

# University of St Andrews



Full metadata for this thesis is available in  
St Andrews Research Repository  
at:

<http://research-repository.st-andrews.ac.uk/>

This thesis is protected by original copyright

NEW REACTIONS INVOLVING SOME  
REACTIVE INTERMEDIATES

A Thesis

presented for the degree of

Doctor of Philosophy

in the Faculty of Science of the

University of St. Andrews

by

Donald Lithgow Brydon, B.Sc.

June, 1967.

United College of St. Salvator  
and St. Leonard, St. Andrews.



I declare that this thesis is my own composition, that the work of which it is a record has been carried out by myself, and that it has not been submitted in any previous application for a Higher Degree.

The thesis describes results of research carried out at the Chemistry Department, United College of St. Salvator and St. Leonard, University of St. Andrews, under the supervision of Professor J.I.G. Cadogan since the 1st October 1964, the date of my admission as a research student.

I hereby certify that Donald Lithgow Brydon, has spent eleven terms at research work under my supervision, has fulfilled the conditions of Ordinance No. 16 (St. Andrews) and is qualified to submit the accompanying thesis in application for the degree of Doctor of Philosophy.

Director of Research.

ABSTRACT

iv

The decompositions of a number of o-substituted N-nitrosoacetanilides in benzene has been investigated. o-Phenyl- and o-carbethoxy-N-nitrosoacetanilide paralleled the anomalous behaviour of o-t-butyl-N-nitrosoacetanilide<sup>78</sup> in that o- and m- substituted phenyl acetates were detected among the products of reaction. The behaviour of N-nitrosoacetanilides with bulky o-groups is rationalised in terms of a rapid expulsion of nitrogen from the intermediate benzenediazonium cation to give a carbonium ion. From the decompositions of o- and p-bromo-N-nitrosoacetanilides the respective dibromobenzenes (ca. 3%) were detected, while from the decompositions of the isomeric iodo-N-nitrosoacetanilides, the corresponding di-iodobenzenes (ca. 20%) were isolated, in addition to the expected products.

N-Nitrosoacetanilide itself, on decomposition in benzene, gave "benzynoid" adducts with the known benzyne traps, 2,3,4,5-tetraphenylcyclopentadienone and 1,3-diphenylisobenzofuran, with suppression of biphenyl formation, but not with furan or anthracene. Phenylazotriphenylmethane, an authentic source of phenyl radicals, did not give an adduct with 2,3,4,5-tetraphenylcyclopentadienone. The formation of benzyne is discounted in the decomposition of N-nitrosoacetanilide and the formation of adducts with the more polarisable arynophiles is interpreted in terms of

a dipolar intermediate which is in equilibrium with precursors of the phenyl radical. Rüchardt's<sup>74,75,76,77</sup> scheme for the decomposition of N-nitrosoacetanilide has been modified to incorporate the equilibrium system.

The isolation of di-iodobenzenes from iodo-N-nitrosoacetanilides prompted extensive investigations which showed that aryl radicals have a strong affinity for iodine in aromatic iodides, and that they abstract iodine from aromatic iodides in a previously unreported homolytic process.

ACKNOWLEDGEMENTS

I should like to thank Professor J.I.G. Cadogan for suggesting the topic of research and for his continued advice and encouragement during the period in which the work was carried out.

In addition, I am indebted to Drs. R.K. Mackie, J.T. Sharp and D.M. Smith for their invaluable advice.

Thanks are also due to the Science Research Council for the award of a Research Studentship for the period during which the work was carried out.

CONTENTS

Page

INTRODUCTION

1) Organic Free Radicals in Solution.	1
2) Sources of Aryl Radicals in Solution.	9
3) Arynes.	26
4) Programme of Research.	33

EXPERIMENTAL

1) Instrumentation.	40
2) Preparation and Purification of Materials.	42
3) Decompositions of Substituted <u>N</u> -nitrosoacetanilides in benzene.	52
4) The Attempted Detection of Benzynoid Intermediates from the Decompositions of Aryl Radical Sources in Solution.	57
5) The Abstraction of Iodine from Aromatic Iodides by Aryl Radicals.	74
6) The Rate of Decomposition of Dibenzoyl Peroxide in Iodobenzene.	90

DISCUSSION

- 1) The Decomposition of Substituted N-nitrosoacetanilides  
in Benzene. 96
- 2) The Attempted Detection of Benzynoid Intermediates  
in the Decomposition of Aryl Radical Sources  
in Solution. 106
- 3) The Abstraction of Iodine from Aromatic Iodides  
by Aryl Radicals. 117

REFERENCES

134

INTRODUCTION

	Page No.
1. <u>ORGANIC FREE RADICALS IN SOLUTION.</u>	1
a) Historical Development.	1
b) Short and Long Lived Radicals.	3
c) Characteristics of Radicals.	5
d) Classification of Reaction in Solution.	6
2. <u>SOURCES OF ARYL RADICALS IN SOLUTION.</u>	9
a) Thermolysis.	9
(i) Diaryl peroxides.	10
(ii) Lead tetrabenzoate and phenyl iodosobenzoates.	14
(iii) Diazo and azo compounds.	15
A) Azo compounds.	15
B) Diazonium compounds.	17
(1) Gomberg Reaction.	17
(2) Diazonium salts.	18
(3) Alkyl nitrite on aromatic amines.	19
C) Acylarylnitrosamines.	19
b) Photolysis.	26
3. <u>ARYNES.</u>	26
a) Historical Development and Evidence of Occurrence.	26
(i) Liquid phase.	26
(ii) Gas phase.	31
b) Structural Considerations.	31
c) Reactions of Arynes.	32
4. <u>PROGRAMME OF RESEARCH.</u>	33

The work to be described in this thesis is concerned with aryl free radicals in solution and aryne intermediates, and there follows a review of these fields up to the present date.

1. ORGANIC FREE RADICALS IN SOLUTION.a) Historical Development

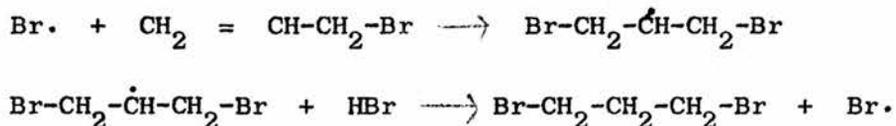
In 1900 the Kekulean concept of the quadrivalency of carbon in organic compounds was seen to require some modification by the discovery of Gomberg<sup>1</sup> that the attempted preparation of hexaphenylethane gave a highly reactive species, which he postulated as the free radical  $\cdot\text{CPh}_3$ . Verification was provided by molecular weight determinations.<sup>2</sup> A 'free radical' or alternatively 'radical' can be defined as an atom or molecule which possesses an unpaired electron in its valence orbitals.

The next milestone was in 1929 when Paneth and Hofeditz<sup>3</sup> established the role of radicals as transient intermediates in chemical reactions by demonstrating the generation of methyl radicals in the pyrolysis of tetramethyl lead. These workers calculated the half-life of the methyl radical under their experimental conditions to be of the order  $10^{-3}$  secs.

The concept of free radicals as intermediates in liquid phase reactions is of more recent development. In 1934, Bäckström<sup>4</sup> postulated aldehyde autoxidation as a free radical chain process and this appears to be the first liquid phase reaction to be definitely ascribed a radical reaction pathway. Grieve and Hey<sup>5</sup>, on isolating biphenyl, 4-chlorobiphenyl, 4-methylbiphenyl and 4-nitrobiphenyl from the decompositions of N-nitrosoacetanilide

and sodium benzenediazotate in benzene, chlorobenzene, toluene and nitrobenzene, rationalised their observations on the basis of the intermediacy of neutral phenyl radicals. At the same time Hey<sup>6</sup> suggested that benzoyl peroxide and phenylazotriphenylmethane were sources of free radicals.

The existence of alternative ionic and radical pathways for a reaction is illustrated by Kharasch and Mayo's<sup>7</sup> observation that if allyl bromide and hydrogen bromide were reacted in the light, or presence of peroxides 1,3-dibromopropane was rapidly produced, whereas when reaction was carried out in the dark with carefully purified reagents the 'Markownikoff product' 1,2-dibromopropane was formed. Some three years later, in 1937, Kharasch<sup>8</sup> et al. and Hey and Waters<sup>9</sup> independently ascribed the formation of the non-ionic product to a radical chain reaction.



Hey and Waters put forward this mechanism in a review of free radical reactions which is now regarded as classic, since it was the first comprehensive collection of radical reactions to be published.

Since that time a vast amount of research has been carried out in this field and the concepts of radicals and homolysis are accepted as corner-stones of chemical theory.

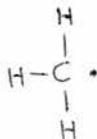
b) Short and Long Lived Radicals.

Radicals in solution can be divided in a purely arbitrary way -into two types; 'long lived' which can be detected at 25° by physical methods such as spectrophotometry, and 'short lived' whose half-life is so short as to preclude such detection. It should be stressed that 'short lived' radicals are transient by virtue of their reactivity and not because of any chemical instability. In a vacuum (1) would be stable.

