovered almost quantitatively. In a repeat reaction, a longer time was allowed for the halogen-metal interconversion, but no reaction occurred.

Since n-butyl lithium is reported to exist as aggregated entities in most solvents,⁵³ we decided to attempt the metallation using two other techniques, namely the use of methyl lithium and of N,N,N',N' - tetramethyl ethylene diamine.⁵⁴

Since methyl lithium is a smaller species than n-butyl lithium, we thought it might approach near enough to the aromatic nucleus for reaction to occur. Two metallations were attempted, both followed by carboxylation and hydrolysis. Hexabromobenzene was recovered unchanged from both reactions.

With regard to N,N,N',N' - tetramethyl ethylene diamine, it has been reported⁵⁴ that it forms a five membered ring chelate

with *n*-butyl lithium, that is very soluble in paraffinic solvents. This chelated species was found to be a more reactive metallating agent than the normal aggregated species. For example, benzene was completely metallated at 30°C, whereas *n*-butyl lithium in the aggregated 'normal' state would not react with benzene even at elevated temperatures.

Hexabromobenzene was treated with a solution of this chelated *n*-butyl lithium, and the mixture carboxylated and hydrolysed. A complete recovery of hexabromobenzene was again achieved.

Further reactions were not attempted, and it is felt that the diazotisation of tetrabromoanthranilic acid⁵⁵ should be investigated.

The possibility that pentachloropyridine could, like hexachlorobenzene, be metallated to produce a trichloropyridyne precursor was of considerable interest.

Accordingly, pentachloropyridine was treated with *n*-butyl lithium in ethereal solution at 40°C, and the mixture carboxylated. An acid which analysed for a tetrachloropyridine carboxylic acid, was isolated in 37% yield, and had the same melting point as that reported for tetrachloroisonicotinic acid.⁵⁶

In a similar reaction, the lithio compound was hydrolysed with water, and the crystalline product obtained after work up

consisted mainly of 2, 3, 5, 6 - tetrachloropyridine, plus a little of the 3, 4, 5, 6, and 2, 4, 5, 6 - tetrachloropyridines.⁵⁷ These could not be separated by G.L.C., but ^1H n.m.r. showed that three aromatic singlets were present, one being very intense (τ 2.90). Recrystallisation of the mixture from alcohol gave pure 2, 3, 5, 6 - tetrachloropyridine in 80% yield.

It was decided to restrict our investigations to an examination of 4-pyridyl lithium only, and not to attempt generation of a 2, 3 - pyridyne from the 2-lithio compound. The reason for this was that other work in these laboratories⁵⁸ had shown that highly halogenated arynes with two halogens ortho to the 'triple bond' were more reactive as dienophiles than highly halogenated arynes with only one halogen 'ortho' to the 'triple bond.' The 2, 3 - pyridyne would have only one ortho halogen.

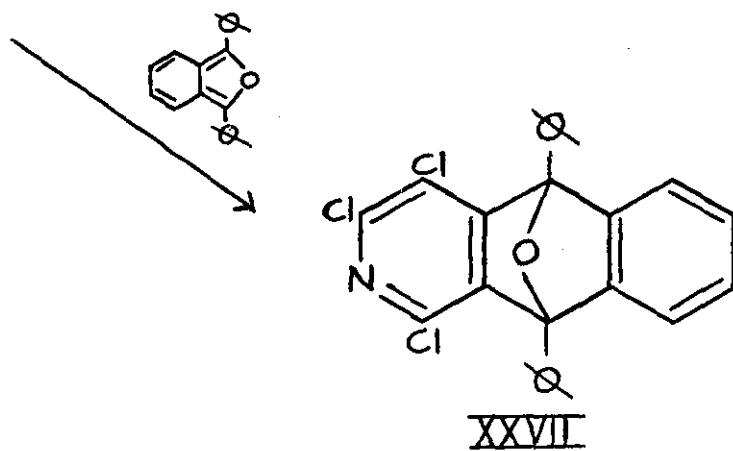
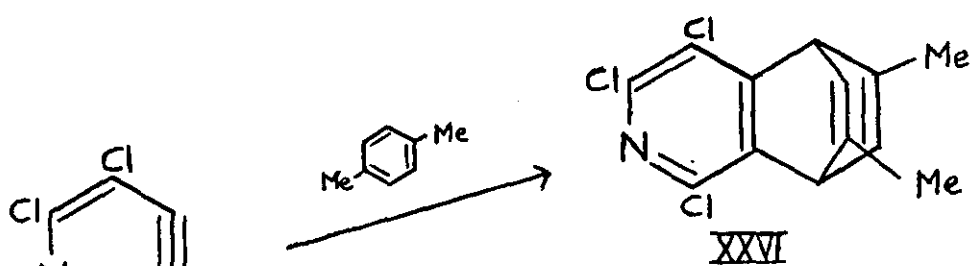
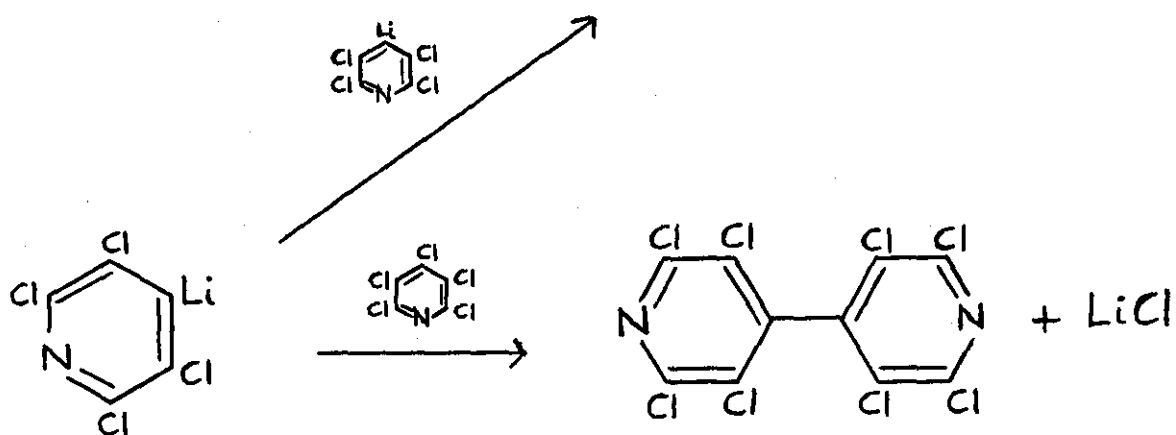
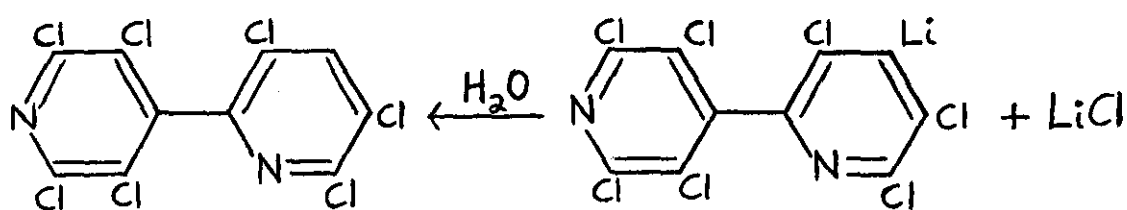
An attempt was first made to trap 2, 5, 6 - trichloro-3, 4 - pyridyne by adding furan to a cold solution (-40°C) of the 4-lithio compound in ether, and allowing the solution to come to room temperature. After hydrolysis and work up, the product was found to consist of hepta and octachlorobipyridyls, as indicated by elemental analysis and ^1H n.m.r. (singlet at τ 2.83 of low intensity). It is suggested that these polychloro-bipyridyls arise via nucleophilic attack by the 4 - lithio compound

on either unreacted pentachloropyridine (leading to octachlorobipyridyls) or on another molecule of the lithio compound, leading after hydrolysis, to heptachlorobipyridyls. An alternative route to the heptachlorobipyridyl could have involved addition of the 4 - lithio compound to the 3, 4 - pyridyne, but this is unlikely, since furan is an excellent aryne trapping agent, and no furan/pyridyne adduct was obtained. In a repeat reaction with furan, the mixture was refluxed for three hours, immediately after addition of the furan. After work up, the mixture was separated by column chromatography into a colourless oil, 2, 3, 5, 6 - tetrachloropyridine, and a little of the hepta and octachlorobipyridyls. The colourless oil was found to be similar to that obtained when pentachlorophenyl lithium was heated with furan. This, coupled with the fact that much tetrachloropyridine was obtained, suggested that the tetrachloropyridyl lithium had cleaved the furan.

In an attempt to prevent bipyridyl formation, it was decided to raise the temperature of the lithio compound quickly, in the presence of a possible aryne co-reactant. A cold solution of the lithio-compound was dripped slowly into refluxing p-xylene. After hydrolysis and removal of solvents, the brown oil was chromatographed on alumina to give a little pentachloropyridine,

some hepta and octachlorobipyridyls, and a colourless oil, which defied all attempted crystallisations. Finally, the oil was rechromatographed once more, and found to be pure by analytical G.L.C. ^1H n.m.r., IR. and elemental analysis proved it to be a 1, 4 adduct of the 3, 4 - pyridyne and p-xylene, (XXVI) in 8% yield.

In an attempt to obtain a higher yield of a pyridyne adduct, 1, 3 - diphenyl isobenzofuran was added to a solution of the 4 - lithio compound in ether, the ether was replaced by 80/100 petrol, and the mixture was refluxed at 80°C for 4 hrs. Column chromatography of the initial crystalline product gave pentachloropyridine, the 1, 4 adduct of the 3, 4 pyridyne and 1, 3 - diphenylisobenzofuran, (XXVII), in 10% yield, and o-dibenzoyl benzene. The latter product arises from oxidation of unreacted 1, 3 - diphenylisobenzofuran. Cook and Wakefield have since confirmed our results on the metallation of pentachloropyridine with n-butyl lithium in diethyl ether.⁵⁹ They have also reported the production of 1, 4 adducts of 2, 5, 6 - trichloro- 3, 4 - pyridyne with mesitylene, benzene and durone,⁶⁰ and have confirmed our results with furan.⁶¹ Musgrave and his co-workers have been unable to trap 2, 5, 6 - trifluoro - 3, 4 - pyridyne.⁶² In a competition reaction between benzene and p-diisopropyl benzene, for the 3, 4 - pyridyne, Cook and Wakefield obtained



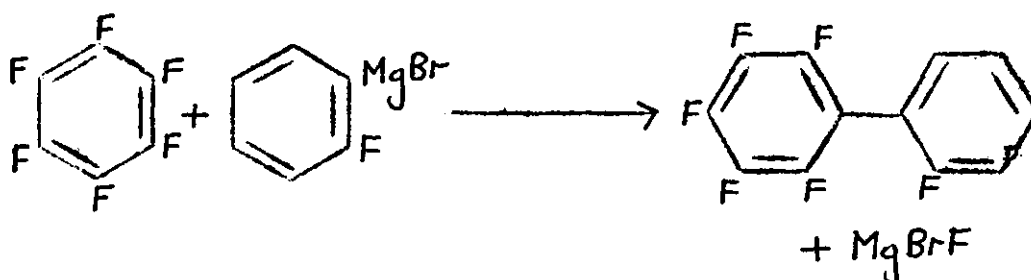
a ratio of benzene to p-diisopropyl benzene adducts of 1:23.⁶¹ This is very similar to the result obtained when tetrachlorobenzene was allowed to compete for benzene and p-xylene.

In the light of these results, we suggest that 2, 5, 6 - trichloro - 3, 4 - pyridine resembles tetrachlorobenzene in showing enhanced electrophilicity when compared with benzene. However, 2, 3, 5, 6 - tetrachloro - 4 - pyridyl lithium differs from pentachlorophenyl lithium in showing a marked tendency to react with itself or its precursor, pentachloropyridine, rather than eliminate lithium halide to give the aryne. As a result of this, solutions of 2, 3, 5, 6 - tetrachloro - 4 - pyridyl lithium give low yields of the pyridine adducts.

The suggestion that charge transfer complex formation is partly responsible for the high yields of 1, 4 addition compounds produced in reactions between highly halogenated arynes and arenes suggested that similar complexes might be formed between a

benzynes precursor and a highly halogenated aromatic reactant. However, adduct formation in these cases would require attack on an electrophile (benzyne) by an electron deficient pi-system. This would not be favourable. We have, however, examined some reactions between benzyne and highly fluorinated benzenes.

Benzynes were generated from orthofluorophenyl magnesium bromide, in the presence of hexafluorobenzene. G.L.C. analysis of the product showed it to contain unreacted hexafluorobenzene and a compound which was shown to be 2, 2', 3, 4, 5, 6 - hexafluorobiphenyl, (XXVIII), isolated in 13% yield. This latter product undoubtedly arose from attack of Grignard reagent on hexafluorobenzene.



When benzyne was generated from 1 - amino - benzotriazole²¹ in the presence of hexafluorobenzene, only biphenylene was produced and isolated in 80% yield. In a final reaction, benzyne was generated from anthranilic acid by aprotic diazotisation¹⁹ in the presence of 1, 2, 4, 5 - tetrafluorobenzene. No Diels Alder adducts were isolated from the reaction mixture.

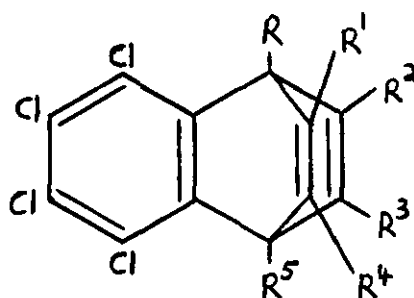
¹H N.M.R. Spectra

The ¹H n.m.r. data for all the 1, 4 adducts discussed are presented in tables 1 and 2.

From these tables, two important structural types (XXIX) and (XXX) may be identified. The structure (XXIX) occurs in the benzene adduct, (X), the naphthalene adduct, (XIX), and the anthracene adduct, (XXI). The structure (XXX), occurs in the anisole adduct, (XVI). The protons H_A and H_A1 in (XXIX) give a triplet in the 60 M/c/sec spectra (centre line broadened and of approximately equal height to that of the outer lines). Close examination of the spectra revealed two additional lines of low intensity at about 7.5 c/sec. on either side of the triplet. Calculation of the spectrum⁹⁶ gave a theoretical spectrum for H_A and H_A1 as part of an AA¹ XX¹ system comparable with the observed spectrum (Spectrum 1). It was assumed that J_{XX}1 = 0, and the values J_{AA}1 = 6.86, J_{AX}1 = 1.33, and J_{AX} = 5.74 c/sec. were obtained (J_{AX} and J_{AX}1 have the same relative signs).

The protons H_A and H_B in (XXX) gave rise to the anticipated eight line multiplets for the AB protons of ABX spectra. The value of J_{AB} (= 7.04 c/sec) was determined directly from the spectrum, and the values of the calculated⁹⁷ coupling constants were J_{AX} = 1.73 c/sec. and J_{BX} = 6.07 c/sec. The calculated spectrum is again comparable with the observed spectrum (Spectrum 2).

Table 1

Benzene and Substituted Benzene Adducts

Chemical Shifts

Coupling Constants

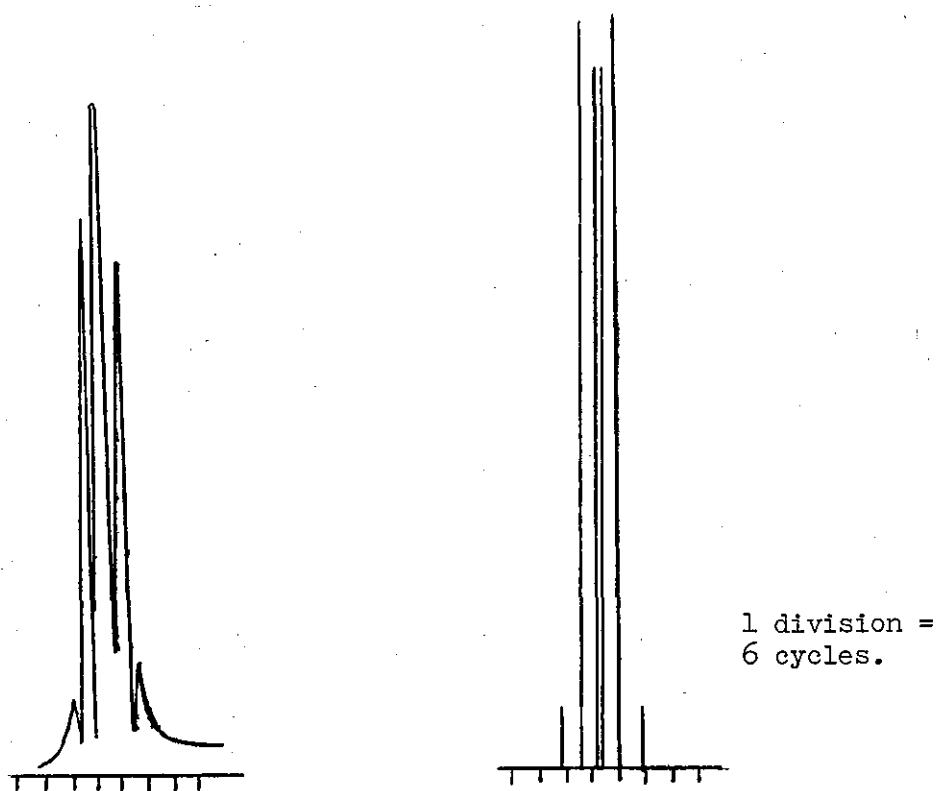
R	R ¹	R ²	R ³	R ⁴	R ⁵	H(R ¹)	H(R ²)	H(R ³)	H(R ⁴)	H(R)	H(R ⁵)	R-R ¹	R-R ²	R ⁵ -R ³	R ⁵ -R ⁴	R-R ³	R-R ⁴	R ⁵ -R ¹	R ⁵ -R ²	R ¹ -R ⁴	R ² -R ³
H	H	H	H	H	H		3.0-3.28	qn		4.5-4.75	qn	5.74	5.74	5.74	5.74	1.33	1.33	1.33	1.33	6.86	6.86
H	Me	H	Me	H	H	8.08d	3.6-3.85	8.08d	3.6-3.85	5.0-5.18		0	5.8	0	5.8	0	1.8	0	1.8	1.8	1.8
							qn		qn	d x d											
Me	H	H	Me	Me	H	4.0	qn		8.08d	7.88s	5.24t	0	0	0	0	0	0	1.8	1.8	1.8	1.8
H	Me	Me	Me	Me	H		8.2s			5.4s		0	0	0	0	0	0	0	0	0	0
Me	Me	Me	Me	Me	Me		8.26s			7.85s		0	0	0	0	0	0	0	0	0	0
OMe	H	H	H	H	H		2.8-3.4o			6.27s	4.5-4.9	0	0	6.07	6.07	0	0	1.73	1.73	7.04	7.04
										n											
H	Me	H	Me	H	H*	8.08d	3.6-3.85	8.08d	3.6-3.85	5.0-5.3		0	5.8	0	5.8	I	1.8	0	1.8	1.8	1.8
							m		m	dxtxd											

s = singlet, d = doublet, t = triplet, qn = quintet, o = octet, and n = nonet.

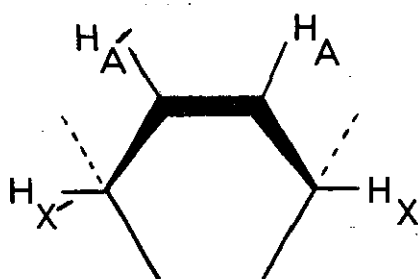
* trichloropyridine adduct (XXVI)

Table 2
Miscellaneous adducts

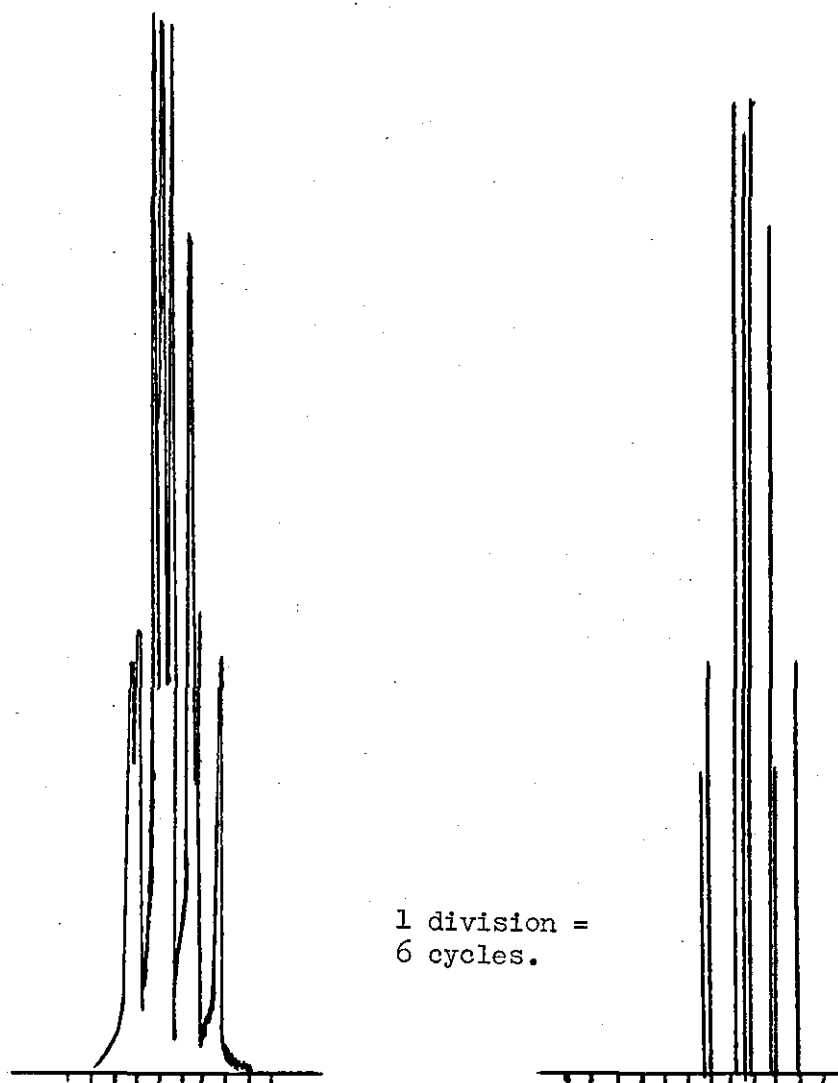
Compound	Chemical Shifts			
	Aromatic Protons	Olefinic Protons	Bridgehead Protons	Methylene Protons
XIX	2.6 — 3.2 m		4.41q	
XXI	2.56 — 3.11m		4.16s	
XXII	2.32 — 3.14 m		4.35q	
XXIII	2.0 — 3.9m			
XXIV		2.82 — 2.98qn	4.1 — 4.22q	
XXV	2.62 — 3.62m			
XVII		3.0 — 3.5 m	4.98 — 5.36m	7.6 — 8.32 o
XXVII	1.9 — 3.8 m			



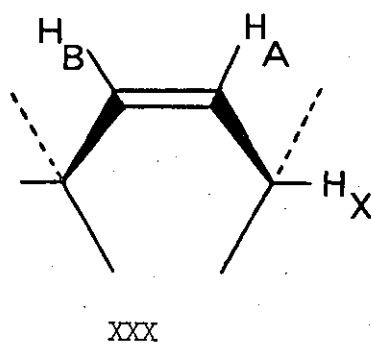
Spectrum 1



XXIX



Spectrum 2



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 ethanolic solutions were determined on a Unicam S.P. 800 spectrophotometer.

^1H n.m.r. spectra were determined at 60 $\text{M}/\text{H}_2\text{O}$ for solutions in carbon tetrachloride, using tetramethyl silane as internal standard, and ^{19}F n.m.r. spectra were determined at 56.5 $\text{M}/\text{H}_2\text{O}$ ^{C.S.} for solutions in carbon tetrachloride using trichlorofluoromethane as internal standard, on a Perkin Elmer spectrophotometer.

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

Carboxylations were carried out by pouring the reaction mixture onto a slurry of solid carbon dioxide in ether (Method 1) or by the passage of a steady stream of dry carbon dioxide through the reaction mixture (Method 2).

Hydrolyses were effected by dilute hydrochloric acid (Method 1) or distilled water (Method 2). All reactions involving the formation of adducts between tetrahalogenbenzynes from the organo-metallic compounds and liquids, were carried out using the liquid as solvent. Reactions with solids were carried out using high boiling petroleum (b.p. 80/100°) as solvent. Solutions of products were dried with anhydrous sodium or magnesium sulphate.

Light petroleum, diethyl ether, and benzene, were dried over sodium wire. Acetone and dichloromethane were dried by storage over magnesium sulphate. Mesitylene and p-xylene were dried by storage over sodium wire, and were freshly distilled as required. 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 nitrated T.L.C. plates were prepared by the method of Berg.⁸⁴ Silver nitrate impregnated silica for column chromatography was prepared by heating a slurry of silica (100g. B.D.H.), distilled water (90 ml.) and silver nitrate (50g.) at 80°C,

under vacuum (rotary evaporator) for seven hours.

Column chromatography was carried out on 'Camag' alumina, Brockmann activity 1. Filtrations of crude products to remove polymeric material were carried out on inactive alumina.

2) Reactions involving pentachlorophenyl magnesium chloride

Preparation of pentachlorophenyl magnesium chloride

Magnesium turnings (2.75g. = 0.40 g.atoms) and hexachlorobenzene (35.5g. = 0.125 moles) in diethyl ether (350 mls.) were brought to a gentle reflux, and 1, 2 - dibromoethane (4.70g. = 0.25 moles) in benzene (50 mls.) (In reactions with other liquid hydrocarbons, the benzene was replaced with the appropriate hydrocarbon) was slowly added over a period of forty-eight hours, to give a dark brown solution.

Preparation of pentachlorobenzoic acid

Pentachlorophenyl magnesium chloride was carboxylated (method 2), and then concentrated hydrochloric acid was added until the mixture was strongly acidic, and the ether and benzene were distilled off. The mixture was filtered, and the solid washed with ammonium hydroxide (2:1, 0.880 ammonia and water) to give a dilute solution of the ammonium salt. This was boiled with charcoal, filtered, acidified, and digested for three hours. The acid was filtered off and dried, to give 55% yield of

beige powder, m.p. 204 - 207°C (lit.⁶³ m.p. 208°C).

Attempted preparation of the tetrachlorobenzene adduct with benzene

Benzene (200 ml.) was added to a prepared solution of pentachlorophenyl magnesium chloride (0.125 moles), and the ether removed by distillation until the boiling point of the distillate was above 75°C. A further quantity of benzene (200 ml.) was added and the mixture was heated under reflux for 12 hrs., cooled and hydrolysed (Method 1). The organic layer was dried and the solvents removed. The dark residue was placed on a short column of alumina and eluted with petrol until there was no increase in weight of the crystalline material (11.5g.). Sublimation at 65 - 70°C (0.1mm.) gave pentachlorobenzene (5.5g.) m.p. and mixed m.p. 82°C (lit.⁶⁴ m.p. 82°C). The residue (6.0g.) was shown to be hexachlorobenzene, m.p. and mixed m.p. 227°C (lit.⁶⁵ m.p. 227°C). The other products, more strongly held on the column, were not investigated.

Reaction of tetrachlorobenzene with p-xylene

After filtration of the products dissolved in light petroleum through alumina, the crystalline material was chromatographed on neutral alumina using petrol (60/80°C) as eluent. This gave a little hexachlorobenzene and 1, 4 - dihydro - 2, 10 - dimethyl - 5, 6, 7, 8 - tetrachloro - 1, 4 - ethononaphthalene,^h (VIII), (50%), m.p. 128 - 130°C, (from ethanol); ν_{\max} 3050,

3000, 2980, 2930, 2905, 2850, 1640, 1450, 1375, 1215, and 760 cm^{-1}

Found: C, 52.5; H, 3.5; Cl, 43.7%.

$\text{C}_{14}\text{H}_{10}\text{Cl}_4$ requires C, 52.5; H, 3.15; Cl, 44.2%

Reaction of tetrachlorobenzene with mesitylene

The eluted mixture was distilled under vacuum ($3.5 \times 10^{-3}\text{mm}$) to give hexachlorobenzene (b.p. $80/100^\circ\text{C}$) and 1, 4 - dihydro - 5, 6, 7, 8 - tetrachloro - 1, 3, 10 - trimethyl - 1, 4 - ethenonaphthalene, (III), (52%), (b.p. 122°C), m.p. 110°C (from ethanol); ν_{max} 3050, 2995, 2980, 2970, 2950, 2880, 2850, 1670, 1440, 1360, 1345, 1275, 1250, 1130, 1075, 810, 795, 730, and 695 cm^{-1}

Found: C, 53.85; H, 3.70; Cl, 42.75%.

$\text{C}_{12}\text{H}_{12}\text{Cl}_4$ requires C, 53.90; H, 3.60; Cl, 42.50%.

3) Reactions involving pentachlorophenyl lithium

Preparation of pentachlorobromobenzene

Pentachlorobenzene (10g. 0.04 moles) in tetrahydrofuran (500ml.) was cooled to -80°C and n-butyl lithium (0.04 moles) was added. After 3hr. at -80°C , bromine (6.8g. 0.04 moles) was added over $\frac{1}{2}$ hr. The mixture was then allowed to warm to room temperature, the solvent removed and the residue taken into ether, washed with aqueous sodium hydroxide, water, and dried. Removal of the solvent and recrystallisation of the residue from ethanol gave pentachlorobromobenzene (12.8g., 80%) m.p. 233°C (lit.⁶⁶ m.p. 238°C).

Preparation of pentachlorophenyl lithium in ether

Method I:- Pentachlorobromobenzene (6.6g., 0.02 moles) in ether (200 ml.) was cooled to -25°C and n-butyl lithium (1 equivalent) added over $\frac{1}{4}$ hr. The mixture was stirred for 1 hr. at -20 to -25°C prior to further reaction.

Method II:- A suspension of hexachlorobenzene (11.4g., 0.04 moles) in ether (400ml.) was cooled to -25°C and n-butyl lithium (1 equivalent) added over $\frac{1}{4}$ hr. The mixture was stirred for 1 hr. at -20 to -25°C prior to further reaction.

Preparation of pentachlorobenzoic acid

Pentachlorophenyl lithium (0.02 moles in 200 mls. ether) was carboxylated (Method 2) and hydrolysed (Method 1), and the ether layer separated and extracted with sodium bicarbonate solution. The bicarbonate extracts were acidified with hydrochloric acid, and then extracted with ether, and the ether layer dried. Removal of the ether gave a crystalline residue, which was recrystallised from ethanol to give pentachlorobenzoic acid, m.p. 207°C (lit.⁶³ m.p. 208°C) in 80% yield.

Reaction of tetrachlorobenzene with benzene

Benzene (200ml.) was added to a solution of pentachlorophenyl lithium (0.02 moles) and the mixture allowed to stand at room temperature for 12 hr. Hydrolysis, followed by drying of the organic layer and removal of solvents gave a brown oil (7.1g.).

Distillation of this material under reduced pressure (10^{-4} mm.) gave pentachlorobenzene b.p. $80 - 81^{\circ}\text{C}$ (51%) and an oily solid b.p. $100 - 102^{\circ}\text{C}$. Recrystallisation of the latter from ethanol gave 1, 4 - dihydro - 5, 6, 7, 8 - tetrachloro - 1, 4 -
othanonaphthalene (X), (37%) m.p. 125°C ; ν_{max} . 3060, 2995,
 2930, 2850, 1585, 1400, 1370, 1330, 1135, 730, 700, 690 and
 675 cm^{-1} .

Found: C, 49.0; H, 2.35; Cl, 49.5%.

$\text{C}_{12}\text{H}_6\text{Cl}_4$ requires: C, 49.3; H, 2.05; Cl, 49.7%.

In a repeat reaction, ether was removed by distillation until the vapour temperature reached 50°C , and the mixture was then heated under reflux for 2 hr. The above work up procedure then gave (X), (62.5%), and no pentachlorobenzene.

Reaction of tetrachlorobenzene with p-xylene

Column chromatography of the crude product obtained after work up, gave hexachlorobenzene and the p-xylene adduct, (VIII), (72.5%).

Reaction of tetrachlorobenzene with mesitylene

Column chromatography of the crude product obtained after work up, gave a little hexachlorobenzene, and the mesitylene adduct, (III), (62.0%).

Reaction of tetrachlorobenzene with durene

Removal of excess durene by vacuum sublimation and chromatography of the residue on alumina gave 1, 4 - dihydro - 5, 6, 7, 8 -

tetrachloro - 2, 3, 9, 10 - tetramethyl - 1, 4 - etheno -
naphthalene, (XIII), (45%), m.p. 207°C (from ethanol); ν_{\max}
 2970, 2940, 2910, 2850, 1640, 1440, 1375, 1360, 1350, 1220,
 1205, 1130, 790, and 635 cm^{-1} .

Found: C, 54.95; H, 4.2; Cl, 40.55%.

$\text{C}_{16}\text{H}_{14}\text{Cl}_4$ requires C, 55.15; H, 4.0; Cl, 40.8%.

Reaction of tetrachlorobenzene with hexamethylbenzene

Gave 1, 4 - dihydro - 1, 2, 3, 4, 9, 10 - hexamethyl - 5, 6, 7, 8 -
tetrachloro - 1, 4 - etheno naphthalene, (XV), (30%), m.p. 242°
 (from ethanol); ν_{\max} 3080, 3000, 2910, 2850, 1630, 1480, 1445,
 1390, 1340, 1125, 1070, 800, and 635 cm^{-1} .

Found: C, 57.2; H, 4.55; Cl, 37.6%.

$\text{C}_{18}\text{H}_{18}\text{Cl}_4$ requires C, 57.45; H, 4.80; Cl, 37.75%.

Reaction of tetrachlorobenzene with naphthalene

Gave 9, 10 - dihydro - 1, 2, 3, 4 - tetrachloro - 9, 10 -
ethenoanthracene, (XIX), (34%), m.p. 166°C (from hexane);
 ν_{\max} 3060, 3000, 1605, 1470, 1375, 1320, 1255, 1220, 1150,
 800, 760, 690, and 650 cm^{-1} .

Found: C, 56.7; H, 2.6; Cl, 41.3%.

$\text{C}_{16}\text{H}_8\text{Cl}_4$ requires C, 56.4; H, 2.35; Cl, 41.55%.

Reaction of tetrachlorobenzene with anthracene

Gave 1, 2, 3, 4 - tetrachlorotriptycene, (XXI), (44%), m.p.

268°C (from cyclohexane). ν_{\max} 3070, 3040, 3020, 2990, 1455, 1365, 1300, 1020, 940, 810, 790, 780, 745, 660, and 665 cm^{-1} .