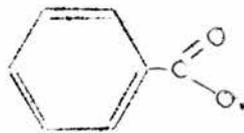
Radicals such as phenyl (1), methyl (2), benzoyloxy (3), and 2-biphenyl (4) are classed as 'short lived'



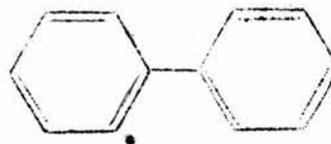
(1)



(2)



(3)



(4)

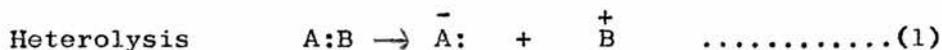
whereas triphenylmethyl (5) and diphenylpicrylhydrazyl (6) are highly stabilised by resonance and are classed as 'long lived' radicals.



c) Characteristics of Radicals.

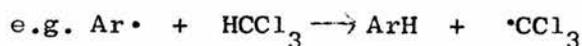
Radicals are highly reactive as a result of their lack of charge which makes electrostatic repulsion forces an insignificant factor compared to ionic species, and as a result of the unpaired electron which releases considerable energy when it forms an electron-pair bond with a substrate. It is noteworthy, in this connection, that no organic compound has been found to be inert to radical attack. The short lifetime of radicals is due to their high reactivity and is not due to any inherent instability.

Ingold<sup>10</sup> in 1938 suggested the following nomenclature for bond fission:

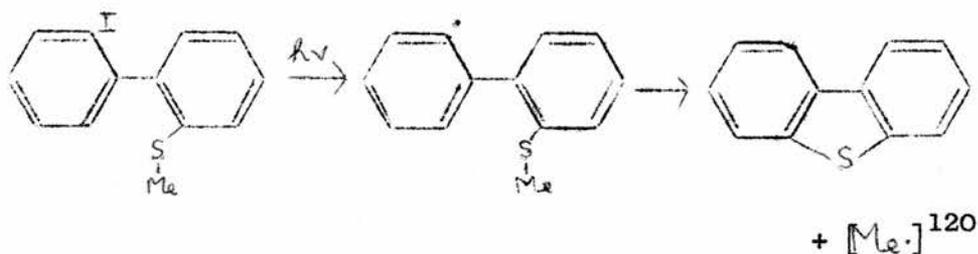


In heterolysis energy is required to separate the charged fragments A and B, but this is offset by the solvation energies of the fragments. Since neutral fragments are formed in homolysis, neither of these energy processes which are based on electrical polarity apply.

From the above considerations, it follows that polar factors are largely absent from homolytic reactions while their heterolytic counterparts are largely governed by such factors.

d. Classification of Reactions in Solution.Reactions involving another moleculea. Abstraction

The group Y is nearly always hydrogen or halogen, whereas the radicals R'· and R· can vary greatly in structure although it is most unusual for R' to be an aryl group.

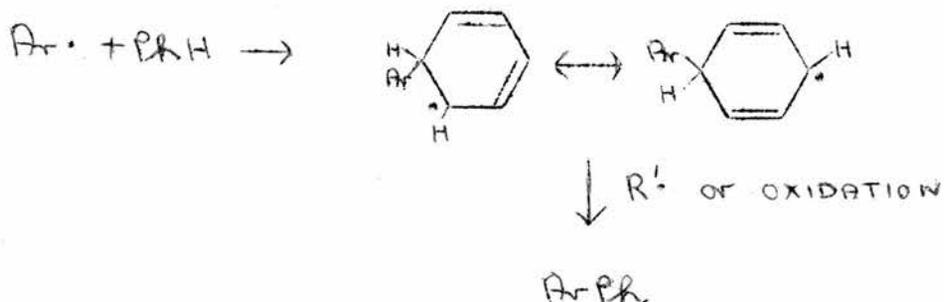
b. Displacement

Displacement is a very rare reaction and applies to cases where R' is an alkyl group, Y is a group of atoms and R· is any type of radical.

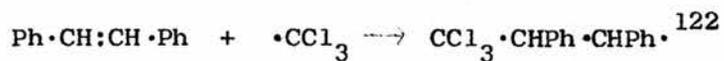
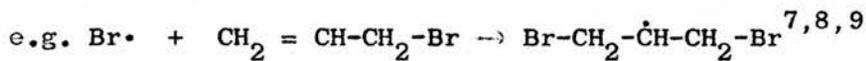
c. Aromatic substitution

Aromatic substitution is a complex reaction which is discussed in detail in section 2. In this class of reaction an aromatic substrate is attacked by a radical which effects substitution such as in the following example where an aryl radical attacks

the benzene ring to give a cyclohexadienyl radical<sup>11,12</sup> which then loses a hydrogen atom by oxidation or by reaction with another radical to give the substitution product.

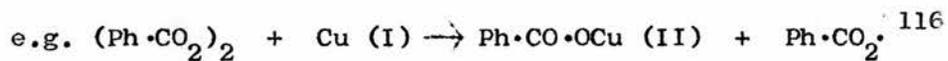
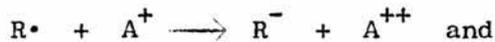


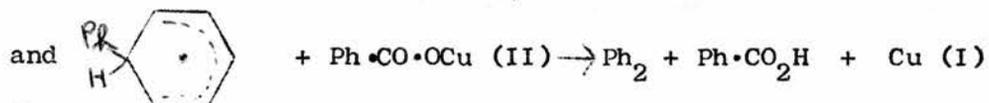
d. Addition to unsaturated systems



Radical addition is an important reaction having widespread applicability in synthesis and as the propagation step in olefin polymerisation.

e. Reaction with metal ions

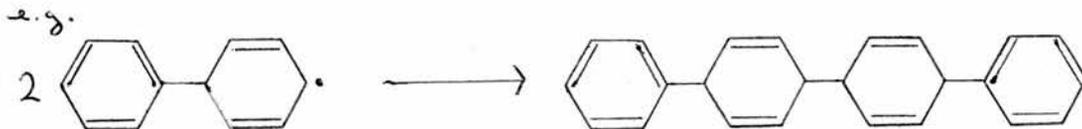
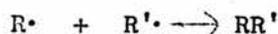




Metals with low redox potentials such as copper and zinc are important in the above types of reactions since they readily accept or donate an electron, because of small energy changes involved.

f. Reactions not involving another molecule

Combination

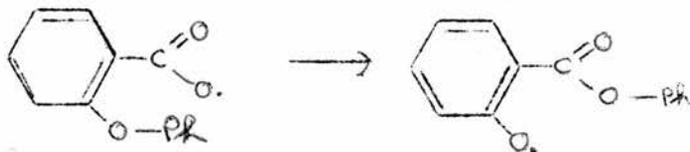


This is characteristic of 'long lived' radicals with which a large enough radical concentration can be built up for reaction to occur appreciably.

g. Rearrangement

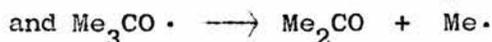
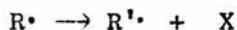


e.g.

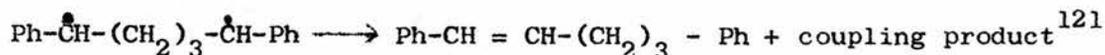


13

h. Decomposition



The decomposition of benzoyloxy radicals in benzene produces a stable molecule and a simpler radical.

i. Disproportionation

Of the above (f) and (g) remove radicals from the system and are classed as termination reactions while the others are classed as propagation reactions.

2. SOURCES OF ARYL RADICALS IN SOLUTION.

Aryl radicals are usually obtained by thermolysis or photolysis of covalent bonds in appropriate compounds.

a) Thermolysis.

From the rate equation for a unimolecular process

$$k = 10^{13} \exp \frac{-E_a}{RT} \text{ sec.}^{-1}$$

it can be calculated that molecules with bonds whose bond dissociation energies are 25 and 32 k.cals./mole will have half lives of one hour at 50°C and 150°C respectively. Molecules with weak bonds of the order of 40 k.cals./mole, or less, dissociate at a useful rate for the generation of radicals at temperatures below 150°C.

1) Diaroyl Peroxides.

Biphenyl was observed as a product of the decomposition of benzoyl peroxide in benzene by Lippmann<sup>14</sup> but because benzoyl peroxide on decomposing in sand<sup>15</sup> also yielded biphenyl, he thought benzene played no part in the reaction. In 1925, it was demonstrated by Gelissen and Hermans<sup>16</sup> that the main products from the decomposition of benzoyl peroxide in refluxing benzene were biphenyl, carbon dioxide and benzoic acid and the participation of benzene in the decomposition was shown by the fact that di-p-chlorobenzoyl peroxide in benzene yielded 4-chlorobiphenyl and not a dichlorobiphenyl and likewise 3-nitrobiphenyl rather than a dinitrobiphenyl was obtained from the decomposition of di-m-nitrobenzoyl peroxide. In 1934, Hey<sup>6</sup> allowed benzoyl peroxide to decompose in chlorobenzene, nitrobenzene and ethyl benzoate and isolated 4-chlorobiphenyl, 2- and 4-nitrobiphenyl and ethyl biphenyl-3- and 4-carboxylates respectively. On the basis of this evidence Hey claimed that phenyl radicals resulted from the decomposition of benzoyl peroxide in aromatic solvents.