Found: C, 61.25; H, 2.5; Cl, 36.0%.

$\text{C}_{20}\text{H}_{10}\text{Cl}_4$ requires C, 61.25; H, 2.55; Cl, 36.15%.

The recrystallisation mother liquors were evaporated and placed on a column of silica and silver nitrate (2:1). Elution with petrol/benzene (9:1) gave a further quantity of (XXI), (10%).

Elution with benzene/ether (7:3) gave 5, 12 - dihydro - 1, 2, 3, 4 - tetrachloro - 5, 12 - ethenonaphthalene, (XXII), (1.7%), m.p. 190°C (from ethanol); ν_{\max} 3070, 1630, 1455, 1365, 880, 750, and 685 cm^{-1} . λ_{\max} ($\log_{10} E$) 243 (4.60); 266 (3.92), 277 (3.79), 288 (3.50), 293 (3.06), 310 (2.78), and 323 (2.70) m μ .

Found: C, 61.65; H, 2.8; Cl, 35.75%.

Reaction of tetrachlorobenzene with anisole

Gave 1, 4 - dihydro - 1 - methoxy - 5, 6, 7, 8 - tetrachloro -

1, 4 - ethenonaphthalene, (XVI), (62%), m.p. 122°C (from cyclohexane),

ν_{\max} 3080, 3060, 3000, 2930, 2840, 1630, 1580, 1450, 1360, 1225, 1175, 1030, 735, 710 and 695 cm^{-1} .

Found: C, 48.15; H, 2.75; Cl, 43.95%.

$\text{C}_{13}\text{H}_8\text{Cl}_4\text{O}$ requires C, 48.45; H, 2.5; Cl, 44.1%.

Further elution of the chromatogram with chloroform gave material which when extracted with aqueous methanol gave 1, 4 - dihydro -

5, 6, 7, 8 - tetrachloro - 1, 4 - etheno-tetralone - 2, (XVII),
(0.8%), m.p. 150° , ν_{\max} 2960, 2930, 1740, 1380, 1270, 1140, 1120,
1070, 740, 710, 690, and 650 cm^{-1} .

Found: C, 46.5; H, 2.15%.

$\text{C}_{12}\text{H}_6\text{Cl}_4\text{O}$ requires C, 46.75; H, 1.95%.

Reaction of tetrachlorobenzene with 1, 3 - diphenyl isobenzofuran

Gave 9, 10 - dihydro - 9, 10 - diphenyl - 1, 2, 3, 4 - tetrachloro -
- 9, 10 - epoxyanthracene, (XXIII), (41%) m.p. 215° (from ethanol),
 ν_{\max} 3060, 3040, 2960, 2910, 2860, 1500, 1455, 1355, 1300, 1290,
1125, 1010, 995, 910, 810, 780, 755, 700 and 660 cm^{-1} .

Found: C, 64.7; H, 3.0; Cl, 29.15%.

$\text{C}_{26}\text{H}_{14}\text{Cl}_4\text{O}$ requires C, 64.6; H, 2.9; Cl, 29.15%.

Reaction of pentachlorophenyl lithium with furan

Gave pentachlorobenzene (51%) and a complex mixture of aliphatic material.

Reaction of tetrachlorobenzene with benzene and p-xylene

Benzene (73g., 1 mole) and p-xylene (106g., 1 mole) were added to a solution of pentachlorophenyl lithium (0.02 moles) in ether (100 mls.), and the mixture was refluxed for 6 hr. The mixture was hydrolysed, the organic layer dried, and the solvent removed. The residue was eluted from alumina with petrol, and analysed by G.L.C. It contained a little hexachlorobenzene and the benzene, (X) and p-xylene, (VIII) adducts in a ratio of 1:24.

.. . . .

4) Reactions of Tetrachloroanthranilic acid

Preparation of tetrachloroanthranilic acid⁶⁷

Tetrachlorophthalic anhydride (143 g., 0.5 moles) was added to ammonia solution (200 ml., 20%), and stirred until the solution became clear. The clear solution was poured into excess dilute sulphuric acid, and the phthalamic acid filtered off and washed with water. The moist phthalamic acid was immediately suspended in a water/ice mixture (1 litre of water, 400 g. of ice), and an alkaline solution of sodium hypochlorite (40 g., 1 mole of sodium hydroxide and 0.5 molar equivalents of sodium hypochlorite) was added. Excess hypochlorite was destroyed by adding sodium bisulphite to the mixture, and warming it at 70/80° for 3 hr. Addition of excess hydrochloric acid to the mixture precipitated tetrachloroanthranilic acid, which was filtered and recrystallised from aqueous methanol, m.p. 175°C (lit.⁶⁷ m.p. 182°) (70% yield).

Reaction of tetrachlorobenzene with benzene

Tetrachloroanthranilic acid (1.38 g., 0.005 moles) in dry ether (50 ml) was added over 20 min. to a solution of iso-amyl nitrate (5 ml.) in benzene (200 ml.) kept at 45°C. The mixture was warmed at 50°C for ½ hr. and the solvent and excess iso-amyl nitrate removed under reduced pressure to yield a yellow oil (1.5 g.) which was placed on alumina (50 g.). Elution with light petroleum yielded, (X), (55%), m.p. and mixed m.p. 125°C, and identical gas chromatographic retention times and infrared spectra.

Reaction of tetrachlorobenzene with anisole.

Gave (XVI), (65%) and (XVII), (1.3%).

Reaction of tetrachlorobenzene with furan.

Tetrachloroanthranilic acid (0.005 moles) in ether (50 ml.) was added over 20 min. to a solution of furan (50 ml.), ^{isoamyl nitrite (3 ml.)} and dichloromethane (100 ml.). The mixture was heated under reflux for $\frac{1}{2}$ hr., the solvents removed under reduced pressure and finally dried by the removal of toluene under reduced pressure. The brown residue when placed on alumina and eluted with benzene/ether (9:1) gave 1, 4 - dihydro - 5, 6, 7, 8 - tetrachloro - 1, 4 - epoxy - naphthalene, (XXIV), 1.0 g., 71.5%, m.p. 118°C (from ethanol), ν_{\max}^{K} 3020, 2920, 2850, 1600, 1560, 1360, 1310, 1280, 1210, 1165, 1125, 1015, 915, 870, 830, 755, 700, and 640 cm^{-1}

Found: C, 42.5; H, 1.05; Cl, 43.5%.

$\text{C}_{10}\text{H}_4\text{Cl}_4\text{O}$ requires C, 42.3; H, 1.1; Cl, 43.5%.

Reaction of tetrachlorobenzene with tetraphenylcyclopentadienone.

Tetrachloroanthranilic acid (0.005 moles) in ether (50 ml.) was added over 20 min. to tetraphenylcyclopentadienone, (1.9 g., 0.005 moles) ^{and iso-amyl nitrite} in dichloromethane (150 ml.) at 40°C. The mixture was heated under reflux for $\frac{1}{2}$ hr. and maleic anhydride (0.005 moles) added. The solvent was removed by distillation and replaced by toluene. The mixture was heated under reflux until the solution became colourless (18 hr.) when aqueous potassium hydroxide

(50 ml., 2N) was added and the mixture heated for a further 3 hr. The organic layer was separated, washed with water, dried and the solvent removed and the oily residue placed on alumina. Elution with benzene:ether (4:1) gave 1, 2, 3, 4 - tetrachloro - 5, 6, 7, 8 - tetraphenyl - naphthalene, (XXV), (lg., 35%), m.p. 290°C (from ethanol); ν_{\max} 3060, 3030, 1600, 1530, 1490, 1440, 1330, 1285, 1210, 1150, 1100, 1070, 1025, 940, 810, 780, 760, 745, 710, and 700 cm^{-1} .

Found: C, 71.9; H, 3.8; Cl, 25.1%.

$\text{C}_{34}\text{H}_{20}\text{Cl}_4$ requires C, 71.6; H, 3.5; Cl, 24.9%.

Reaction of tetrachlorobenzene with benzene and p-xylene.

Tetrachloroanthranilic acid (1.38 g., 0.005 moles) in dry ether (50 ml.) was added over 20 min. to a solution of iso-amyl nitrate (5 ml.) in benzene (78 g., 1 mole) and p-xylene (106 g., 1 mole) kept at 45°C. The mixture was warmed at 50°C for $\frac{1}{2}$ hr. and the solvents removed. The residue was analysed by G.L.C. It contained the benzene, (X), and p-xylene, (VIII) adducts in a ratio of 1:19.5.

4) Reductions of Adducts.

Reduction of 1, 4 - dihydro - 5, 6, 7, 8 - tetrachloro - 1, 4 - othenonaphthalene.

Compound (X) (150 mg.) in ethanol (50 ml.) was reduced by hydrogen at atmospheric pressure in the presence of a pre-reduced palladium on carbon catalyst. Uptake of hydrogen stopped after

the absorption of 24 ml. (22.4 ml = 2 moles). After the removal of catalyst and solvent, the residue gave 5, 6, 7, 8 - tetrachloro - 1, 4 - ethanotetralin, (XI), (150 mg., 100%) m.p. 135 - 136°C (from ethanol); ν_{\max} 2950, 2940, 2865, 1480, 1450, 1435, 1380, 1305, 1180, 995, 760, and 685 cm^{-1} ; δ 6.4 (m) (>C-H); 8.0 - 8.95 (m) (>CH_2).

Found: C, 48.8; H, 3.5; Cl, 47.8%.

$\text{C}_{12}\text{H}_{10}\text{Cl}_4$ requires C, 48.7; H, 3.4; Cl, 48.0%.

Reduction of compound (VIII)

Gave 2, 10 - dimethyl - 5, 6, 7, 8 - tetrachloro - 1, 4 - ethanotetralin, (IX), m.p. 82 - 88°C; ν_{\max} 2950, 2930, 2870, 1443, 1390, 1380, 1320, 1170, 1050, 920, and 675 cm^{-1} ; δ 6.65 (>CH); 7.7 - 8.2 (m) (>CH - Me); 8.9 - 9.2 (m) (>CH_2); 9.3 (d) ($J = 7\text{c/sec}$) (>CH - Me).

Found: C, 52.2; H, 4.55; Cl, 43.35%.

$\text{C}_{14}\text{H}_{14}\text{Cl}_4$ requires C, 51.9; H, 4.35; Cl, 43.8%.

Reduction of compound (III)

Gave 5, 6, 7, 8 - tetrachloro - 1, 3, 10 - trimethyl - 1, 4 - ethanotetralin, (VI), m.p. 45 - 55°C; ν_{\max} 2990, 2965, 2935, 2900, 2885, 2860, 1465, 1390, 1380, 1340, 1240, 1100, 890, 805 and 675 cm^{-1} ; δ 6.62 (m) (>CH), 7.7 - 8.45 (m) (>CH - Me), 8.9 - 9.2 (m) (>CH_2), 8.32 (s) ($-\text{CH}_3$), 9.35 (d) ($J = 6\text{ c/sec.}$) (>CH - Me).

Found: C, 53.4; H, 4.65; Cl, 42.05%.

$C_{15}H_{16}Cl_4$ requires C, 53.3; H, 4.75; Cl, 42.0%.

Reduction of compound (XIII).

Gave 5, 6, 7, 8 - tetrachloro - 2, 3, 9, 10 - tetramethyl - 1, 4 - ethanotetralin, (XIV), m.p. 126 - 140°; ν_{\max} 2970, 2930, 2910, 2870, 2850, 1465, 1440, 1385, 1320, 1170, 1115, 810 and 680 cm^{-1} ; τ 6.84 (m) ($\rightarrow CH$), 7.58 - 8.2 (m) ($\rightarrow CH - Me$), 9.36 (d) ($J = 7$ c/sec.) ($\rightarrow CH - Me$).

Found: C, 54.85; H, 5.15; Cl, 40.7%.

$C_{16}H_{18}Cl_4$ requires C, 54.55; H, 5.1; Cl, 40.35%.

Reduction of compound (XVI)

Gave 1 - methoxy - 5, 6, 7, 8 - tetrachloro - 1, 4 - ethanotetralin, (XVIII), m.p. 66°; ν_{\max} 2970, 2960, 2900, 2860, 2825, 1455, 1360, 1340, 1290, 1220, 1200, 1155, 1120, 1020, 945, 860, 800, 690, and 675 cm^{-1} ; τ 6.38 (m) ($\rightarrow CH$), 6.70 (s) (O-Me), 7.9 - 8.6 (m) ($-CH_2$).

Found: C, 47.55; H, 3.6; Cl, 43.5%.

$C_{13}H_{12}Cl_4O$ requires C, 47.85; H, 3.7; Cl, 43.4%.

Reduction of compound (XIX)

Gave 9, 10 - dihydro - 1, 2, 3, 4 - tetrachloro - 9, 10 - ethanoanthracene, (XX), m.p. 186°; ν_{\max} 3070, 3040, 2980, 2950, 2910, 2875, 1480, 1460, 1380, 1315, 1300, 1225, 1160, 1140, 1110, 770, and 680 cm^{-1} ; τ 2.65 - 3.05 (m) (Ar - H), 5.14 (m) ($\rightarrow CH$), 8.3 (m) (CH_2).

Found: C, 55.7; H, 3.1; Cl, 41.15%.

$C_{16}H_{10}Cl_4$ requires C, 55.8; H, 2.9; Cl, 41.3%.

Pyrolysis of compound (X) - The compound (105 mg.) was placed in a pyrex tube (500 ml.) capacity) evacuated and flushed with nitrogen. The tube was re-evacuated (10^{-1} mm.), sealed and heated for 13 hr. at 375°C . The tube was opened and the contents dissolved in ether and percolated through a short alumina column (20 g.). After removal of the solvent, the residue (58 mg.) was sublimed under reduced pressure and gave 1, 2, 3, 4 - tetrachloronaphthalene, (XII), 34 mg. (35%) m.p. 194°C (lit. 68° m.p. 198° .)

Reaction of tetrachlorobenzynes with benzene in the presence of silver ions

Tetrachlorobenzynes were generated from pentachlorophenyl lithium (0.02 moles) in the presence of benzene (50 ml.) and silver oxide, bromide and nitrate (200 mg.) in separate experiments. G.L.C. analysis of the products on a 2%, 5 ft. silicone column at 180°C , showed the presence of the adduct (X) only. In similar reactions the tetrachlorobenzynes were generated from tetrachloroanthranilic acid (2.80 g. = 0.01 moles) in the presence of benzene and the silver compounds (100 mg.). G.L.C. analysis of the products again showed the presence of compound (X) only.

Reaction of tetrafluorobenzynes with benzene in the presence of silver ions

Pentafluorobromobenzene (12.4 g. = 0.05 moles), in diethyl ether (200 ml.), was treated at -40°C with one equivalent of n-butyl lithium solution, and small quantities (200 mg.) of the silver

compounds were added in separate experiments. After warming up to and standing at room temperature overnight, the mixtures were hydrolysed (method 2) and the organic layers were separated and dried. Examination of the products by analytical G.L.C. on a 5ft., 10% silicone column at 150°C, and comparison of the result with G.L.C. standards, showed that the mixtures contained the 1, 4 cycloadduct⁴¹ only. No 2,3,4,5 - tetrafluoro biphenyl or tetrafluorobenzocyclooctatene^{et}₄₀ could be detected in the products.

Attempted preparations of pentabromophenyl lithium

Reaction of hexabromobenzene with n-butyl lithium

Hexabromobenzene (1.38g., 0.0025 moles) was suspended in dry ether (250 ml.) and the mixture cooled to -80°C. One equivalent of n-butyl lithium solution was added and the mixture was stirred for 3 hr. and then carboxylated (method 2) and hydrolysed (method 1). The organic layer was extracted with aqueous sodium hydroxide solution, and these extracts were acidified and ether extracted. Drying of the acidic ether extracts, followed by removal of the ether, gave a brown solid (10 mg.). The neutral material was found to contain unreacted hexabromobenzene (1.3 g.). In a repeat reaction a longer time (9 hr.) was allowed before carboxylation, but the hexabromobenzene was again recovered unchanged.

Use of N. N. H.¹ N.¹ - tetramethylethylene diannino - n-butyl lithium complex

Hexabromobenzene (2.3 g., 0.0042 moles) in ether (200 ml.) was

treated at -20°C with a mixture of n-butyl lithium (2.0 ml.) and N, N, $^1\text{N}^1$ - tetramethylethylenediamine (1.0g.) in ether, and the mixture stirred for 3 hr. After carboxylation and work up, all the hexabromobenzene was recovered unchanged.

Reaction of hexabromobenzene with methyl lithium

A suspension of hexabromobenzene (1.38 g., 0.0025 moles) in ether (200 ml.) was treated with methyl lithium solution (one equivalent) at -50°C . After three hours at -50°C , the solution was carboxylated. Work up of the mixture gave back all the hexabromobenzene.

Reactions involving tetrachloro-4-pyridyl lithium

Preparation of tetrachloro - 4 - pyridyl lithium

Pentachloropyridine (5.1 g = 0.02 moles) in diethyl ether (200 ml.) was cooled to -40°C and one equivalent of n-butyl lithium added.

The mixture was stirred for 1 hr. at -40°C prior to further reaction.