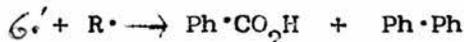
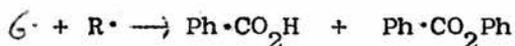
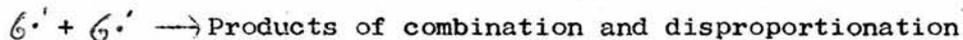
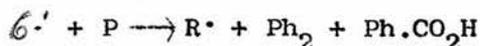
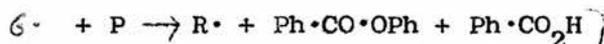
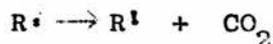
In aliphatic solvents benzoyl peroxide decomposed to give benzene<sup>16</sup>, and chlorobenzene was the main product from decomposition in carbon tetrachloride<sup>17</sup>. At a later date Hermans<sup>18</sup> proposed a reaction scheme involving the formation of intermediate complexes

with the solvent. It was left to Hey<sup>6</sup> to appreciate the radical nature of the decomposition of aroyl peroxides in organic solvents. Brown<sup>19</sup> further demonstrated the homolytic nature of the decomposition, showing that there was no direct relationship between the rates of decomposition of substituted benzoyl peroxides and the ionisation constants of the corresponding carboxylic acids, which would have been expected for a heterolytic process.

At the present time it is known that the decomposition of benzoyl peroxide in a monosubstituted benzene ( $C_6H_5X$ ) gives benzoic acid, carbon dioxide, the monosubstituted biphenyl derivatives<sup>20,21,22</sup> (2-, 3-, and 4- $XC_6H_4.C_6H_5$ ), the corresponding isomeric monosubstituted derivatives of phenyl benzoate and, in some instances, considerable amounts of high boiling residue from which have been isolated terphenyl derivatives<sup>23,24</sup> and tetrahydroquaterphenyls<sup>24,25</sup>. A small amount of phenyl benzoate is often produced<sup>26</sup> and dihydrobiaryls have been reported.<sup>24,27</sup> No gaseous hydrogen is evolved on decomposition of peroxides in benzene<sup>28</sup> but there is considerable evidence for the generation of reducing agents in reaction between peroxides and aromatic solvents.<sup>29,30,31</sup>

Much work has been done on the kinetics of the decomposition of benzoyl peroxide in benzene.<sup>32,33,34,35,36,37</sup>

Gill and Williams<sup>37</sup> suggested the following mechanism for the decomposition of benzoyl peroxide in benzene:-



where P is peroxide

R· is a benzoyloxy radical

R<sup>·</sup> is a phenyl radical



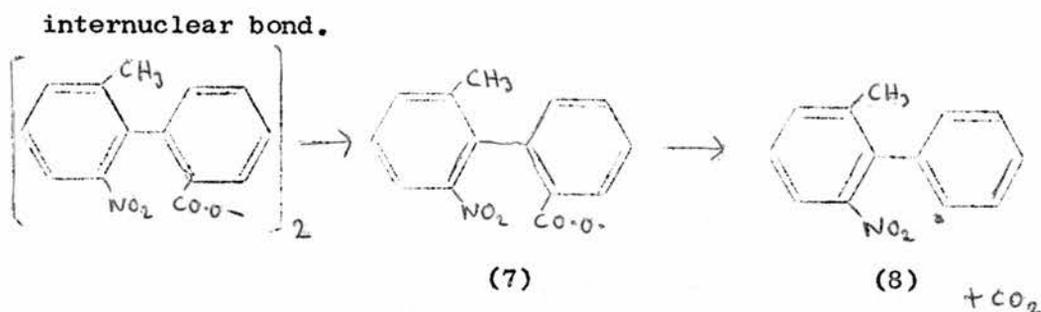
In dilute solutions the kinetics are first order, corresponding to scission of the -O-O- bond and formation of two benzoyloxy radicals,

while at higher concentrations the rate of decomposition increases due to radical induced decomposition of the peroxide and obeys the rate equation:

$$-\frac{d[P]}{dt} = k_a[P] + k_b[P]^{\frac{3}{2}}$$

With more "reactive" solvents than benzene, such as naphthalene<sup>38</sup> and anthracene,<sup>39</sup> benzoyloxylation is significant and this is interpreted as reaction of the more reactive solvents with the benzoyloxy radicals before they can decompose to phenyl radicals and carbon dioxide.

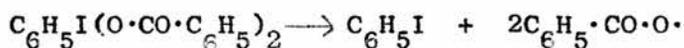
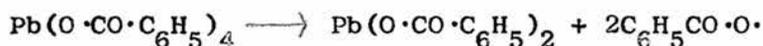
Decomposition of optically active o-(2-methyl-6-nitrophenyl) benzoyl peroxide<sup>40</sup> in benzene, carbon tetrachloride and bromotrichloromethane yielded products whose configurations were retained to the extent of 25-50%, 40-55% and 90% respectively. This can be taken as (i) proof of the existence of (8) since (7) cannot racemise and (ii) illustration of the very short lifetime of (8) since racemisation occurs simply by rotation of the



The course of arylation reactions with peroxides is altered in the presence of catalytic amounts of aromatic nitro compounds<sup>41</sup> and molecules which act as electron acceptors in charge transfer complexes<sup>42</sup>, in that the yields of biaryl and acid are increased approximately twofold.

ii) Lead tetrabenzoate and phenyl iodosobenzoates.

Hey, Stirling and Williams<sup>43</sup> have demonstrated that these compounds decompose in a manner analogous to benzoyl peroxide.



The compounds were allowed to decompose at 125° for 72 hours in nitrobenzene whereupon it was found that the ratios of isomeric nitrobiphenyls were almost identical with that from benzoyl peroxide at the same temperature. The iodoso compound has also been used to phenylate pyridine<sup>44</sup>. It was thus concluded that

aryl radicals were involved.

Lynch and Pausacker<sup>79</sup> verified the above reaction scheme but also showed that benzoyloxylation occurred simultaneously with phenylation, and investigated the decomposition of iodosobenzene dianisate and di-p-toluate in chlorobenzene.

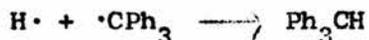
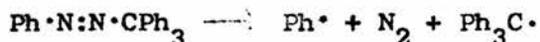
More recently Leffler<sup>80</sup> et al. carried out kinetic work on the decomposition of phenyl iodosobenzoate and found that phenyl benzoate is formed ( $\sim 0.1$  moles/mole dibenzoate) in which the phenyl moiety of the ester comes exclusively from the phenyliodine moiety of the dibenzoate, and that in presence of benzoic anhydride reaction is fast after a prolonged induction period.

iii) Diazo and azo compounds.

A) Azo compounds.

Azo compounds usually do not give phenyl radicals unless associated with an incipient stable radical. Thus Ph-N=N-Ph is stable but Ph-N=N-CPh<sub>3</sub> is not, and so the latter, phenylazotriphenylmethane, is a much used source of phenyl radicals. The thermolysis of this compound in benzene was first investigated by Hey<sup>6</sup> and found to yield nitrogen, biphenyl and triphenylmethane.

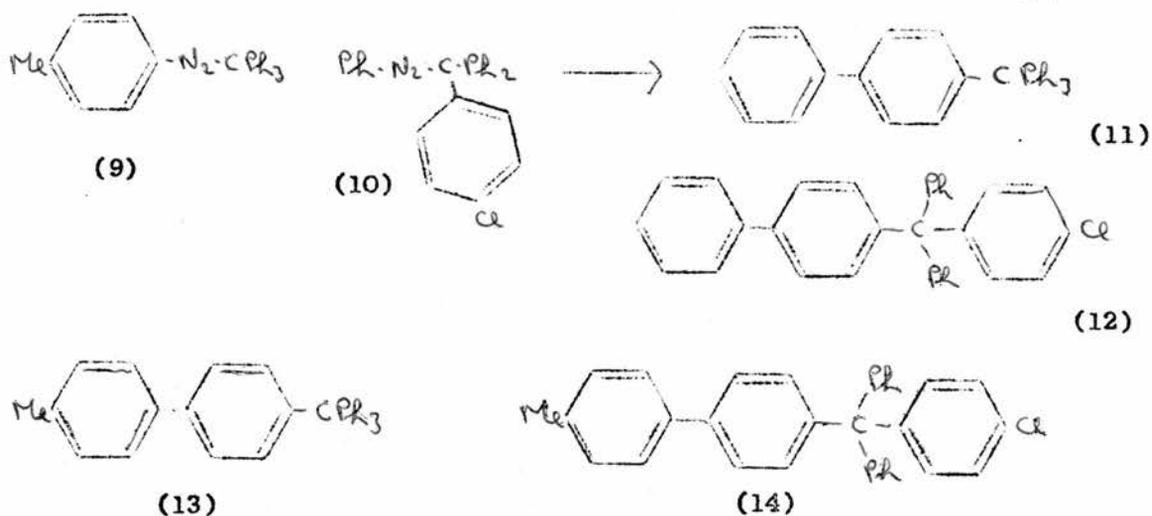
Wieland<sup>23</sup> et al. proposed the following scheme for decomposition in aromatic solvents



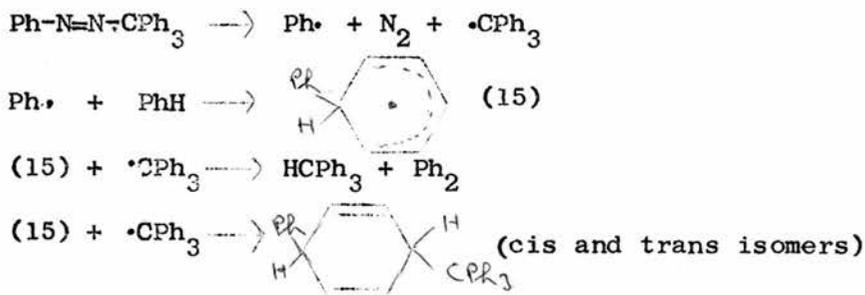
Arylazotriphenylmethanes have been shown to decompose according to first order kinetics<sup>46,47,48</sup>. Huisgen and Nakaten also demonstrated the correctness of Wieland's mechanism and concluded that free aryl radicals were intermediates.

Davies, Hey and Williams<sup>117</sup> investigated the decomposition of a number of substituted arylazotriarylmethanes in toluene and the decomposition of phenylazotriphenylmethane in various solvents, and found little difference in the rates of decomposition, however, the energies and entropies of activation varied to a greater extent but tended to compensate one another.

In 1962 Eliel<sup>49</sup> suggested that the radicals produced on homolysis of arylazotriphenylmethanes are constrained within a "solvent cage" but this has been discounted<sup>50,51</sup> and Hey, Perkins and Williams<sup>52</sup> conclusively showed the presence of free radicals by allowing an equimolar mixture of (9) and (10) to decompose in benzene.



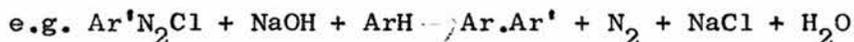
to give (11), (12), (13) and (14) in equal amounts after dehydrogenation of the dihydrobiphenyls. On this basis the following reaction scheme was suggested:



## B) Diazonium compounds.

### (1) Gomberg Reaction.

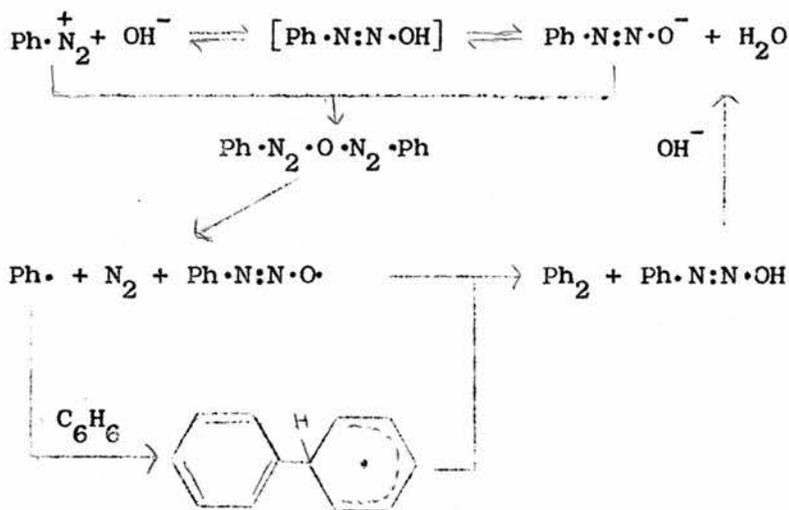
Essentially the reaction consists of the decomposition of diazohydroxides or diazoacetates in aqueous-aromatic heterogeneous systems:



The reaction is of little use for preparative work since yields of biaryls are low and large amounts of tars are formed, but has considerable historical significance being the first example of homolytic aromatic substitution<sup>5</sup>.

For the period before 1957 the reaction has been reviewed.<sup>53,54</sup>

In 1964, Merz and Ruchardt<sup>74</sup> postulated the following reaction scheme for the Gomberg reaction. (See also<sup>75,76,77</sup> in connection with acylarylnitrosamines).



## 2) Diazonium salts.

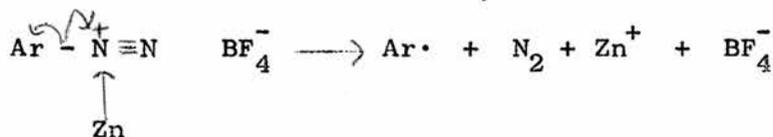
The simplest arylation effected by a diazonium salt involves its thermal decomposition



in a first order process<sup>57,58</sup>.

Diazonium trifluoroacetates<sup>59</sup> have been used in this way and it is possible that the covalent form of the salt, which is in equilibrium with the ionic form, homolyses to produce aryl radicals.

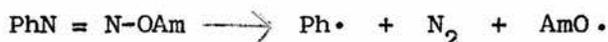
Some diazonium salts, such as fluoborates, require the presence of a catalyst such as zinc<sup>60</sup> (a metal with a low redox potential) before they will generate radicals, probably by a sequence:



Many esoteric combinations of diazonium salts and catalysts have been used to produce aryl radicals.

3) Alkyl nitrite on aromatic amines.

In 1962 Cadogan<sup>55</sup> reported the arylation of benzene using various aromatic amines in the presence of amyl nitrite, without determining the mechanism of the process. Later,<sup>56</sup> the reaction was confirmed to be a radical phenylation by comparison of the ratio of isomeric chlorobiphenyls obtained from the reaction of aniline with amyl nitrite in chlorobenzene. Although the mechanism of the reaction has not been fully determined, it is likely to involve an in situ diazotisation followed by decomposition e.g.



Regardless of mechanistic detail this is by far the simplest and most convenient method of conversion of aromatic amines to unsymmetrical biaryls.

C) Acylarylnitrosamines.

In 1897 N-nitrosoacetanilide was used in arylation<sup>61</sup> but it was not until 1934 that it was more fully investigated by Grieve and Hey<sup>5</sup>, who suggested that it was a source of free radicals. Later Butterworth and Hey<sup>62</sup> showed that the decomposition of N-nitrosoacetanilide followed first order kinetics and that the rate was virtually independent of the solvent. Consequently, they suggested the following mechanism:-

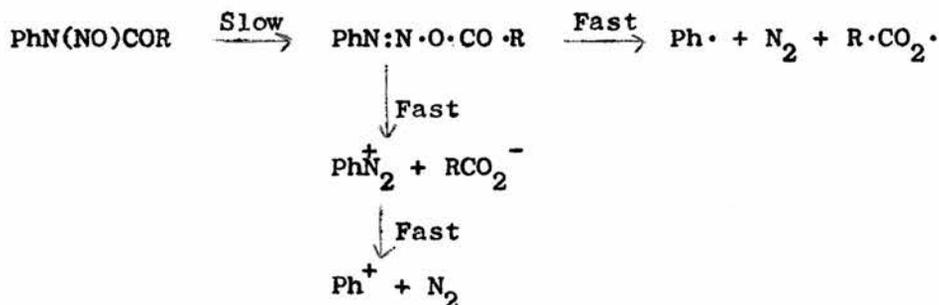


However, in 1949 Huisgen and Horeld<sup>63</sup> showed that the rate of coupling of diazonium ions in the system with  $\beta$ -naphthol was identical with the rate of nitrogen evolution in the absence of the phenol. Thus formation of the diazo-ester, which can undergo homolysis or heterolysis, must be the rate determining step in the decomposition of N-nitrosoacetanilide.

Huisgen and co-workers<sup>64</sup> proposed that the nitrosoamide was converted to diazo-ester by intramolecular rearrangement.