Hydrolysis of tetrachloro - 4 - pyridyl lithium

A solution of the lithio compound (0.02 moles) was hydrolysed (method 2), the organic layer separated and dried, and the ether removed to give a brown solid (4.0 g.). Elution from a short column of alumina with petrol (60/80 $^{\circ}\text{C}$) gave white crystals. ^1H n.m.r. showed this to be a mixture of 2,3,5,6 - tetrachloropyridine, (80%), 3,3,5,6, - tetrachloropyridine, (5%),

and 2,4,5,6 - tetrachloropyridine, (15%). These could not be separated by G.L.C., but ^1H n.m.r. spectroscopy showed that three aromatic singlets were present at τ 2.14, 2.70, 2.90, (integration ratio 1:3:16). Recrystallisation of the mixture from alcohol gave 2,3,5,6 - tetrachloropyridine, (2.5g.), m.p. 90°C , (lit. 57a m.p., 91°C), ν_{max} 3040, 1520, 1400, 1375, 1340, 1315, 1230, 1170, 1070, 925, 715, 680, 640 cm^{-1} . Overall yield of tetrachloropyridines = 80%.

Carboxylation of tetrachloro - 4 - pyridyl lithium

A solution of the lithio compound (0.05 moles) was carboxylated, (method 2), and hydrolysed, (method 1). The organic layer was extracted with aqueous sodium hydroxide solution, and these extracts were acidified and ether extracted. Drying of the acidic ether extracts, followed by removal of the ether gave buff crystals (11.1 g.). Recrystallisations from water gave tetrachloroisonicotinic acid, (70%), m.p. 222°C , (lit. 56 m.p. 224°C), ν_{max} 2900 - 2450, 1765, 1550, 1400 1335, 1250, 1235, 1180, 1100, 680 cm^{-1} .

Found: C, 54.05; Cl, 28.05; N, 5.5

$\text{C}_6\text{HCl}_4\text{NO}_2$ requires C, 54.35; Cl, 27.6; N, 5.4%

Reaction of tetrachloro-4-pyridyl lithium with furan

Furan (50ml.) was added to a solution of the lithio compound (0.02 moles) at -40°C , and the solution was allowed to warm up to and stand at room temperature overnight. The mixture was

hydrolysed, (method 2), the organic layer dried, and the solvents removed to give a brown residue (5.2 g.). This residue was column chromatographed on neutral alumina using petrol (60/80°C) as eluent, when pentachloropyridine (0.55g.) was obtained. Elution with 90% petrol (60/80°C), 10% benzene gave a mixture of octachloro and heptachloro bipyridyls, (2.5 g.), ν_{\max} 3040, 1575, 1525, 1365, 1320, 1210, 1180, 1150, 1100, 1070, 1045, 840, 760, 700, 675 cm^{-1} , (δ 2.83).

Found: C, 29.0; H, 0.5

$\text{C}_{10}\text{Cl}_8\text{N}_2$ requires C, 27.8%

$\text{C}_{10}\text{HCl}_7\text{N}_2$ requires C, 30.1; H, 0.25%

In a similar reaction, the mixture was refluxed for 3 hr. immediately after the addition of the furan. Column chromatography of the product on neutral alumina gave a colourless oil, (2.5 g.), 2,3,5,6 - tetrachloropyridine (2.3g.) and the hepta and octachlorobipyridyl mixture, (0.5 g.). G.L.C. analysis of the oil showed it to be a complex mixture.

Reaction of trichloro- 3,4 - pyridyne with p-xylene

A solution of the lithio compound (0.04 moles) at -20°C , was dripped slowly into boiling p-xylene (500ml.). After the addition was completed the mixture was cooled, hydrolysed, (method 2), and the organic layer dried. Removal of the solvents by distillation followed by elution of the products from a short column of alumina with petrol (60/80°C) gave an

oil (4.5g.). Column chromatography of this oil on neutral alumina gave pentachloropyridine, (1.26 g.), the hepta and octachloro-bipyridyl mixture, (2.3 g.), and 1, 3, 4 - trichloro - 5, 8 - dihydro - 6, 9 - dimethyl - 5, 8 - ethenoisocquinoline, (XXVI), (0.9 g. = 8%), colourless oil, ν_{\max} 3040, 2950, 2920, 2850, 1570, 1520, 1395, 1370, 1320, 1220, 1160, 1135, 1070, 920, 825, 765, 715, 700, 675, 640 cm^{-1}

Found: C, 54.7; H, 3.9; Cl, 36.85; N, 5.2;

$\text{C}_{13}\text{H}_{10}\text{Cl}_3\text{N}$ requires C, 54.45; H, 3.5; Cl, 37.15; N, 4.9%.

Reaction of trichloro-3, 4 - pyridine with 1, 3 - diphenyl isobenzofuran

1, 3 - diphenyl iso-benzofuran (5.4 g.) was added to a solution of tetrachloro - 4 - pyridyl lithium (0.02 moles) in ether at 0°C . The ether was distilled off and replaced by petrol ($80/100^\circ\text{C}$) and the mixture was heated under reflux for four hours, cooled, washed with water, the organic layer separated, dried, and the solvents removed. Column chromatography of the residue on neutral alumina using petrol ($60/80^\circ\text{C}$) as eluent gave pentachloro-pyridine and 2-aza - 1, 3, 4 - trichloro - 9, 10 - dihydro - 9, 10 - diphenyl - 9, 10 - epoxyanthracene, (XXVII) (10%), m.p. 203°C , (from ethanol), ν_{\max} 3060, 1545, 1540, 1500, 1450, 1370, 1320, 1285, 1165, 1120, 1010, 985, 940, 910, 850, 790, 775, 755, 700, 680, 630 cm^{-1} ,

Found: C, 66.7; H, 3.3; Cl, 23.8; N, 3.1

$\text{C}_{25}\text{H}_{14}\text{Cl}_3\text{NO}$ requires C, 66.6; H, 3.1; Cl, 23.6; N, 3.1%.

Reactions of benzyne with hexafluoro - and 1, 2, 4, 5 -
tetrafluorobenzene

(a) Benzyne generated from o-fluorophenyl magnesium bromide

O-Fluorobromobenzene (8.75 g. = 0.05 moles) was added to a suspension of magnesium turnings (1.34 g. = 0.055 g. atom) in diethyl ether (100 ml.) and hexafluorobenzene (25.0 g.), and the reaction was initiated with 1,2 - dibromoethane (0.2 g.). After the reaction had subsided, the mixture was refluxed for 3 hr., the ether removed by fractional distillation, and the mixture cooled and hydrolysed (method 1). The organic layer was dried, and was shown by G.L.C. analysis to contain ether, hexafluorobenzene, ortho-fluorobromobenzene and a less volatile product. Fractional distillation of the mixture gave

2, 2¹, 3, 4, 5, 6 - hexafluorobiphenyl, (XXVIII), (12%), m.p.
60°C, (from ethanol), ν_{\max} 3080, 1660, 1620, 1545, 1500,
1450, 1395, 1330, 1275, 1240, 1200, 1120, 1070, 995, 955, 880,
810, 790, 765, 710, 640 cm.⁻¹.

Found: C, 55.25; H, 1.35; F, 43.5

C₁₂H₄F₆ requires C, 54.95; H, 1.55; F, 43.5%.

(b) Benzyne generated from 1-aminobenzotriazole

1-aminobenzotriazole (0.67 g. = 0.005 moles), prepared by the method of Campbell and Rees,²¹ in hexafluorobenzene (10 ml) and dichloromethane (10 ml.), was added dropwise to a solution of lead tetra-acetate (5.2 g. = 0.01 moles) in hexafluorobenzene (15 ml.) and dichloromethane (20 ml.), over a period of 20 min.

Examination of the products by T.L.C. on silica gel showed that they contained no unreacted 1-aminobenzotriazole. The mixture was washed with water, filtered through kieselguhr to remove lead dioxide, and the organic layer dried. G.L.C. analysis showed that the mixture contained biphenylene (80% yield) in addition to hexafluorobenzene.

(c) Benzynes generated from benzene diazonium - 2 - carboxylate
Anthranilic acid, (13.7 g. = 0.1 moles) in acetone (75 ml.), was slowly added to a gently refluxing mixture of iso-amyl nitrate (12.7 g.), 1,2,4,5 - tetrafluorobenzene (23.5g.) and dichloromethane (25 ml.). After the addition was completed (3 hr.), the mixture was heated under reflux for two hours. No product derived from benzyne and the tetrafluorobenzene was detected.

SECTION 2.

The Reactions of Tetrachloro and Tetrafluoro benzynes
with Styrene and α -Methyl Styrene

INTRODUCTION

The reactions of benzyne with styrenes have been reported in two publications.^{28, 69} In the reaction of benzyne with vinyl naphthalene, the hydrocarbon chrysene was obtained,²⁸ while 9 - methyl - phenanthrene derivatives were produced in the reactions of benzyne with isoeugenol and isosafrole.⁶⁹ Surprisingly however, Simmons was unable to isolate any products from the reaction of benzyne with ~~benzene~~ ^{styrene}.³¹

In view of the high reactivities of tetrahalogenobenzenes towards aromatic hydrocarbons, the reactions of tetrafluorobenzenes with simple styrenes were of considerable interest, and we decided to investigate them. In principle, the aryne could undergo different types of addition to those previously reported,^{28, 69} for example, cycloaddition to give a cyclobutane derivative, or 1, 4 addition across the aromatic ring.

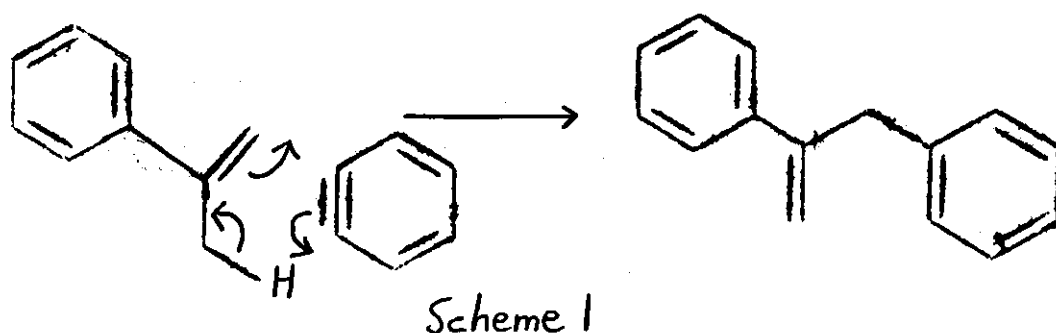
DISCUSSION

Tetrachlorobenzyne was generated from pentachlorophenyl lithium in the presence of a 25 molar excess of styrene. After removal of solvents, the residue was eluted from alumina with petrol, and the crystalline eluent was column chromatographed on neutral alumina to give hexachlorobenzene and 1, 2, 3, 4, - tetrachloro - 9, 10 - dihydrophenanthrene, (1), in 33.5% yield. The structure was determined on the basis of elemental analysis,

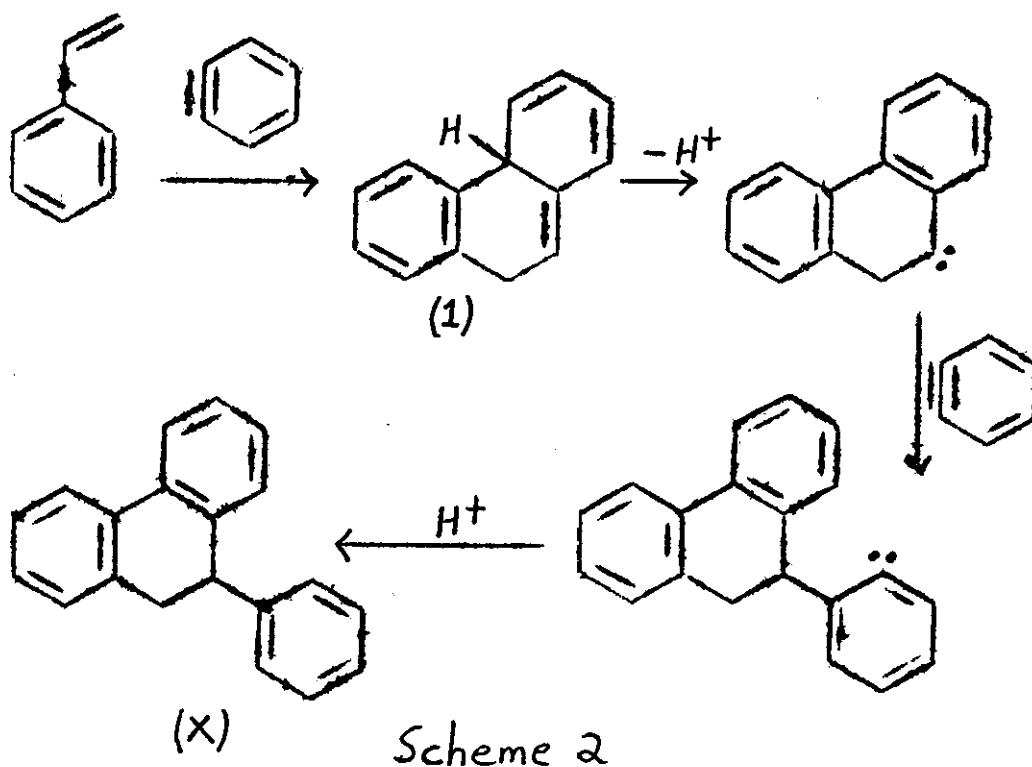
^1H n.m.r. and ir. spectra. In a similar reaction, tetrafluorobenzyne, generated from pentafluorophenyl lithium, was reacted with a 5 molar excess of styrene. Removal of the solvents and elution of the crude products from alumina with petrol gave a white crystalline compound. Recrystallisation of this compound from ethanol gave 1, 2, 3, 4 - tetrafluoro - 9, 10 - dihydrophenanthrene, (II), in 60.5% yield. The structure was determined on the basis of elemental analysis, ^1H n.m.r. and ir. spectra, and the fact that on prolonged reflux of, (II), in p-cymene in the presence of palladium on carbon, 1, 2, 3, 4 - tetrafluorophenanthrene, (III), was obtained in quantitative yield.

In a further investigation of the reactions of simple styrenes with tetrahalogenobenzyne, α -methyl styrene was reacted with tetrachlorobenzyne. Column chromatography of the crude product on neutral alumina, gave three fractions, which were, in order of elution, 1, 2, 3, 4 - tetrachloro-9-methyl-9,10-dihydrophenanthrene, (IV), (6.9%), α - (2,3,4,5 - tetrachlorobenzyl) styrene, (V), (15.3%), and 1, 2, 3, 4 - tetrachloro-9-methylphenanthrene, (VI), (10.6%). The corresponding three compounds were obtained from the reaction of tetrafluorobenzyne with α -methyl styrene, the yields being 20.6% 1, 2, 3, 4 tetrafluoro-9-methyl-9,10-dihydrophenanthrene, (VIII), 28.2% α - (2,3,4,5-tetrafluorobenzyl) styrene, (VIII), and 5.1% 1, 2, 3, 4-tetrafluoro-9-methyl phenanthrene, (IX). The dihydrophenanthrenes and phenanthrenes presumably are formed via initial Diels Alder addition of the

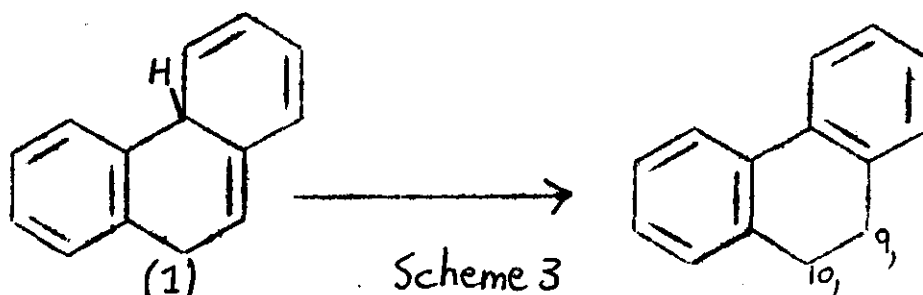
aryne across the ring and exocyclic double bond, while the α -tetrahalogenobenzyl styrenes arise by an insertion reaction of the aryne onto the α -methyl group of the styrene.



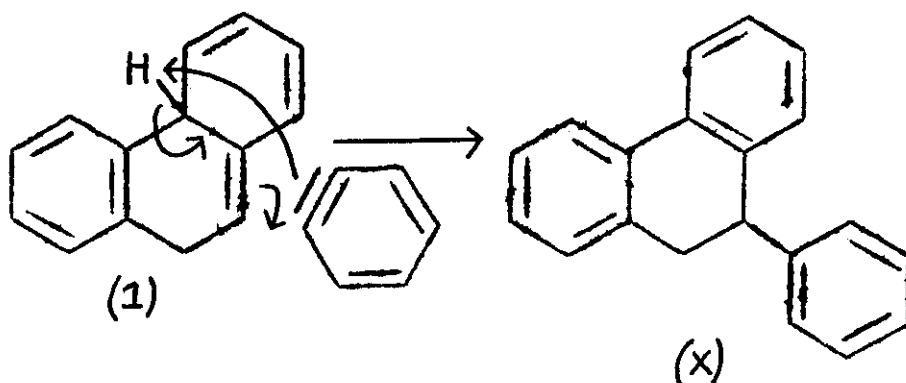
After much of this work had been completed, Dilling reported that he had obtained 9-phenyl-9,10-dihydrophenanthrene, (X) in good yield, by generating benzyne from *o*-fluorophenyl magnesium bromide in the presence of a 5 molar excess of styrene.⁷⁰ He also suggested a possible mechanism for the reaction, viz.



Dilling's mechanism is unlikely, since in reactions involving Grignard and organolithium reagents, it is improbable that a proton should be lost and then regained to give for example the 1, 2, 3, 4 - tetrahalogeno-9,10 -dihydrophenanthrenes. A more likely mechanism for the formation of the 9, 10 - dihydrophenanthrenes would involve attack of the aryne on the styrene to give intermediate (1) (scheme 2), followed by either inter or intramolecular transfer of a hydrogen atom from the ring junction to the 9-position.



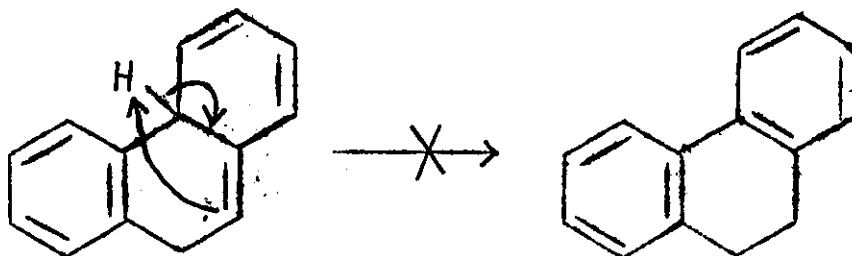
Dilling's 9-phenyl-9,10-dihydrophenanthrene (X) could arise by insertion of a second benzyne onto the 9 position of intermediate (1) and simultaneous abstraction of the ring-junction proton. This would involve a six-membered transition state, viz.



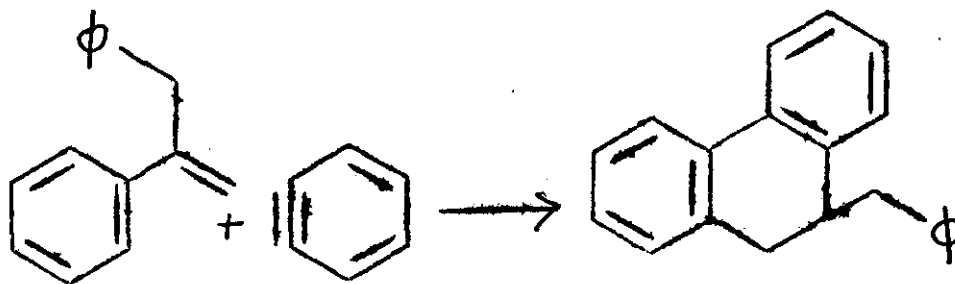
This type of mechanism has been postulated for the attack of benzyne on olefins.³¹

It was surprising that we had been unable to isolate 9-tetrahalogenophenyl - dihydrophenanthrenes from our reactions, and in an attempt to force the production of 9-tetrafluorophenyl - 9, 10 dihydrotetrafluoro phenanthrene, tetrafluorobenzynes was generated in the presence of a $\frac{1}{2}$ molar equivalent of styrene. G.L.C. analysis of the product showed two major components present. These were separated by column chromatography on alumina, and shown to be 1, 2, 3, 4 - tetrafluoro - 9, 10 - dihydrophenanthrene, (II), (25.0%), and 1, 2, 3, 4 - tetrafluorophenanthrene, (III), (18.5%), by mixed melting points, and comparison of G.L.C. retention times, with standard samples. This result suggested that the 'excess' benzyne dehydrogenated either the dihydrophenanthrene or intermediate (I), since no trace of 9-tetrafluorophenyl - 9, 10 dihydrotetrafluorophenanthrene could be detected.

With reference to this last point, it has recently been shown in these laboratories⁷¹ that generation of tetrafluorobenzene in the presence of 1, 2, 3, 4 - tetrafluoro - 9, 10 - dihydrophenanthrene, does not lead to dehydrogenation of the dihydrophenanthrene, and we tentatively suggest that production of phenanthrenes in these reactions, probably arises by dehydrogenation of intermediate (1) by the benzyne. It is also of interest to note that recent work on the reaction of tetrafluorobenzene with deuterium labelled styrene⁷¹ has shown that the hydrogen lost from intermediate (1) does not transfer intra-molecularly to form the dihydrophenanthrene, i.e.



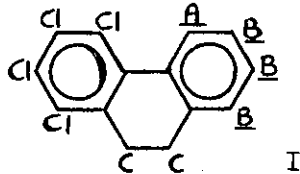
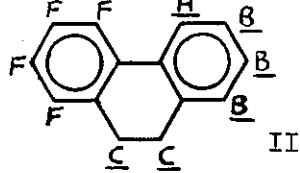
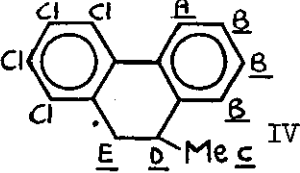
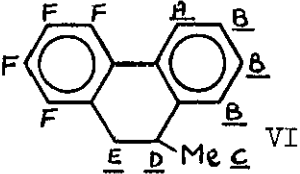
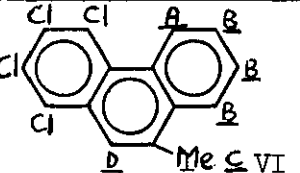
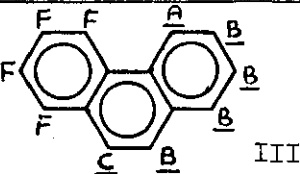
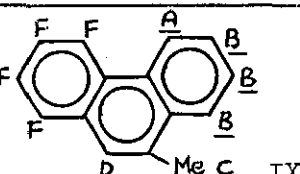
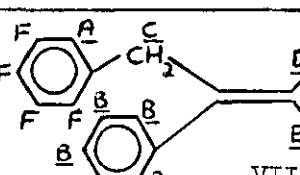
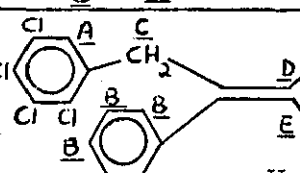
Shortly after our work on styrenes was concluded, Wolthuis and Cady reported the reaction of benzyne with α -methyl styrene.⁷² Their results differed slightly from ours, in that a small quantity of a dihydrophenanthrene formed from the reaction of benzyne with the initially formed α -benzyl styrene, was isolated, i.e.



We conclude that if the corresponding compounds were formed in our reactions, they were formed in very low yields.

¹H n.m.r. spectra.

s=singlet, d=doublet, t=triplet, m=multiplet.

Compound	Chemical Shifts and Coupling Constants.				
	A	B	C	D	E
 I	1.76-2.04m	2.62-2.9m	6.86-7.44m		
 II	1.97-2.31m	2.6-2.87m	7.05-7.30s		
 IV	1.76-2.02m	2.6-2.9m	8.6-8.88d J _{CD} =6c/s	6.9-6.35m	6.9-6.35r
 VII	1.97-2.25m	2.58-2.9m	8.6-8.9d J _{CD} =6c/s	6.83-7.4m	6.83-7.4r
 VI	1.72-2.06m	2.1-2.4m	7.27s	1.28-1.5m	
 III	1.5-2.4m	1.5-2.4m	0.9-1.25m		
 IX	1.8-2.12m	2.17-2.55m	7.38s	0.9-1.25m	
 VIII	2.98-3.47m	2.5-2.88m	6.19s	4.94t	4.49s
 V	2.55-2.88m	2.55-2.88m	6.14s	5.09t	4.49s

EXPERIMENTAL

All General Methods are as reported in Section 1, (experimental).

Reaction of tetrachlorobenzene with styrene

Styrene (104g. = 1 mole) was added to a solution of pentachlorophenyl lithium (0.04 mole) and some ether was distilled from the mixture until the boiling point of the vapour was 55°C. The mixture was then refluxed for 2 hours, hydrolysed, (method 2) and the organic layer dried. The excess styrene and ether were removed by vacuum distillation, and the crude residue was eluted from a short alumina column with petrol, (60/80°C.), to yield 7.2g. of oily crystals. These were separated by column chromatography on neutral alumina, to give hexachlorobenzene, (3.55g.), and 1, 2, 3, 4 - tetrachloro - 9, 10 - dihydrophenanthrene, (1), (3.35g. = 33.5%), m.p. 114°C, (from ethanol); ν_{\max} 3010, 2955, 2920, 2900, 1520, 1490, 1400, 1380, 1370, 1340, 1310, 1200, 1180, 885, 785, 770, 750, 740, 725, 690 cm^{-1}

Found: C, 52.7; H, 2.5; Cl, 44.6.

$\text{C}_{14}\text{H}_8\text{Cl}_4$ requires C, 52.85; H, 2.55; Cl, 44.6%.

Reaction of tetrachlorobenzene with α - methyl styrene

A sample (900mg.) of the initial crude product (12.2g.) was column chromatographed on neutral alumina (100g.) using 80% petrol (60/80°C), 20% benzene as eluent. Four fractions were obtained, and shown to contain (a) hexachlorobenzene, (96.7mg. = 11.4%);

(b) 1, 2, 3, 4 - tetrachloro - 9 - methyl - 9, 10, -

dihydrophenanthrene, (IV), (67.4 mg. = 6.9%), m.p. 148°C, (from ethanol), ν_{\max} 3060, 2980, 2890, 1480, 1450, 1425, 1380, 1360, 1250, 1195, 1175, 1125, 1105, 1060, 1020, 865, 785, 770, 760, 750, 720, 690 cm^{-1} ;

Found: C, 53.85; H, 3.15; Cl, 42.3;

$\text{C}_{15}\text{H}_{10}\text{Cl}_4$ requires C, 54.3; H, 3.05; Cl, 42.7%;

(c) α - (2, 3, 4, 5 - tetrachlorobenzyl) styrene, (V), (150 mg. = 15.3%), colourless oil, ν_{\max} 3080, 3040, 2930, 2860, 1700, 1535, 1495, 1450, 1425, 1360, 1215, 1190, 1090, 1000, 830, 755, 700 cm^{-1} .

Found: C, 53.90; H, 3.05; Cl, 42.5%; and

(d) 1, 2, 3, 4 - tetrachloro - 9 - methyl - phenanthrene, (VI), (103mg. = 10.6%), m.p. 202°C, (from benzene), ν_{\max} 3050, 2950, 2920, 2850, 1610, 1575, 1540, 1435, 1405, 1355, 1330, 1290, 1240, 1185, 1120, 885, 865, 810, 780, 745, 730, 700, 680 cm^{-1} ;

Found: C, 54.5; H, 2.9; Cl, 42.5.

$\text{C}_{15}\text{H}_8\text{Cl}_4$ requires C, 54.6; H, 2.45; Cl, 42.5%.

Reaction of tetrafluorobenzene with styrene

Pentafluorobromobenzene (12.4g. = 0.05 moles), in dry diethyl ether (300ml.) and styrene (23.0g. = 0.25 moles) was cooled to - 40°C, and one equivalent of n-butyl lithium solution was added. After $\frac{1}{2}$ hour, the mixture was allowed to warm to and stand at room temperature overnight, hydrolysed, (method 2), and the organic layer separated and dried. The ether and styrene were removed by vacuum distillation,

and the brown residue was eluted from a short alumina column with petrol (60/80°C) to give 8.3g. of crystalline product. Recrystallisation from ethanol gave 1, 2, 3, 4 - tetrafluoro - 9, 10 - dihydrophenanthrene, (II), (7.5g. = 60.5%), m.p. 88°C, ν_{\max} 3010, 2950, 2920, 2860, 1620, 1515, 1470, 1450, 1400, 1345, 1120, 1100, 1050, 1030, 990, 955, 880, 850, 775, 745 cm^{-1} .

Found: C, 66.4; H, 3.15; F, 30.2

$\text{C}_{14}\text{H}_8\text{F}_4$ requires C, 66.7; H, 3.2; F, 30.15%

In a similar reaction, the amount of styrene was reduced to 3.10g.

= 0.025 moles. G.L.C. analysis at 170°C on a 5ft., 2% S.E. 52

column, showed the oil (6.0g.) obtained after elution from alumina,

to be composed of two major (90% of mixture) and four very minor

components. Column chromatography of a portion of the oil (1.0g.)

on neutral alumina (100g.), using petrol (60/80°C) as eluent,

separated the major components, which were shown to be (a) 1, 2, 3, 4 -

tetrafluoro - 9, 10 - dihydrophenanthrene, (II), (516 mg. = 25%),

and (b) 1, 2, 3, 4 - tetrafluorophenanthrene, (III), (387mg. =

18.5%), m.p. 174°C, (from ethanol), ν_{\max} 3040, 1665, 1630, 1540,

1520, 1500, 1450, 1400, 1350, 1325, 1290, 1260, 1210, 1175, 1135,

1115, 1050, 1030, 990, 875, 840, 815, 750, 710, 640 cm^{-1} .

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%.

The more volatile minor products were not identified, but comparison

with G.L.C. standards, suggested that they were fluorinated biphenyls.

Reaction of tetrafluorobenzynes with α - methyl styrene

G.L.C. analysis of the oil obtained after filtration of the crude product through an alumina column, showed the presence of three major components. Column chromatography of the oil on neutral alumina, using petrol (60/80°C) as eluent, gave (a) α - (2, 3, 4, 5 - tetrafluorobenzyl) styrene, (VIII), (28.2%), colourless oil, ν_{\max} 3090, 3060, 2920, 2860, 1630, 1525, 1490, 1445, 1365, 1225, 1110, 1050, 950, 915, 860, 780, 705, cm^{-1} .

Found: C, 67.25; H, 3.9; F, 28.45;

$\text{C}_{15}\text{H}_{10}\text{F}_4$ requires C, 67.7; H, 3.8; F, 28.55%;

(b) 1, 2, 3, 4 - tetrafluoro - 9 - methyl - 9, 10 - dihydrophenanthrene, (VII), (20.6%), m.p. 92°C, (from ethanol), ν_{\max} 3080, 2980, 2940, 2880, 2860, 1650, 1625, 1580, 1515, 1470, 1450, 1390, 1360, 1310, 1260, 1180, 1120, 1050, 1035, 970, 950, 850, 770, 760, 735, 645 cm^{-1} .

Found: C, 67.8; H, 3.85; F, 28.4%.

and (c) 1, 2, 3, 4 - tetrafluoro - 9 - methyl phenanthrene, (IX), (5.1%), m.p. 178°C, (from ethanol), ν_{\max} 3040, 2950, 2920, 2850, 1665, 1620, 1510, 1490, 1450, 1400, 1330, 1260, 1200, 1150, 1130, 1075, 1060, 1035, 995, 860, 760, 640 cm^{-1} .

Found: C, 68.4; H, 3.35; F, 28.4;

$\text{C}_{15}\text{H}_8\text{F}_4$ requires C, 68.2; H, 3.05; F, 28.75.

Dehydrogenation of (II)

1, 2, 3, 4 - tetrafluoro - 9, 10 - dihydrophenanthrene, (II),
(200mg.) was dissolved in p-cymene (50 ml.) and 10% palladium on carbon catalyst (100mg.) was added. The mixture was heated under reflux while a slow stream of nitrogen was passed during five days, filtered, and the p-cymene distilled off under vacuum. Recrystallisation of the residue from ethanol gave 1, 2, 3, 4 - tetrafluorophenanthrene, (III), (100%).

SECTION 3.

The Reactions of Tetrachloro and Tetrafluoro benzyne with
Bicyclohepta (2,2,1) ene, and Bicyclohepta (2,2,1) diene.

INTRODUCTION

Few examples of arynes undergoing 1, 2 - cycloadditions are known. With simple olefines, benzyne undergoes an insertion reaction, probably involving a six-centered transition state³¹ (see main introduction). 1, 2 - Cycloaddition compounds have been formed with methyl vinyl ether,⁷³ and the strained olefines, bicyclohepta (2,2,1) ene, and bicyclohepta (2,2,1) diene.³¹

These are unusual cases, because the benzyne cannot undergo the insertion reaction. With methyl vinyl ether, there are no protons β to the attacking carbon, for the benzyne to abstract. The reactions of benzyne with bicyclohepta (2,2,1) ene and bicyclohepta (2,2,1) diene were of considerably more interest to us. 1, 2 - Cycloaddition undoubtedly occurs instead of insertion, because although β hydrogens are available, the product obtained by insertion would have a double bond at the bridge-head position.

Simmons³¹ obtained fairly low yields of exclusively exo - 1,2 adducts with bicyclohepta (2,2,1) ene and bicyclohepta (2,2,1) diene (10% and 15 - 21% respectively). He also reported isolating an unidentified saturated product in low yield from the reaction with bicyclohepta (2,2,1) diene. He suggested steric hindrance to explain the stereospecificity of the reactions, and postulated that the absence of rearranged products excluded the existence of benzyne as a dipolar species, and concluded that the products

arose by a concerted mechanism.

Examination of molecular models of bicyclohepta (2,2,1) one and bicyclohepta (2,2,1) diene suggested to us that serious steric hindrance would be involved in the formation of an endo - 1, 2 cycloaddition product with bicyclohepta (2,2,1) one. However, we could see no steric reason why attack of an aryne from beneath bicyclohepta (2,2,1) diene should not occur. In view of the high reactivity of highly halogenated arynes in addition reactions, we decided to investigate the reactions of tetrachloro and tetrafluorobenzynes with bicyclohepta(2,2,1) one and bicyclohepta (2,2,1) diene.