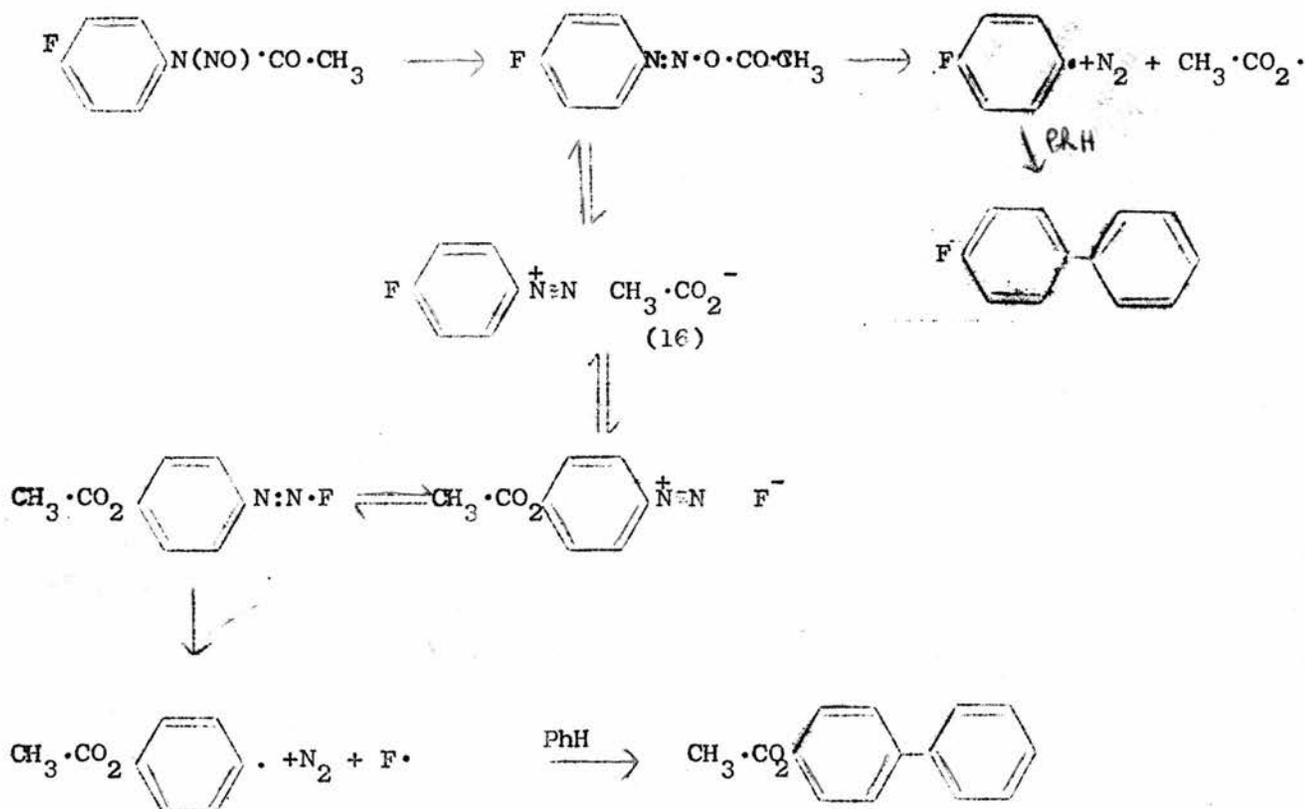


The same conclusion was reached independently by Hey, Stuart-Webb and Williams<sup>65</sup> after a most comprehensive investigation. Further verification came from De Tar<sup>66</sup>, based on his work on the decomposition of N-nitrosoacetanilide in methanol, methanol and sodium acetate and methanol and sulphuric acid. On the basis of this work he modified Huisgen's reaction scheme:



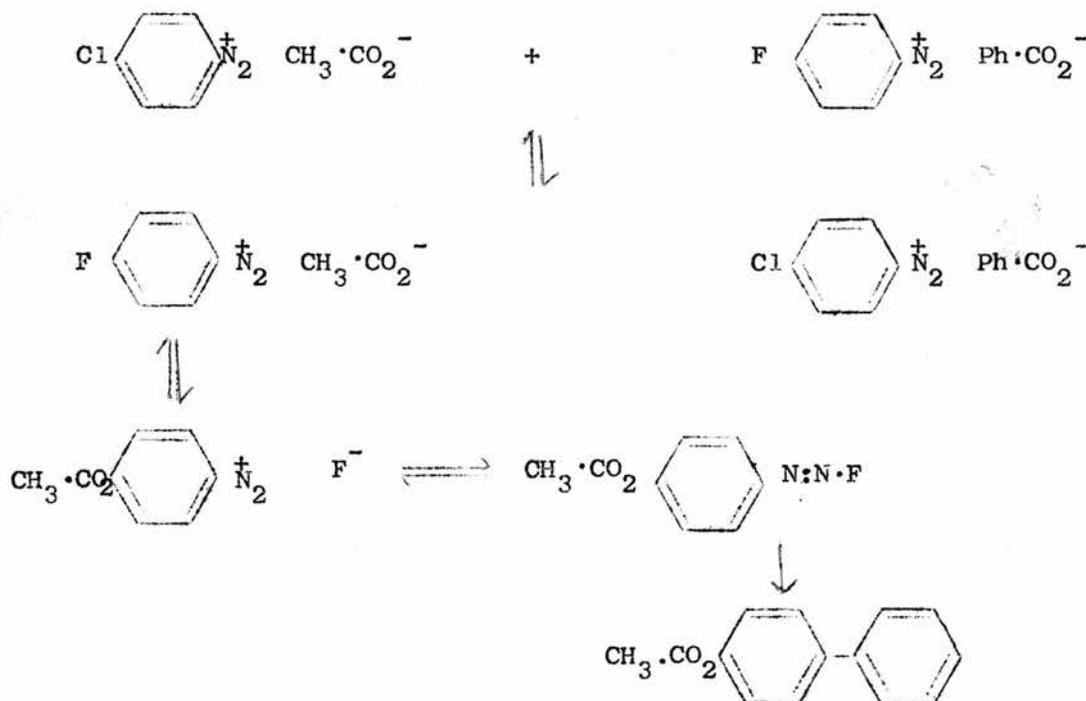
Further light was cast on the rearrangement of the nitroso amide by Barben and Suschitzky,<sup>67</sup> who on decomposition of o- and p-fluoro-N-nitroso-acetanilides and -benzanilides in benzene, obtained mixtures of the 2- and 4-fluorobiphenyls with the corresponding 2- and 4-acylbiphenyls. Decomposition of m-fluoro-N-nitrosoacylanilides gave only 3-fluorobiphenyl. Suschitzky rationalised this data on the basis of the formation of the diazo 'ion pair' (16) with a subsequent nucleophilic substitution in the case of the activated o- and p-isomers.

e.g.

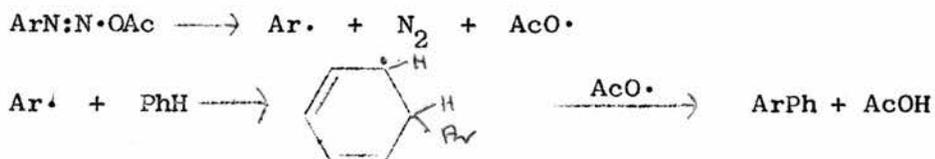


No other p-substituted N-nitrosoacetanilides gave 4-acetoxybiphenyl and the behaviour of the fluoro derivatives was attributed to the high electronegativity of the fluorine atom.

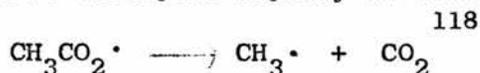
However, evidence for the existence of 'ion pairs' with other acylarylnitrosamines is provided by Miles and Suschitzky<sup>68</sup> who allowed a mixture of N-nitroso-p-chloroacetanilide and N-nitroso-p-fluorobenzanilide to decompose in benzene, with the subsequent isolation of the crossed product, 4-acetoxybiphenyl



In all these cases the overall substitution process was assumed to be as follows:-



Certain aspects of the reaction of acylarylnitrosamines were puzzling however, <sup>IN PARTICULAR</sup> the low yields of carbon dioxide and methyl radicals and the high yields of acetic acid.<sup>59,70,71</sup> These facts were not consistent with the existence of free acetoxy radicals which are known to decompose rapidly as follows:-

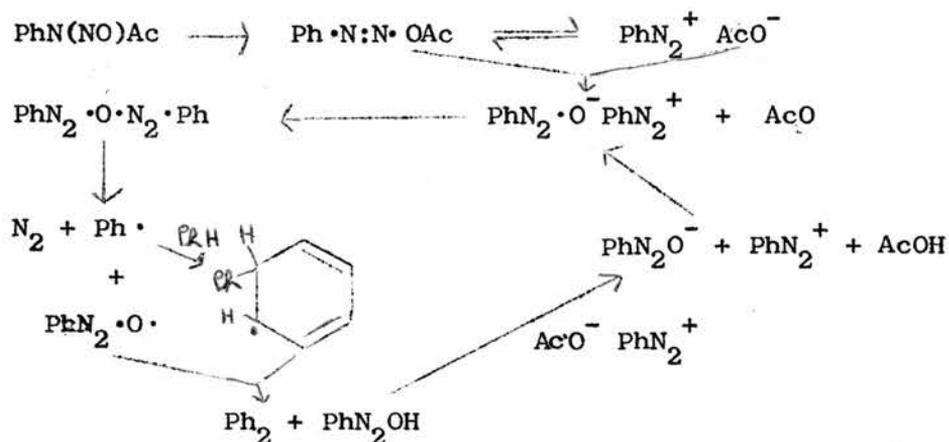


Further, there was the absence of quaterphenyls and dihydrobiphenyls, which would be expected to be formed by dimerisation and disproportionation of intermediate cyclohexadienyl radicals.