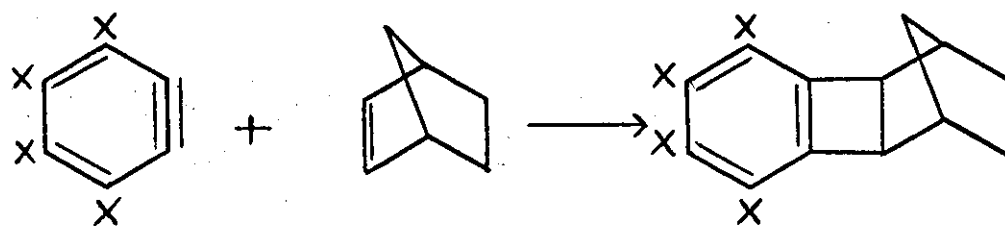
DISCUSSION

Tetrachlorobenzynes was generated from pentachlorophenyl lithium in the presence of bicyclohepta (2,2,1) one, and after work up, the white crystalline product was column chromatographed on alumina to give a little hexachlorobenzene and exo - 3,4 - tetrachlorobenzotricyclo (4.2.1.0^{2,5}) non-3-ene, (I), in 25% yield. The structure of this adduct was assigned on the basis of elemental analysis, ir. and n.m.r. spectra. The adduct was shown to be the exo-adduct because the resonance due to protons at positions 5 and 8 appear as a sharp singlet.⁷⁴ Tetrafluorobenzynes, generated from pentafluorophenyl lithium, gave the corresponding tetrafluoro adduct with bicyclohepta (2,2,1) one, (II), in 36% yield.

Tetrachlorobenzynes, generated from pentachlorophenyl lithium gave a good yield of crystalline material with bicyclohepta (2,2,1) diene. This was shown to be a mixture of hexachlorobenzene and two other components by analytical thin-layer chromatography on silica gel/silver nitrate. Column chromatography on silica gel/silver nitrate gave hexachlorobenzene, exo - 3, 4 - tetrachlorobenzotricyclo (4.2.1.0.^{2,5}) nona - 3, 7 - diene, (III), (50%) and tetrachlorobenzonortricyclene, (IV), (22%). The structure of (III), was assigned on the basis of elemental analysis, ir. and n.m.r. spectra, and the fact that (I) was obtained on hydrogenation of (III) in the presence of a palladium/carbon catalyst. The structure of (IV) was assigned on the following evidence. Elemental analysis and molecular weight determination showed the compound to be isomeric with (III). The absence of resonance due to olefinic protons in the p.m.r. proved that one additional ring was present in (IV) as compared with (III). The symmetrical nature of (IV) was evident from the relative simplicity of the p.m.r. spectrum.

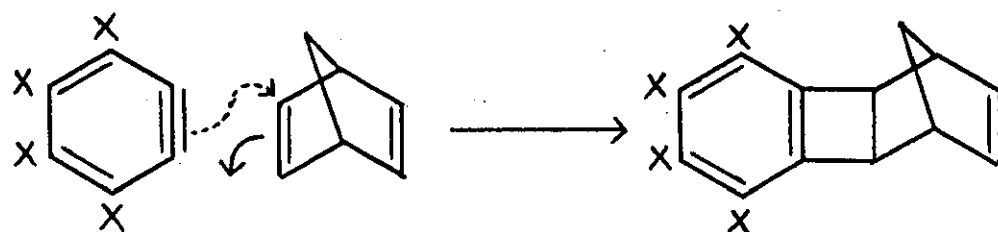
The analogous compounds were isolated from the reaction of tetrafluorobenzynes with bicyclohepta (2,2,1) diene, the nortricyclene adduct, (VI), in 6% yield, and the 1, 2 adduct, (V), in 24% yield.

The possible mechanisms of formation of these adducts were interesting. The most likely mechanism of formation of the nortricyclene adducts involves concerted addition of the aryne



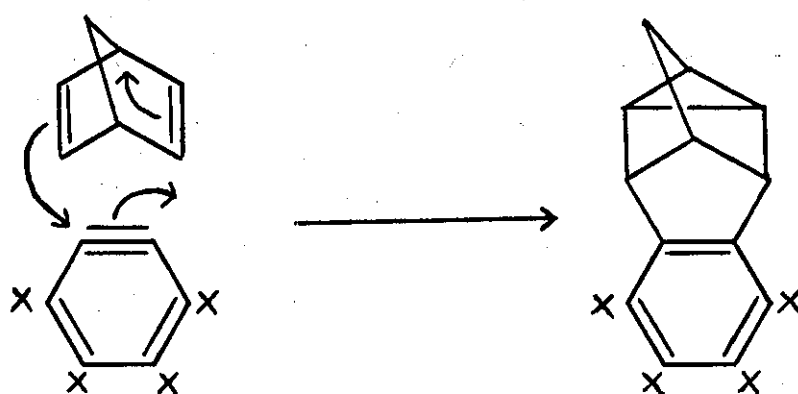
I, X = Cl

II, X = F



III, X = Cl

V, X = F

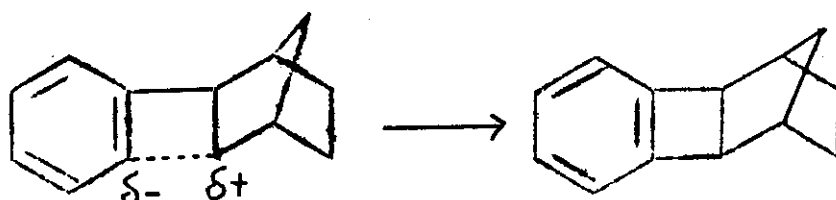


IV, X = Cl

VI, X = F

Scheme 1

across the 2 and 6 positions of the homoconjugated diene, the arynes attacking from beneath the diene, i.e. from the endo position. The similar additions of maleic anhydride and tetracyano-ethylene were suggested as occurring by a concerted mechanism.⁷⁵ However, the formation of the 1, 2 addition products should occur by a non - concerted mechanism, on the basis of the Woodward - Hoffmann rules, which forbid concerted $2 + 2$ thermal additions.⁴⁸ Moriconi and Kelly have obtained $2+2$ adducts with chlorosulphonyl isocyanate and a variety of compounds,⁷⁶ including bicyclohepta (2,2,1) ene and bicyclohepta (2,2,1) diene.⁷⁷ In one of their communications,⁷⁶ they reiterate the suggestion of Graf,⁷⁸ that the addition of chlorosulphonyl isocyanate to a double bond occurs by a pseudo-concerted reaction,⁷⁹ involving a 1, 4 dipolar species, in which the charged species are aligned for bonding. They suggest that this species then collapses to the products so fast, as to forbid rotation and give stereospecific products. This mechanism could be operating in the reactions of arynes with bicyclohepta (2,2,1) diene and bicyclohepta (2,2,1) ene. A rapid collapse of the 1, 4 dipolar species to 1, 2 adduct, would prevent rearranged products from being formed. It is interesting to note at this point, that Japanese workers have recently reported the non-stereospecific additions of benzyne to vinyl ethers.⁸⁰ Another possible mechanism for these reactions, could be a near - concerted process,⁸¹ in which no formal charges are present in the intermediate, i.e.



Since it is virtually impossible to distinguish between these two mechanisms practically, further speculation is pointless. However, we suggest that one of these mechanisms is operating rather than a concerted mechanism as originally suggested by Simmons.³¹

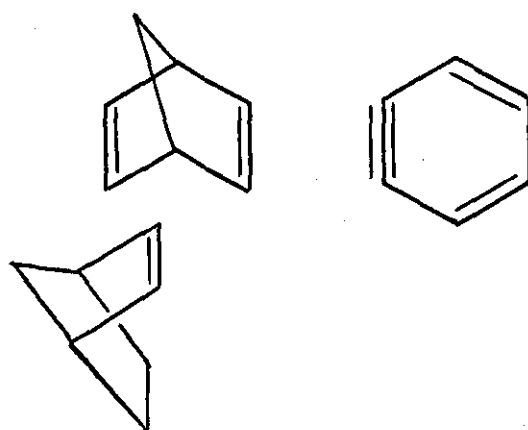
In an attempt to investigate these reactions further, we varied the conditions of the original reaction between tetrafluorobenzene and bicyclohepta (2,2,1) diene. Firstly, the reaction was repeated using cyclohexane as solvent instead of diethyl ether. This gave a ratio of nortricyclene to 1, 2 adduct, of 1:4, compared to a ratio of 1:6 obtained when ether was the solvent. Secondly, the tetrafluorobenzene was generated from pentafluorophenyl magnesium bromide in bicyclohepta (2,2,1) diene, and the ratio of adducts was now 1:5 in favour of the 1, 2 adduct. The first result showed that a solvent effect occurs in going from a bicycloheptadiene/cyclohexane to a bicycloheptadiene/ether solvent. A 1, 4 dipolar species would be more easily formed in the more polar solvent, ether, and consequently an increase in the ratio of 1, 2 to nortricyclene

adducts would be expected. This increase was in fact observed. The Grignard precursor result is difficult to interpret, since both solvent and temperature effects are involved.

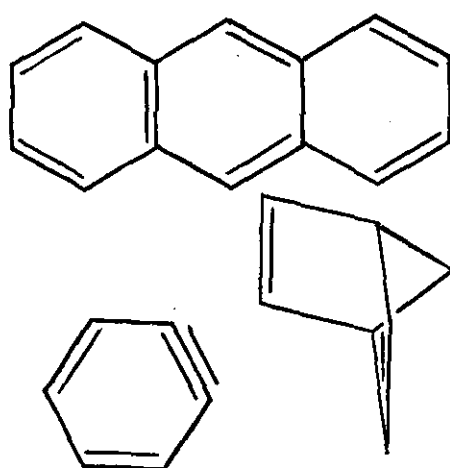
Shortly after the above work had been published in preliminary form,⁸² Friedman reported obtaining a nortricyclene adduct from the reaction of bicyclohepta (2,2,1) diene with benzyne generated from benzene diazonium - 2- carboxylate.⁸³ He also claimed to have observed interesting effects with this reaction. Firstly, when excess equimolar quantities of bicyclohepta (2,2,1) diene and bicyclohepta (2,2,1) ene were together reacted with benzyne, only two adducts were obtained, namely the 1, 2 adducts of bicyclohepta (2,2,1) diene and bicyclohepta (2,2,1) ene with benzyne. None of the nortricyclene adduct was detected. Secondly, the addition of anthracene to the reaction of benzyne and bicyclohepta (2,2,1) diene resulted in 1, 2 adduct formation being eliminated. The only product isolated from the reaction, in addition to triptycene, was the nortricyclene adduct.

Friedman suggested that these results might be explained by the participation of charge-transfer complexes in the reactions. In the reaction of benzyne with bicyclohepta (2,2,1) diene and bicyclohepta (2,2,1) ene, the nortricyclene adduct might be prevented from forming by the initial production of a charge-transfer complex between bicyclohepta (2,2,1) diene and bicyclohepta (2,2,1) ene. This could be orientated such that the bicyclohepta (2,2,1) ene double bond sits between the double bonds of the bicyclohepta

(2,2,1) diene (see scheme 3), thus preventing the 'underside' attack of the benzyne necessary for the formation of nortricyclene adduct. In the case of the anthracene, a double bond of the bicyclohepta (2,2,1) diene sits across the anthracene (see scheme 4) which acts as a diene, and prevents benzyne from attacking the 1, 2 positions. We have investigated these effects in the reactions of tetrachloro and tetrafluorobenzyne with bicyclohepta (2,2,1) diene. Tetrafluorobenzyne, generated from pentafluorophenyl lithium, was reacted with bicyclohepta (2,2,1) diene in ether solution, in the presence of an equimolar quantity of bicyclohepta (2,2,1) one and varied quantities of anthracene. When the product mixtures were analysed by G.L.C., the ratios of nortricyclene, (VI) to 1, 2 adduct, (V), were identical in all of the reactions to those obtained in the original reaction with bicyclohepta (2,2,1) diene only, i.e. 1:6. Tetrachlorobenzyne, generated from pentachlorophenyl lithium was also reacted with bicyclohepta (2,2,1) diene in the presence of bicyclohepta (2,2,1) one and anthracene, and again the ratios of nortricyclene, (IV), to 1, 2 adduct, (III), were found to be identical to those of the original reaction with tetrachlorobenzyne and bicyclohepta (2,2,1) diene only, namely 1:2. In all of the reactions, the corresponding bicyclohepta (2,2,1) one 1, 2 adducts, (I and II), and tetrahalotriptycenes were detected.



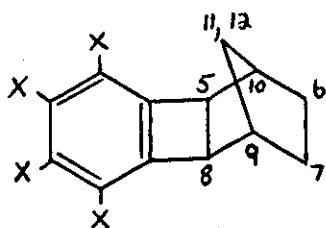
Scheme 3



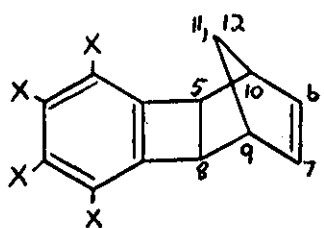
Scheme 4

In order to approach Friedman's reaction conditions more closely, the tetrachlorobenzyne reactions were repeated, with the benzyne generated from tetrachlorobenzenediazonium - 2 - carboxylate. The ratios of nortricyclene, (IV), to 1, 2 adduct, (III), were again identical to those obtained from the lithio-compound reactions and a simple reaction between tetrachlorobenzyne generated from the diazonium carboxylate and bicyclohepta (2,2,1) diene, namely 1:2.

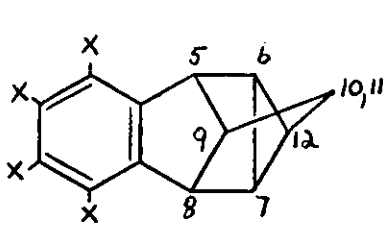
¹H n.m.r.



I and II



III and V



IV and VI

Compound	Chemical Shift(s) and Coupling Constants (J)				
I X=Cl	H _{5,8} 6.8s	H _{9,10} 7.54*	H _{6,7} 8.2-8.88m	H _{11,12} 8.88-9.12m	
II X=F	H _{5,8} 6.77s	H _{9,10} 7.59*	H _{6,7} 8.05-8.8m	H _{11,12} 8.8-9.1m	
III X=Cl	H _{6,7} 3.8t	H _{5,8} 6.9s	H _{9,10} 7.07*	H ₁₁ 8.42-8.75d J ₁₁₋₁₂ =10c/s	H ₁₂ 9.0-9.27d J ₁₂₋₁₁ =10c/s
IV X=Cl	H _{5,8} 6.61*	H ₉ 7.58*	H ₁₂ 8.05t J _{12-6,7} =6c/s	H _{10,11} 8.28*	H _{6,7} 8.58d J _{6,7-12} =6c/s
V X=F	H _{6,7} 3.77t	H _{5,8} 6.82s	H _{9,10} 7.05*	H ₁₁ 8.35-8.45d J ₁₁₋₁₂ =10c/s	H ₁₂ 8.9-9.18d J ₁₂₋₁₁ =10c/s
VI X=F	H _{5,8} 6.58*	H ₉ 7.55*	H ₁₂ 8.04t J _{12-6,7} =6c/s	H _{10,11} 8.21*	H _{6,7} 8.58d J _{6,7-12} =6c/s

s=singlet, d=doublet, t=triplet, m=multiplet, *=unresolved.

EXPERIMENTAL

All General Methods are as reported in Section 1, (experimental).

Reaction of tetrachlorobenzene with bicyclohepta (2,2,1) ene

Bicyclohepta (2,2,1) ene (9.4g. = 0.1 moles) was added to a solution of pentachlorophenyl lithium (0.04 moles) in ether (500ml.) at -20°C. The ether was partly removed by distillation, and replaced by petrol (80/100°C) until the vapour temperature reached 50°C., and the mixture was then heated under reflux for 12hr. Hydrolysis (method 2), followed by drying of the organic layer and removal of solvents gave a brown oil (11.6g.), which was eluted from a short alumina column with petrol (60/80°C.) to give a white crystalline product (7.4g.). Column chromatography of this product on neutral alumina gave hexachlorobenzene, (4.0g.), bicyclohepta (2,2,1) ene, (0.30g.) and exo - 3,4 - tetrachlorobenzotricyclo (4,2,1,0^{2,5}) non - 3 - ene, (1), (25%), m.p. 110°C, (from ethanol), ν_{\max} 2965, 2880, 1470, 1450, 1370, 1310, 1275, 1230, 1200, 1160, 1135, 1105, 1080, 960, 910, 820, 775, 720, 640 CM.⁻¹.

Found: C, 50.0; H, 3.3; Cl, 46.25;

C₁₃H₁₀Cl₄ requires C, 50.7; H, 3.3; Cl, 46.0%

Reactions of tetrachlorobenzene generated from pentachlorophenyl lithium with bicyclohepta (2,2,1) diene

Elution of the initial crude product (13.5g.) from a short alumina column with petrol (60/80°C) gave a white crystalline product (10.2g.).

Analytical gas chromatography showed the presence of hexachlorobenzene and two other products in the mixture. Thin layer chromatography on silver nitrate/silica gel⁸⁴ separated the components, and column chromatography of the mixture on silica gel/silver nitrate gave three fractions, hexachlorobenzene, 1, 2, 3, 4 - tetrachlorobenzonortricyclene, (IV), (22%), m.p. 190°C, (from ethanol), ν_{\max} 3015, 2965, 2950, 2870, 1450, 1400, 1370, 1345, 1300, 1240, 1210, 1150, 825, 795, 750, 685 cm^{-1} .

Found: C, 50.7, H, 2.9; Cl, 46.3;

$\text{C}_{13}\text{H}_8\text{Cl}_4$ requires C, 51.0; H, 2.65; Cl, 46.35%. and exo - 3, 4 tetrachlorobenzotricyclo (4.2.1.0^{2,5}) nona - 3, 7 - diene, (III), (50%), m.p. 102°C, (from ethanol), ν_{\max} 3035, 3000, 2980, 2960, 2960, 2890, 1625, 1400, 1370, 1320, 1290, 1270, 1200, 1190, 1130, 820, 790, 700, 680 cm^{-1} .