To account for these anomalies, Huisgen<sup>69</sup> proposed that actual free radicals were not involved but that acetoxy radicals obtained a hydrogen atom within a complex of solvent molecules and reactant. In this view, Eliel<sup>49</sup> put forward evidence for a "cage reaction" for the decomposition of N-nitrosoacetanilide, but later retracted,<sup>72</sup> stating that there was no "cage reaction" in the decomposition of N-nitrosoacetanilide in benzene, (on the basis of the results of a reaction carried out in the presence of a low concentration of iodine, which gave iodobenzene). It has also been shown by Denney et al.<sup>73</sup> that there is no "cage reaction" in the decomposition of

N-nitrosoacetanilide in ether, and that in benzene, radical acceptors (e.g. styrene) suppress formation of biphenyl but do not affect the yield of nitrogen.

The next advance in the elucidation of the mechanism of the decomposition of N-nitrosoacetanilides was provided by Rüchardt et al.<sup>74,75</sup> who suggested the intermediacy of aryl diazo ethers ( $\text{Ar-N=N-O-N=N-Ar}$ ) which would decompose to give the long lived diazotate radical,  $\text{Ar-N=N-O}\cdot$ , which would account for the absence of quaterphenyls and dihydrobiphenyls as decomposition products, the relatively stable diazotate radical being assumed to scavenge the intermediate aryl cyclohexadienyl radicals, thus suppressing their dimerisation. In 1966 Binsch and Rüchardt<sup>76</sup> reported the E.S.R. identification of the diazotate radical in the decomposition of N-nitrosoacetanilide in benzene and later<sup>77</sup> reported E.S.R. data for  $\text{p-Bu}^t\text{-C}_6\text{H}_4\text{-N=N-O}\cdot$ ,  $\text{p-D-C}_6\text{H}_4\text{-N=N-O}\cdot$  and  $\text{Ph-N}^{15}\text{=N-O}\cdot$  obtained from the appropriate nitrosoacylanilides. Rüchart's proposed reaction scheme for the decomposition of N-nitrosoacetanilide in benzene is:-



This mechanism was assumed by most workers in the field to be satisfactory. It did not fit all the facts however. Thus, in 1964 evidence was obtained by Cadogan and Hibbert<sup>78</sup> for the participation of an aryne in the decomposition of o-t-butyl-N-nitrosoacetanilide in benzene, following the isolation of 2-t-butyltriptycene when anthracene was added to the reaction. In absence of anthracene a 46% yield of a mixture of o- and m-t-butylphenyl acetates was obtained. It was clear, therefore, that anomalies, possibly a result of steric factors, in the decompositions of arylacylnitrosamines existed, and such anomalies might involve the participation of arynes.

b) Photolysis.

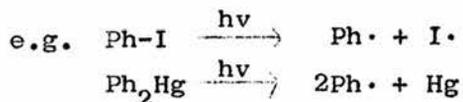
Energy to homolyse covalent bonds can be supplied by irradiation with ultra-violet light of suitable wavelength or with ionising radiation emanating from nuclear sources.

$$E = \frac{2.8579 \times 10^8}{\lambda} \text{ calories/mole}$$

where  $\lambda$  = wavelength of light in Å

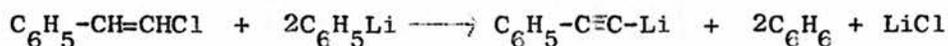
E = energy in calories/mole

Phenyl radicals have been produced by photolysis of diphenylmercury,<sup>81,82</sup> tetraphenylead,<sup>82,83</sup> triphenylbismuth<sup>84</sup> and iodobenzene<sup>82</sup> while Kharasch et al.<sup>85,86</sup> have photolysed iodoaromatics in dilute benzene solution to effect arylation of the benzene.

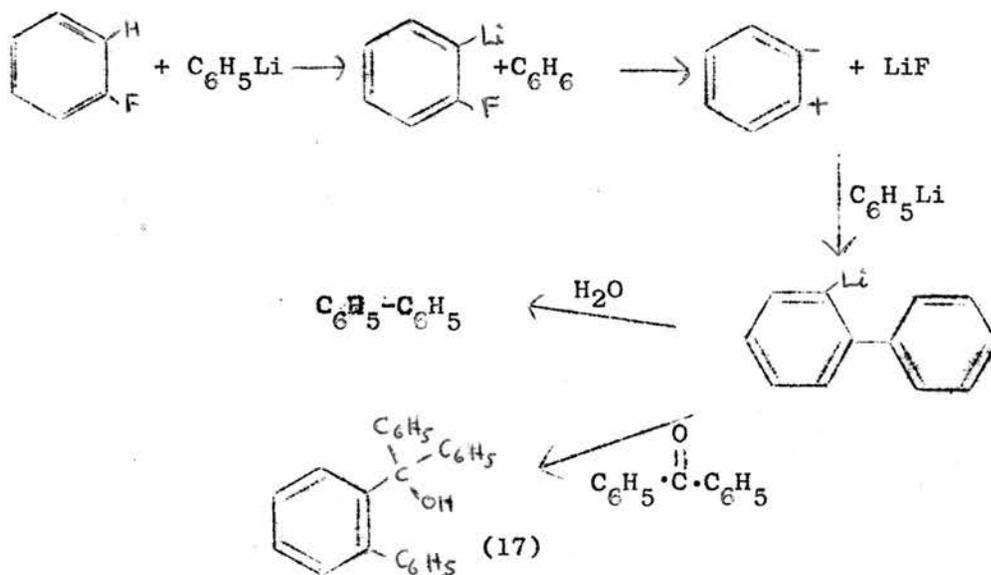
3) ARYNES.a) Historical Development and Evidence of Occurrence.i) Liquid phase.

Benzyne or dehydrobenzene, a transient intermediate, represented by the formula  $\text{C}_6\text{H}_4$ , obtained by the removal of two ortho hydrogen atoms from a benzene molecule was first suggested in 1902<sup>87</sup> but it was not until 1942 that it was seriously considered. Wittig<sup>88</sup> found that the products of reaction of phenyllithium with fluorobenzene depended on the subsequent treatment of the reaction mixture, when

water was added biphenyl was the product while with added benzophenone o-biphenyldiphenylcarbinol (17) was obtained. The key to the problem was provided by the discovery that olefinic derivatives such as o-chlorostyrene on treatment with phenyllithium were readily converted into acetylenic compounds, presumably by substitution of the metal into the  $\beta$ -position followed by elimination of metal halide <sup>89</sup>

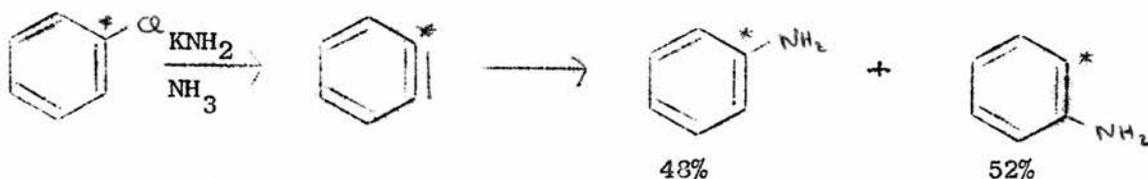


As a result Wittig postulated the following mechanism with the dehydrobenzene permanently polarised in the sense shown:-

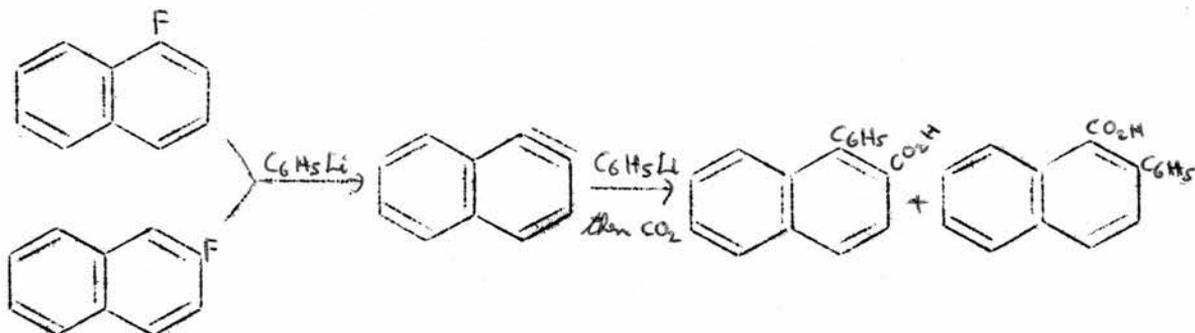


Compelling evidence in favour of the intermediacy of benzyne was provided by Roberts<sup>90</sup> et al., who allowed  $[1\text{-}^{14}\text{C}]$ -chlorobenzene to react

with potassium amide in liquid ammonia, to obtain the two labelled anilines in approximately 50% yield:



Wittig's error in thinking that benzyne was permanently polarised was demonstrated by Huisgen<sup>91</sup> and Rist who showed that reaction of 1- and 2-fluoronaphthalene with phenyllithium followed by carbonation gave 2-phenyl-1-naphthoic acid and 1-phenyl-2-naphthoic acid in the same 2:1 ratio. (Another product from 2-fluoronaphthalene was 3-phenyl-2-naphthoic acid).