Found: C, 50.8; H, 3.0; Cl, 46.35%.

In two similar separate reactions, A and B, anthracene, (17.8g. = 0.1 mole), (reaction A) and bicyclohepta (2,2,1) ene, (9.4g. = 0.1 mole), (reaction B), were added to the starting materials. G.L.C. analysis of reaction A at 200°C. on a 5ft. S.E. 52 column showed both (III) and (IV) to be present in a ratio of 2.2:1. T.L.C. on silica gel showed the presence of tetrachlorotriptycene in the mixture. G.L.C. analysis of reaction B showed (I), (III), and (IV) to be present in ratios of 1.6:2.0:1. It was established that (I), (III), and (IV) had identical G.L.C. response, by comparing

standard samples with the peak areas.

Reactions of tetrachlorobenzene generated from tetrachloroanthranilic acid with bicyclohepta (2, 2, 1) diene

Tetrachloroanthranilic acid (1.38g. = 0.005 moles) in dry ether (50ml.) was added over 20 min. to a solution of iso-amyl nitrate (5ml.) and bicyclohepta (2, 2, 1) diene (9.2g. = 0.1 moles) kept at 45°C. The mixture was warmed at 50°C. for $\frac{1}{2}$ hr., the solvents and excess iso-amyl nitrate then removed under reduced pressure, and the brown residue eluted from a short alumina column with petrol (60/80°C) to give a white crystalline solid (400mg.). This was shown to contain (III) and (IV) in a ratio of 1.85:1 which represented overall yields of 17% (III) and 9.2% (IV). In two similar reactions, C and D, anthracene (17.8g. = 0.1 moles), (reaction C), and bicyclohepta (2,2,1) ene, (9.4g. = 0.1 moles), (reaction D) respectively were added to the reaction mixture before addition of the anthranilic acid. G.L.C. analysis of reaction C showed (III) and (IV) present in a ratio of 1.95:1.0, while G.L.C. of reaction D showed (I), (III), and (IV) present in ratios of 1.6:1.9:1.0.

Reaction of tetrafluorobenzene with bicyclohepta (2, 2, 1) ene

Bicyclohepta (2, 2, 1) ene, (18.8g. = 0.2 moles) was added to a solution of pentafluorophenyl lithium (0.05 moles) at -40°C. After the reaction mixture had warmed up to and stood at

room temperature overnight, it was hydrolysed (method 2) and the organic layer dried. The solvent was removed by fractional distillation, and the yellow liquid was eluted from a short alumina column to give a colourless oil containing two minor and one major component, as shown by G.L.C. analysis on a 5ft. S.E. 30 column, programmed from 100° to 170°C. The components were separated by preparative G.L.C. on a 10ft. Silicone column at 200°C. The minor components were identified as 4-bromo-nonafluorobiphenyl, and 2,2,1 3,3,1 4,4,1 5,5¹,6 - nonafluorobiphenyl by comparison of their G.L.C. retention times and ¹⁹F n.m.r. spectra with those of standard samples.⁸⁵ The major product was exo - 3,4 - tetrafluorobenzotricyclo (4.2.1.0^{2,5}) non-3-ene, (II), (36%), colourless oil, ν_{\max} 2970, 2880, 1490, 1400, 1290, 1260, 1200, 1165, 1140, 1080, 1000, 960, 930, 910, 860, 805, 765, 755, 650 cm^{-1}

Found: C, 63.65; H, 4.01; F, 31.7

$\text{C}_{13}\text{H}_{10}\text{F}_4$ requires C, 64.5; H, 4.15; F, 31.4%.

Reaction of tetrafluorobenzynes generated from pentafluorophenyl lithium with bicyclohepta (2,2,1) diene

Bicyclohepta (2,2,1) diene (18.4g. = 0.2 moles) was added to a solution of pentafluorophenyl lithium (0.05 moles) in ether (200mls.) at -40°C. After hydrolysis (method 2), drying of the organic layer, and removal of solvents by fractional distillation, the product was eluted through a short alumina column with petrol

(60/80°) and gave a yellow oil (5.0g.). This was shown by analytical G.L.C. to contain two major products, which were separated by preparative G.L.C. and gave exo-3,4-tetrafluorobenzotri-cyclo (4,2,1,0^{2,5}) nona-3,7- diene, (V), (24%), m.p. 70°C,

(from ethanol), ν_{\max} 3085, 3000, 2980, 2890, 1650, 1575, 1485, 1400, 1325, 1280, 1265, 1185, 1135, 1100, 1080, 1060, 1000, 985, 960, 915, 895, 820, 780, 720, 655 cm^{-1}

Found: C, 64.85; H, 3.4; F, 32.0

$\text{C}_{13}\text{H}_8\text{F}_4$ requires C, 65.0; H, 3.35; F, 31.65%

and tetrafluorobenzonortricyclene, (VI), (4%), m.p. 78°C,

(from ethanol), ν_{\max} 3020, 2965, 2950, 2870, 1490, 1400, 1295, 1270, 1205, 1150, 1115, 1085, 1050, 1030, 975, 955, 940, 890, 820, 800, 780, 685 cm^{-1}

Found: C, 65.0; H, 3.5; F, 31.2%

In four similar reactions, E, F, G, and H, the following conditions were altered: in reaction E, the diethyl ether was replaced by cyclohexane; anthracene, (0.5 moles) and (0.2 moles), was added to reaction mixtures F and G respectively, and bicyclohepta (2,2,1) ene (0.2 moles) was added to reaction mixture H. In reaction E, the ratio of (VI) to (V) was found to be 1:4, the yields of adducts being 27.0% (V) and 6.8% (VI). In reactions F, G and H, G.L.C. analysis showed that the ratio of (VI) to (V)

was 1:6 in each case. In reactions F and G, tetrafluorotriptycene⁴¹ was shown to be present by comparison with a standard G.L.C. sample.⁸⁵ In reaction H, the ratio of (II) to (VI) was found to be 4:1.

Reaction of tetrafluorobenzene generated from pentafluorophenyl magnesium bromide with bicyclohepta (2,2,1) diene

Pentafluorobromobenzene (12.4g. = 0.05 moles) was added to magnesium turnings (1.34g. = 0.055 moles) and ether (50ml.). A few drops of 1, 2 dibromoothane were added to the mixture and after the reaction had subsided, the mixture was heated at 30°C until all the magnesium had reacted. The ether was gradually removed by distillation, and replaced by bicyclohepta (2,2,1) diene until the vapour temperature of the mixture reached 80°C and the mixture was heated under reflux for 5 hr. The mixture was hydrolysed (method 1) and the organic layer separated, dried, and the solvents removed to leave a black oil. Elution of this material from a short column of alumina with petrol (60/80°C), gave a yellow oil (6.5g.) which was found to contain (V) and (VI) in a ratio of 5:1, by analytical G.L.C.

Reductions

Compound (III), (100mg.) in ethanol (50 ml.) was reduced by hydrogen in the presence of palladium on carbon catalyst. After removal of catalyst and solvent, the residue gave (I), (100mg., 100%)

Compound (V) gave compound (II) in a similar reduction.

SECTION 4.

The Reactions of Tetrachlorobenzene with Aliphatic Ethers.

INTRODUCTION

Ethers have been widely used for many years as solvents for reactions involving arynes; yet no products resulting from the cleavage of ether linkages by arynes have been reported. This is not surprising since most aryne reactions have been carried out in the presence of much stronger nucleophiles than the ether. Into this category would come not only co-reactants, but aryne precursors, such as organometallic reagents. The cleavage of thio-ethers by benzyne have been recently reported,⁸⁶ and we anticipated that the more electrophilic tetrahalogenobenzyne, might cleave simple aliphatic ethers in the absence of a stronger nucleophile. The cleavage of aromatic ethers by tetrahalogenobenzyne is not observed, since the aryne attacks the nucleophilic aromatic π - system, and 1, 4 addition products are formed.^{41, 87}

DISCUSSION

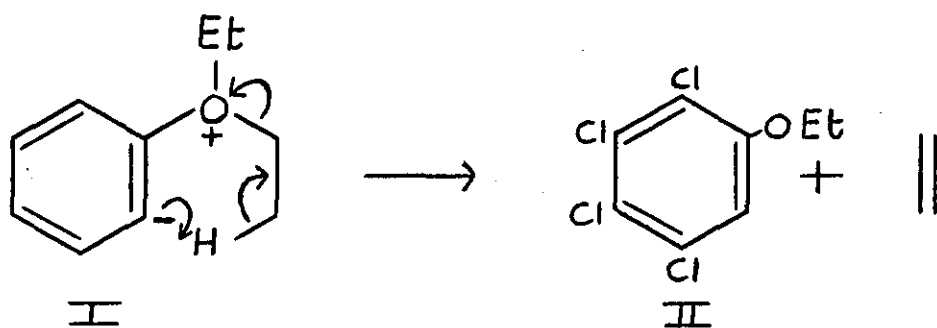
Tetrachlorobenzyne was generated by aprotic diazotisation of tetrachloroanthranilic acid, in the presence of carefully purified diethyl ether. After work up, the initial product was column chromatographed on alumina and 2, 3, 4, 5 - tetrachlorophenetole,⁸⁸ (II), (63%), and 2, 3, 4, 5 - tetrachlorophenyl - 3¹ methyl - butyl ether, (III), (10%) were obtained. The latter product presumably arose by the addition of 3-methylbutan - 1 - ol to tetrachlorobenzyne. 3-Methylbutyl nitrate (iso-amyl nitrate) was used as the source of nitrosating agent in the aprotic diazotisation.

Two mechanisms were possible for the formation of the tetrachlorophenetole; abstraction of a proton β - to the oxygen, by an initially formed betaine, (1), followed by elimination of ethylene (mechanism 1), or abstraction of a proton from solution by the initially formed betaine and loss of ethyl carbonium ion or an equivalent process (mechanism 2). Both these mechanisms are outlined in Scheme 1.

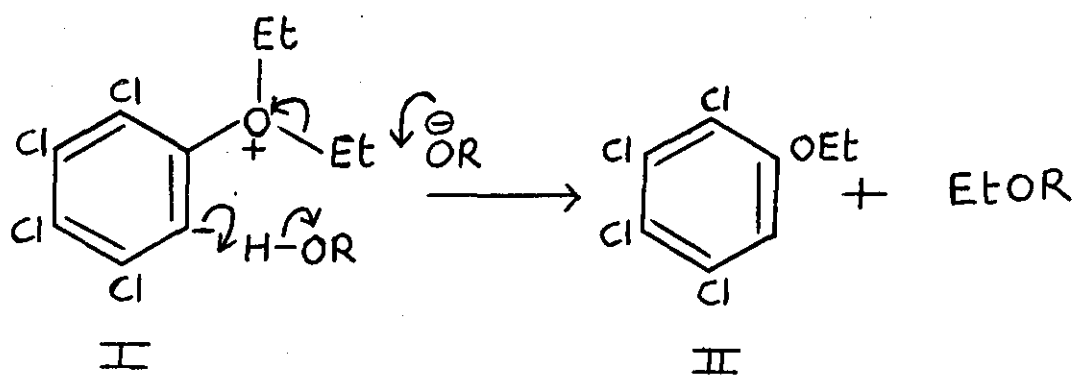
These mechanisms could be substantiated by either detecting an olofin in the reaction mixture, or proving that the aryl proton in the product is derived from the reaction medium. Since the most readily available protons in the reaction medium are those arising from the anthranilic acid, the diethyl ether cleavage was repeated, using tetrachloroanthranilic acid, which had the protons replaced by deuterium. The tetrachlorophenetole obtained from the reaction was found to contain no aryl deuterium, by comparison of the integrated ^1H n.m.r. trace with that of the standard sample.

In an attempt to detect any ethylene generated from the cleavage of the diethyl ether, the reaction gases were blown through a solution of bromine in carbon tetrachloride. After removal of excess bromine, the solution was analysed by G.L.C. but no 1,2-dibromoethane was detected in the solution.

If mechanism 1 was operating, unsymmetrical ethers, in which one of the alkyl groups contained no β hydrogens, should cleave to give only one tetrachlorophenyl alkyl ether. However,



Mechanism 1



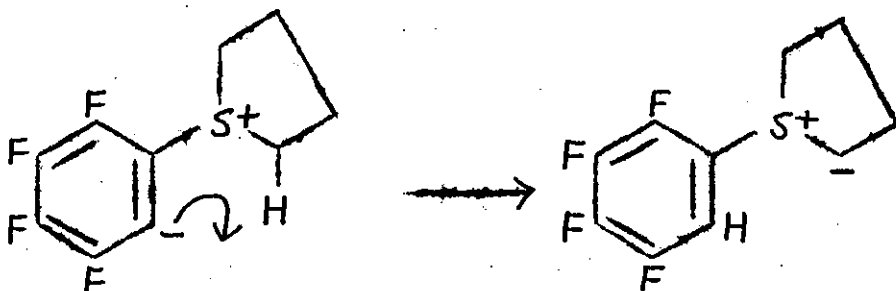
Mechanism 2

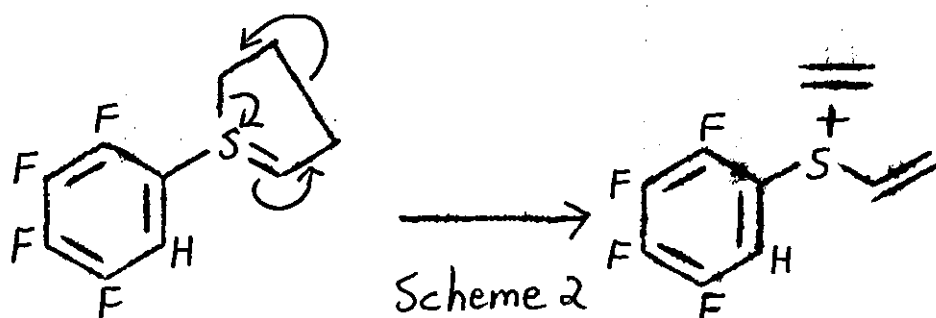
Scheme 1

mechanism 2 would not necessarily lead to the exclusive formation of one product.

We investigated these points by cleaving methyl tert-butyl, methyl n-butyl, and methyl cyclohexyl ethers, with tetrachlorobenzene. Examination of the products by analytical G.L.C., and comparison with standards of the possible cleavage products showed that all of these ethers were cleaved to give exclusively 2, 3, 4, 5 - tetrachloroanisole.⁸⁹ Cyclohexene was isolated in the case of the reaction with cyclohexyl methyl ether, and was identified by comparison with a standard sample using G.L.C. No cyclohexene was present in the cyclohexyl methyl ether used for the cleavage. We conclude from this result that mechanism 1 is operating in the reactions of tetrachlorobenzene with aliphatic ethers.

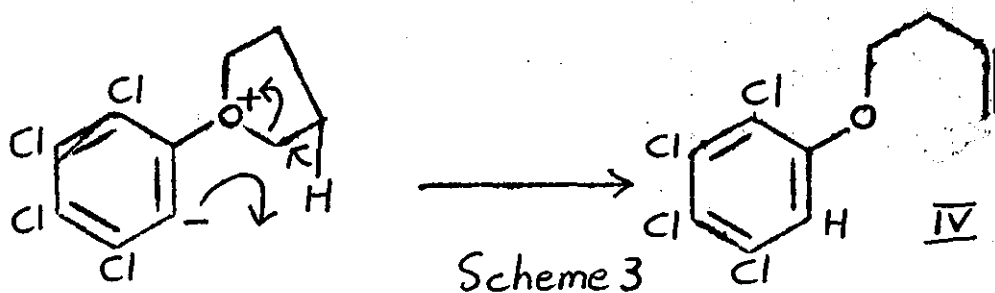
The abstraction of an α - proton to form an ylid is well known with thioethers,⁹⁰ and Brewer has shown that tetrafluorobenzene reacts with tetrahydrothiophene to yield 2, 3, 4, 5 - tetrafluorophenyl vinyl sulphide.⁹¹ The driving force for the abstraction of a proton α - to a positively charged sulphur would be the formation of an ylid, viz.





With oxygen, the absence of suitable d- orbitals would presumably preclude a similar reaction with tetrahydrofuran. However, since scale molecular models indicated that the abstraction of a proton β - to oxygen in a betaine derived from an arylmagnesium and tetrahydrofuran would be difficult, we decided to investigate the reaction of tetrachlorobenzene with tetrahydrofuran.

After work up, the major product from this reaction was found to be the 2, 3, 4, 5 - tetrachlorophenyl - 3¹ methyl-butyl ether, (III). A small quantity of an unknown compound, (IV), was detected by G.L.C., and reduction of the crude reaction mixture in the presence of palladium on carbon was shown to reduce this unknown compound, (IV), to 2, 3, 4, 5 - tetrachlorophenyl-n-butyl ether, (V), by comparison with a standard sample on G.L.C. columns of widely differing polarities. It is reasonable to assume that compound (IV) was the ether cleavage product of the T.H.F., namely 2,3,4,5 - tetrachlorophenyl-but-3-enyl ether (scheme3).



This result showed that little cleavage of tetrahydrofuran occurs with tetrachlorobenzene, and the cleavage that does occur involves the usual six-centered transition state associated with mechanism 1.