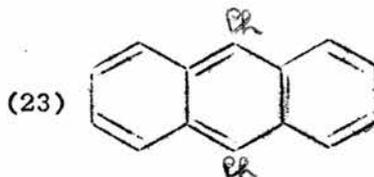
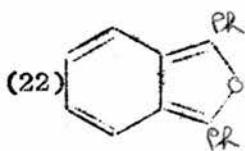
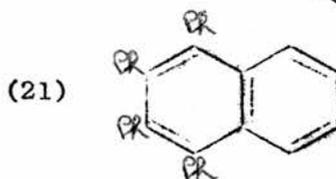
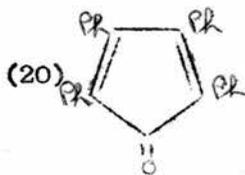
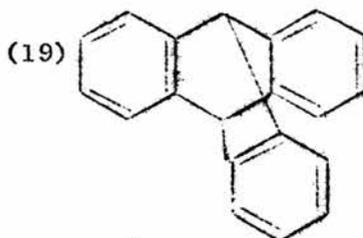
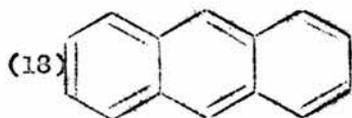


Wittig and Pohmer<sup>92</sup> argued that benzyne should act as a dienophile. *o*-Bromofluorobenzene in furan was treated with lithium amalgam and 1,4-dihydronaphthalene-1,4-endoxide was isolated in 76% yield.



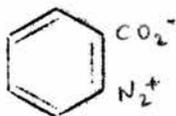
Pyrrole derivatives<sup>93</sup> and cyclopentadiene<sup>94</sup> gave similar Diels-Alder type adducts with benzyne but non-cyclic dienes do not give adducts,<sup>95</sup> probably because benzyne has not a long enough lifetime to await the non-cyclic dienes assuming the requisite cis conformation.

Benzyne forms an adduct with anthracene<sup>96,97</sup> (18) to give triptycene (19), with 1,2,3,4-tetraphenyl-1,3-cyclopentadienone<sup>97,98</sup> (20)<sup>98</sup> to give 1,2,3,4-tetraphenylnaphthalene (21) and with 1,3-diphenylisobenzofuran<sup>93</sup> (22) to give, after reduction, 9,10-diphenylanthracene.(23)

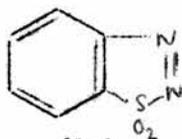


These cycloadditions provided a diagnostic test for the occurrence of dehydroaromatic intermediates and led to the discovery of the following methods of generating benzyne without having recourse to organo-metallics or strong bases:-

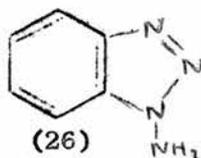
- i) Thermolysis<sup>99</sup> of benzenediazonium o-carboxylate (24)!
- ii) Diazotisation<sup>100</sup> of anthranilic acid with amyl nitrite
- iii) Thermolysis<sup>101</sup> of benzenethiadiazole (25).
- iv) Oxidation<sup>102</sup> of 1-aminobenzotriazole (26) with lead tetraacetate or nickel oxide



(24)



(25)



(26)

The similarity in all methods of generating benzyne (only a representative sample has been listed above), is that the benzyne precursors possess 'good leaving groups'. Nitrogen is a particularly good example of such a leaving group, thus the acquisition of two electrons by the diazonium function in the cases described above readily leads to aryne formation.

The 'hetarynes' have been recently reviewed.<sup>103</sup>

ii) Gas phase.

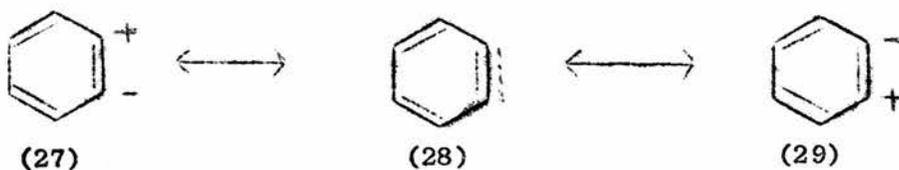
Biphenylene was obtained by the decomposition of bis-*o*-iodophenylmercury and phthaloyl peroxide under reduced pressure at 600°C,<sup>104</sup> and also by the flash photolysis of benzenediazonium 2-carboxylate and *o*-iodophenyl mercuric iodide by Berry, Spokes and Stiles<sup>105</sup> who also obtained a U.V. spectrum attributed to gaseous benzyne. Later Berry et al.,<sup>106</sup> with time resolved mass spectroscopy, noted the appearance of a peak attributable to mass 76, which gave way to a peak attributable to mass 152, on the flash photolysis of benzenediazonium-2-carboxylate. This he attributed to the formation of benzyne which dimerised to biphenylene and estimated the benzyne lifetime at 250-300  $\mu$ secs. Similar investigations on the 3- and 4-carboxylates led to Berry<sup>107</sup> et al. claiming the existence of 1,3- and 1,4-dehydrobenzenes. Thermolysis of *o*-diiodobenzene<sup>108</sup> followed by mass spectroscopy gave a peak at  $m = 76$ .

Little work has been done on arynes in the gas phase in comparison to the volume of solution work. It is conceivable that "gas phase" and "liquid phase" benzyne are quite different transient entities.

b) Structural Considerations .

By convention, benzyne is written as  and although Roberts<sup>90</sup> et al. and Coulson<sup>109</sup> have argued as to the possibility of an acetylenic bond between two sp hybridised carbon atoms existing in such an environment, benzyne is best described as a

resonance hybrid of the three canonical forms:<sup>110</sup>



(27) and (29) are the so called 'singlet benzyne' in which two anti-parallel electrons reside in a  $sp^2$  orbital, while in (28) one electron resides in each of the two adjacent  $sp^2$  orbitals and there is some degree of bonding due to overlap of the orbitals.

Some contribution to the resonance hybrid by triplet (diradical) benzyne must also be considered.

### c) Reactions of Arynes.

Dehydroaromatic compounds have a pronounced electrophilic character as evidenced by the addition of phenyllithium to benzyne<sup>33</sup> and the amination of halobenzenes<sup>90</sup>. Such nucleophilic additions to arynes have been discussed by Wittig.<sup>111</sup>

The role of arynes as dienophiles has been discussed in section (a) but it is worthy of notice that tetrafluorobenzyne has been found to be a very powerful dienophile.<sup>112</sup>

The orientation of addition to the triple bond in substituted benzyne has been studied by Huisgen and Sauer<sup>110</sup> and Roberts and co-workers<sup>114</sup>, but the most thorough study has been carried out by

de Graaf<sup>115</sup>, who found that the orientation of the addition of amide ion to the 'triple bond' depends on both the inductive effect and the conjugative effect of the substituent group for both 3- and 4-substituted benzyne.

#### 4) PROGRAMME OF RESEARCH.

The original intention was to follow up the work of Cadogan and Hibbert<sup>73</sup> with an investigation of decompositions of o-substituted N-nitrosoacetanilides to determine which ones, if any, decomposed via an aryne intermediate. In addition, it was of interest to discover whether the decomposition of unsubstituted N-nitrosoacetanilide proceeded, if only in part, via the intermediacy of benzyne or a closely related species.

During the course of these investigations, a novel radical abstraction reaction of iodine from aromatic iodides was discovered and investigated extensively. This discovery arose from the observation that o-, m-, and p-iodo-N-nitrosoacetanilide on decomposition in benzene gave o-, m-, and p-di-iodobenzene as by-products.