¹H n.m.r. Spectra

Compound	Chemical Shifts and Coupling Constants				
	A	B	C	D	E
	3.07 s	6.11 s			
	3.13 s	8.4-8.64 t J _{BC} = 7.02	5.76-6.11 q		
	3.08 s	8.58 s			
	3.10 s	8.82-9.22 t	8.1-8.82 m	8.1-8.82 m	5.82-6.17 m
	3.09 s	8.82-9.22 d J _{BC} = 6.0	5.82-6.17 m	7.92-8.54 m	5.82-6.17 m

s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet

EXPERIMENTALGeneral Methods

All ethers were purified by repeated fractional distillations from LiAlH_4 . Other general methods are as described in Section I (experimental).

Reactions of tetrachlorobenzene with ethers

(a) Diethyl ether. - Tetrachloroanthranilic acid (2.8 g. = 0.1 moles) in diethyl ether (50 ml.) was added to a solution of iso-amyl nitrate (5 ml.) in diethyl ether (150 ml.) at 38°C over a period of $\frac{1}{2}$ hr. The reaction gases were blown through bromine in carbon tetrachloride by a slow stream of nitrogen, but no 1, 2 - dibromoethane was detected by G.L.C. The solvents of the reaction mixture were removed by distillation to give a brown oil (3.0 g.), which was column chromatographed on neutral alumina using petrol ($60/80^\circ\text{C}$) as eluent, to give 2,3,4,5 - tetrachlorophenyl, ethyl ether, (II), (63%) m.p. 55°C , (from ethanol), (lit.⁸⁸ m.p. 56°C), ν_{max} 3070, 2980, 2910, 1570, 1540, 1430, 1385, 1355, 1280, 1175, 1100, 1050, 875, 815, 735 cm^{-1} .

Found: C, 37.2; H, 2.65; Cl, 54.4

Calculated for $\text{C}_8\text{H}_6\text{Cl}_4\text{O}$: C, 36.95; H, 2.35; Cl, 54.55% and

2,3,4,5 - tetrachlorophenyl, 3¹ - methyl - butyl, ether, (III), (10%), m.p. 62°C , ν_{max} 3030, 2950, 2860, 1565, 1540, 1430, 1385, 1360, 1285, 1245, 1180, 1100, 1055, 1000, 850, 835, 740 cm^{-1}

Found: C, 43.6; H, 3.95; Cl, 46.7

$C_{11}H_{12}Cl_4O$ requires C, 43.75; H, 4.0; Cl, 46.95%

(b) Reactions of tetrachlorobenzene with n-butyl, t-butyl and cyclohexyl methyl ethers.

These reactions were carried out similarly. The products from the reactions were analysed by G.L.C. at 170°C on a 5ft. silicone column (2% S.E. 30) and the chromatographs were compared with standards prepared independently. Tetrachloroanisole, (VI), and tetrachlorophenyl, 3^l - methyl butyl ether, (III), were the only ethers detected in each of the reactions.

In the reaction of tetrachlorobenzene with cyclohexyl methyl ether, column chromatography on alumina gave a fraction which was shown by G.L.C. at 70°C on silicone (S.E. 30, 10%) apiezon -L (10%) and polythene glycol adipate (10%) columns, to contain cyclohexene by comparison with a standard sample. No. cyclohexene could be detected by G.L.C. in the methyl cyclohexyl ether used as starting material.

Reactions of tetrachlorobenzene with (a) methanol, (b) n-butanol, and (c) t-butanol

Tetrachloroanthranilic acid (1.4g. = 0.005 moles) in acetone (20 ml.) was added to a solution of iso-amyl nitrate (5 ml.) and the alcohol (15 ml.) in dichloromethane (150 ml.) at 40°C. Removal of the solvents by distillation and column chromatography of the products on neutral alumina using petrol (60/80°C) as eluent, gave:-

(a) 2,3,4,5 - tetrachlorophenyl, methyl ether, (VI), (52%), m.p. 82°C, (lit.⁸⁹ m.p. 83°C), (from cyclohexane), ν_{\max} 3090, 2955, 2860, 1575, 1465, 1425, 1400, 1360, 1290, 1250, 1180, 1100, 1050, 850, 730 cm^{-1} .

Found: C, 34.4; H, 2.0; Cl, 57.45

Calculated for $\text{C}_7\text{H}_4\text{Cl}_4\text{O}$: C, 34.2; H, 1.65; Cl, 57.7%

(b) 2,3,4,5 - tetrachlorophenyl, n-butyl ether, (V), (28%), colourless oil, ν_{\max} 3095, 2960, 2880, 1575, 1465, 1440, 1390, 1360, 1245, 1180, 1100, 1065, 1035, 935, 830, 740 cm^{-1} .

Found: C, 41.5; H, 3.75; Cl, 50.6

$\text{C}_{10}\text{H}_{10}\text{Cl}_4\text{O}$ requires: C, 41.7; H, 3.5; Cl, 50.35% (c) 2,3,4,5 - tetrachlorophenyl, t-butyl-ether, (VII), (46%), colourless oil, ν_{\max} 3090, 2990, 2940, 2880, 1570, 1535, 1465, 1415, 1395, 1365, 1260, 1160, 1100, 1030, 990, 875, 845, 825, 750, 690, 640 cm^{-1} .
Found: C, 41.35; H, 3.8; Cl, 50.4%.

Reaction of tetrachlorobenzene with tetrahydrofuran

Tetrachloroanthranlic acid (5.6 g. = 0.02 moles) in tetrahydrofuran (100 ml.) was added to a solution of iso-amyl ^{nitrite} ~~nitrate~~ (7 ml.) in tetrahydrofuran (200 ml.) at 40°C. After the solvents had been removed by distillation, the crude product (6.2 g.) was dissolved in chloroform and analysed by G.L.C. at 180°C on a 5ft. silicone (2% S.E. 30) column. The only volatile components were compound (III) and an unknown compound, (IV). The chloroform was removed, and the crude mixture dissolved in sulphur-free benzene, and reduced with hydrogen at atmospheric pressure using palladium on carbon as catalyst.

G.L.C. examination of the products showed compounds (III) and (V) to be present, but the peak due to (IV) had disappeared.

Deuteration of tetrachloroanthranilic acid

A suspension of tetrachloroanthranilic acid (2.8 g. = 0.01 moles) and anhydrous potassium carbonate (2.1 g. = 0.015 moles) in deuterium oxide was heated at 60°C for 24 hr. in a dry atmosphere. The free acid was liberated by the addition of deuterium chloride to the mixture.

The process was repeated until the tetrachloroanthranilic acid contained no protons, as indicated by ^1H n.m.r. and ir. spectroscopy.

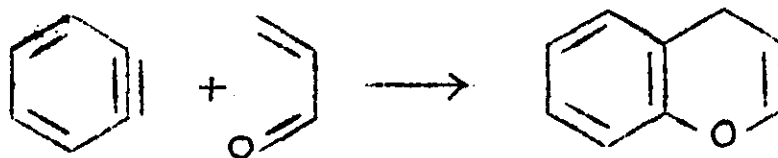
SECTION 5.

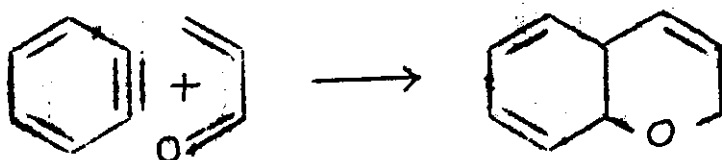
The Reactions of Tetrachlorobenzene with Acrolein
and Crotonaldehyde.

INTRODUCTION

The Diels-Alder condensation between α,β unsaturated carbonyl compounds and common dienophiles has been fairly widely studied.⁹² Acrolein, crotonaldehyde, methyl vinyl ketone, benzalacetone and certain other compounds have been used as heterodienes, and several ethylenic hydrocarbons, vinyl and allyl ethers, esters of acrylic acid, acrylonitrile etc., have been used as dienophiles in these condensations. High yields (circa. 80%) have been reported for many of the reactions. It is surprising that no examples of arynes forming Diels-Alder type adducts with α,β unsaturated carbonyl compounds have been reported, since good methods are available for generating arynes in the presence of carbonyl compounds e.g. benzenediazonium - 2 - carboxylate.¹⁸

We decided to investigate the reactions of α,β unsaturated carbonyl compounds with tetrachlorobenzynes, since tetrahalogenobenzyne had generally proved to be more electrophilic than benzyne itself. Addition of an aryne across an α,β unsaturated carbonyl compound would be a novel and possibly useful method of preparing benzopyran derivatives.





DISCUSSION

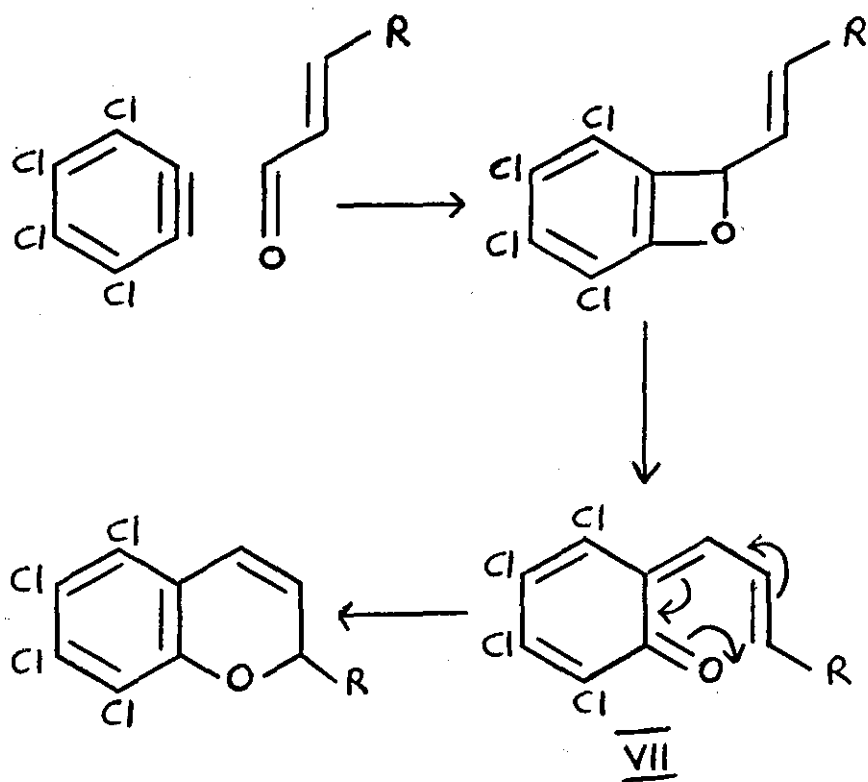
Tetrachlorobenzene was generated by aprotic diazotisation of tetrachloroanthranilic acid in the presence of crotonaldehyde. Column chromatography of the products on neutral alumina using petrol as eluent gave 2,3,4,5 - tetrachlorophenyl, 3¹ - methyl butyl ether (I) (10%) and 5,6,7,8 - tetrachloro-2-methyl-2-H-chromene, (II) (34%).

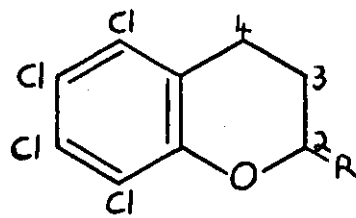
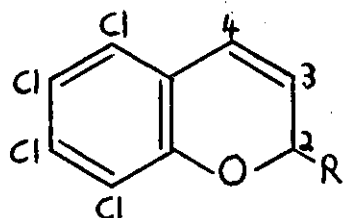
The structure of (II) was assigned on the basis of elemental analysis, ¹H n.m.r., i.r., and uv. spectra, and the fact that reduction of (II) with hydrogen in the presence of palladium on carbon gave 5,6,7,8 - tetrachloro-2-methyl-chroman, (III). The ¹H n.m.r. spectrum of (II) was analysed by first order methods, (see table), and compared with the data quoted for 2-H-chromene,⁹³ and 4-H-chromene.⁹⁴ The ¹H n.m.r. spectrum of the chroman, (III), proved the structure of (II), since spin-spin decoupling experiments

proved that the multiplet centred at τ 5.78 (methine proton) was spin-spin coupled to the methyl group (τ 8.52). The uv. spectrum of compound (II) showed the presence of a styrene type chromophore, which was absent in (III). The ir. spectrum of (II) showed the absence of carbonyl absorption and the presence of a styrene type double bond.

In a similar experiment, acrolein was reacted with tetrachlorobenzene to give 5,6,7,8 - tetrachloro-2-H-chromen, (IV), (17%). Reduction in the presence of palladium on carbon gave the corresponding chroman, (V).

Unless a methyl migration is invoked, it is evident that compounds (II) and (IV) cannot arise via 1, 4 addition of tetrachlorobenzene across the $\alpha\beta$ unsaturated carbonyl system. A possible mechanism for the production of these compounds (see scheme 2) would involve addition of tetrachlorobenzene across the carbonyl group of the reactant, to form a benzoxetene structure, followed by ring opening to give a quinone methide, (VII). This could then give the 2-H-chromen by undergoing an electrocyclic ring closure of the type which Ollis and Sutherland suggested might occur in the biosynthesis of the 2,2-dimethylchromen system.⁹⁵





Compound	Chemical Shifts and Coupling Constants			
	2-H	3-H	4-H	R
IV	5.05 dxd J_{2-3} 3.4 J_{2-4} 1.7	4.0 dxt J_{3-4} 10.3 J_{3-2} 3.4	3.15 dxt J_{4-3} 10.3 J_{4-2} 1.7	
II	4.91 qxdxd J_{2-R} 6.4 J_{2-3} 3.4 J_{2-4} 1.7	4.19 dxd J_{3-2} 3.4 J_{3-4} 10.3	3.32 dxd J_{4-3} 10.3 J_{4-2} 1.7	8.5d J_{R-2} 6.4
V	5.76 t J_{2-3} 5.4	7.9m	7.16 t J_{4-3} 6.8	
III	5.78m	8.0m	7.2m	8.52 d J_{R-2} 6.0

EXPERIMENTAL

All general methods are as reported in Section 1 (experimental).

Reaction of tetrachlorobenzene with crotonaldehyde

Tetrachloroanthranilic acid (5.6 g. = 0.02 moles) in acetone (50 ml.) was added to a mixture of freshly redistilled crotonaldehyde (50 ml.) and iso-amyl nitrate (5 ml.) in dichloromethane (100 ml.) at 40°C. The solvents were removed by distillation, and the yellow oil was eluted from a short column of alumina with petrol (60/80°C) and gave a colourless oil. The product was chromatographed on neutral alumina using petrol (60/80°C) as eluent to give (a) 2, 3, 4, 5 - tetrachlorophenyl - 3¹ - methyl - butyl ether (10%) and (b)

5.6.7.8 - tetrachloro - 2 - methyl - 2 - H - Chromen,

(II) (34%), m.p. 56°C, (from ethanol), ν_{\max} 3070, 2960, 2940, 2860, 1640, 1565, 1450, 1410, 1360, 1320, 1260, 1210, 1170, 1090, 1040, 870, 825, 770, 700 cm^{-1} ,

$\lambda_{\max}(\log_{10} E)$ 233 (4.48); 237.5 (4.49); 245.5 (4.31); 280 (3.85); 290 (3.78) $\text{m}\mu$ (in hexane).

Found: C, 42.2; H, 2.65; Cl, 49.65;

$\text{C}_{10}\text{H}_6\text{Cl}_4\text{O}$ requires C, 42.25; H, 2.15, Cl, 49.9%.

Reaction of tetrachlorobenzene with acrolein

Gave 5. 6. 7. 8 - tetrachloro - 2 - H - chromen, (IV), (17%), m.p. 150°C (from ethanol), ν_{\max} 3070, 2980, 1635, 1560, 1450, 1405, 1360, 1335, 1250, 1220, 1160, 1055, 1010, 960, 890, 850, 760, 685 cm^{-1} $\lambda_{\max}(\log_{10} E)$ 233 (4.36); 237.5 (4.38);

246 (4.17); 231 (3.70); 291 (3.62) $m\mu$ (in hexane).

Found: C, 40.15; H, 1.4; Cl, 52.6

$C_9H_4Cl_4O$ requires: C, 40.0; H, 1.5; Cl, 52.6%.

Reduction of (II)

Compound (II), (100mg.) in ethanol (50 ml.) was reduced by hydrogen at atmospheric pressure in the presence of a palladium on carbon catalyst. After the removal of catalyst and solvent, the residue gave 5, 6, 7, 8 - tetrachloro - 2 - methyl - chroman, (III), m.p.

82°C, (from ethanol), ν_{\max} 2990, 2960, 2950, 2860, 1550, 1440, 1400, 1325, 1190, 1140, 110, 1065, 995, 940, 890, 830, 770, 740, 715, 650 CM^{-1} λ_{\max} ($\log_{10}E$) 226 (4.10) $m\mu$. (in hexane).

Found: C, 42.2; H, 3.2; Cl, 49.3

$C_{10}H_8Cl_4O$ requires C, 42.0; H, 2.8; Cl, 49.6%

Reduction of (N): - Gave 5, 6, 7, 8 - tetrachloro-chroman, (V), m.p.

102°C, (from ethanol), ν_{\max} 2960, 2920, 2850, 1560, 1465, 1430, 1400, 1360, 1315, 1260, 1180, 1065, 1030, 950, 870, 800, 740, 710, 650 CM^{-1} λ_{\max} ($\log_{10}E$) 226 (4.10) $m\mu$. (in hexane)

Found: C, 39.8; H, 2.7; Cl, 51.85

$C_9H_6Cl_4O$ requires C, 39.75; H, 2.2; Cl, 52.1%.

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