EXPERIMENTAL

	Page
1) <u>INSTRUMENTATION.</u>	40
2) <u>PREPARATION AND PURIFICATION OF MATERIALS.</u>	42
a) Solvents.	43
b) Di-aryl Peroxides.	43
c) Phenylazotriphenylmethane.	45
d) Acylarylnitrosamines.	46
e) Iodo Compounds.	48
i) From amino compounds.	48
ii) From halobenzenes.	49
iii) Preparation of phenyl iodoso-di- <u>p</u> -nitrobenzoate.	50
f) Miscellaneous Compounds.	51
i) 2,3,4,5-Tetraphenylcyclopentadienone.	51
ii) Phenyl acetates.	51
iii) <u>m</u> -Bromobenzenediazonium fluoroborate.	51
3) <u>DECOMPOSITIONS OF SUBSTITUTED <u>N</u>-NITROSOACETANILIDES IN BENZENE.</u>	52
a) <u>o</u> -Methyl- <u>N</u> -nitrosoacetanilide.	52
b) <u>o</u> -Carbethoxy- <u>N</u> -nitrosoacetanilide.	53
c) <u>o</u> -Chloro- <u>N</u> -nitrosoacetanilide.	54
d) <u>o</u> -Phenyl- <u>N</u> -nitrosoacetanilide.	54
e) Bromo- <u>N</u> -nitrosoacetanilides.	55
i) <u>o</u> -Bromo- <u>N</u> -nitrosoacetanilide.	55
ii) <u>m</u> -Bromo- <u>N</u> -nitrosoacetanilide.	56
iii) <u>p</u> -Bromo- <u>N</u> -nitrosoacetanilide.	56

	Page
4) <u>THE ATTEMPTED DETECTION OF BENZYNOID INTERMEDIATES IN THE DECOMPOSITIONS OF ARYL RADICAL SOURCES IN SOLUTION.</u>	57
a) Decomposition of <u>N</u> -Nitrosoacetanilides.	57
i) Decomposition of <u>N</u> -nitrosoacetanilide in benzene.	57
ii) Decomposition of <u>N</u> -nitrosoacetanilide in benzene in the presence of 2,3,4,5-tetraphenylcyclopentadienone.	57
iii) Competition reaction of 2,3,4,5-tetraphenylcyclopentadienone and furan with benzyne.	59
iv) Decomposition of <u>N</u> -nitrosoacetanilide in furan in the presence of 2,3,4,5-tetraphenylcyclopentadienone.	60
v) Decomposition of <u>N</u> -nitrosoacetanilide in benzene in the presence of anthracene.	62
vi) Decomposition of <u>N</u> -nitrosoacetanilide in pyridine in the presence of 2,3,4,5-tetraphenylcyclopentadienone.	63
vii) Decomposition of <u>N</u> -nitrosoacetanilide in tetrahydrofuran in the presence of 2,3,4,5-tetraphenylcyclopentadienone.	64
viii) Decomposition of <u>N</u> -nitrosoacetanilide in benzene in the presence of 1,3-diphenylisobenzofuran.	65
ix) Decomposition of <u>o</u> -iodo- <u>N</u> -nitrosoacetanilide in benzene in the presence of 2,3,4,5-tetraphenylcyclopentadienone.	66
x) Decomposition of <u>o</u> -iodo- <u>N</u> -nitrosoacetanilide in furan and benzene.	67

- xi) The reaction of o-di-iodobenzene with 2,3,4,5-tetraphenylcyclopentadienone in benzene. 67
- xii) The reaction of dibenzoyl peroxide with o-di-iodobenzene in benzene in the presence of 2,3,4,5-tetraphenylcyclopentadienone. 67
- b) Decomposition of Dibenzoyl Peroxide in Benzene in the Presence of 2,3,4,5-Tetraphenylcyclopentadienone. 68
- c) Decomposition of Phenylazotriphenylmethane in Benzene in the Presence of 2,3,4,5-Tetraphenylcyclopentadienone. 69
- d) Aniline and Amyl Nitrite. 70
- i) The reaction of aniline with amyl nitrite and 2,3,4,5-tetraphenylcyclopentadienone in benzene. 70
- ii) The reaction of aniline with amyl nitrite and 2,3,4,5-tetraphenylcyclopentadienone in dichloromethane. 70
- iii) The reaction of aniline with amyl nitrite and 2,3,4,5-tetraphenylcyclopentadienone in benzene in the presence of anhydrous magnesium sulphate. 71
- iv) The reaction of aniline with amyl nitrite, acetic acid and 2,3,4,5-tetraphenylcyclopentadienone in benzene in the presence of anhydrous magnesium sulphate. 72

e) The Gomberg Reaction.	72
f) Reaction of Benzenediazonium Fluoroborates with Strong Bases.	73
i) The reaction of <u>m</u> -bromobenzenediazonium fluoroborate with sodium methoxide in the presence of 2,3,4,5-tetraphenylcyclopentadienone in benzene.	73
ii) The reaction of benzenediazonium fluoroborate with <u>n</u> -butyl lithium in benzene in the presence of 2,3,4,5-tetraphenylcyclopentadienone.	73
iii) The reaction of benzenediazonium fluoroborate with <u>n</u> -butyl lithium in furan.	74
5) <u>THE ABSTRACTION OF IODINE FROM AROMATIC IODIDES BY ARYL RADICALS.</u>	74
a) The Decomposition of <u>o</u> -Iodo- <u>N</u> -nitrosoacetanilide in Benzene.	74
b) The Decomposition of <u>m</u> -Iodo- <u>N</u> -nitrosoacetanilide in benzene.	76
c) The Decomposition of <u>p</u> -Iodo- <u>N</u> -nitrosoacetanilide in benzene.	77
d) The Decomposition of Di- <u>p</u> -chlorobenzoyl Peroxide in Iodobenzene.	78
e) The Decomposition of Di- <u>p</u> -bromobenzoyl Peroxide in Iodobenzene.	79
f) The Decomposition of Di- <u>p</u> -chlorobenzoyl Peroxide in Bromobenzene.	80
g) The Decomposition of Di- <u>p</u> -bromobenzoyl Peroxide in Bromobenzene.	80

h) The Decomposition of Di- <u>p</u> -chlorobenzoyl Peroxide in 2-Iodobiphenyl.	80
i) The Decomposition of Di- <u>p</u> -iodobenzoyl Peroxide in Benzene.	81
j) The Decomposition of Di- <u>m</u> - and Di- <u>o</u> -bromobenzoyl Peroxide and Di- <u>p</u> -methylbenzoyl Peroxide in Iodobenzene.	82
k) The Decomposition of Di- <u>o</u> -bromobenzoyl Peroxide in a Mixture of Benzene and Iodobenzene.	83
l) The Decomposition of Di- <u>m</u> - and Di- <u>p</u> -bromobenzoyl Peroxides in Mixtures of Benzene and Iodobenzene.	83
m) The Decomposition of <u>p</u> -Chloro- <u>N</u> -nitrosoacetanilide in Iodobenzene, Iodobenzene and Benzene, and Benzene.	86
n) The Decomposition of Di- <u>p</u> -nitrobenzoyl Peroxide in Iodobenzene.	88
o) The Decomposition of Di- <u>p</u> -cyanobenzoyl Peroxide in Iodobenzene.	89
6) <u>THE RATE OF DECOMPOSITION OF DIBENZOYL PEROXIDE IN IODOBENZENE.</u>	90
a) Development of Experimental Technique.	90
b) The Rate of the Decomposition of Dibenzoyl Peroxide in Bromobenzene.	91
c) The Rate of the Decomposition of Dibenzoyl Peroxide in Iodobenzene.	92

Abbreviations

(a) Gas-liquid chromatography	G.L.C.
(b) Moles per mole of radical source	m/m
(c) Melting point	m.p.
(d) Infra-red	I.R.
(e) Thin layer chromatography	T.L.C.
(f) Boiling point	b.p.
(g) Nuclear magnetic resonance	N.M.R.

## 1. INSTRUMENTATION.

Infra-red spectra were recorded on Grubb Parsons Type G.S.2A, Perkin-Elmer Model 137 or Model 237 spectrophotometers. Liquids were examined as thin films and solids as Nujol mulls.

Ultra-violet spectra were recorded on a Unicam S.P.800 Ultraviolet Spectrophotometer.

A Perkin-Elmer Nuclear Magnetic Resonance Spectrometer, Model R-10, with probe temperature of  $33.5^{\circ}\text{C}$ , operating at 60 Mc./sec., was used for the determination of proton magnetic resonance spectra.

For gas-liquid chromatography four instruments were used:

- (i) A Perkin-Elmer model F11 was used for qualitative examination of reaction mixtures and for purity tests on reagents. This instrument had both  $1/8''$  o.d., 2 metre packed columns and  $1/16''$  o.d., 50 metre capillary columns, with nitrogen as the carrier gas and a flame ionisation detector.
- (ii) A Griffin and George D6 gas-density-balance chromatograph operating with nitrogen as the carrier gas was used both qualitatively and quantitatively with  $3/16''$  i.d. columns (2 metres long).

With a gas density balance detector the area (A) of a peak traced out by the recorder is directly proportional to the molecular weight (M) of the compound giving rise to the peak, according to the relationship.<sup>123</sup>

$$n = \frac{kA}{M-m}$$

where  $n$  is the number of moles of compound.

$m$  is the molecular weight of the carrier gas.

$k$  is a constant particular to the machine.

Thus for two compounds (1) and (2):

$$\frac{n_1}{n_2} = \frac{A_1}{A_2} \frac{(M_2 - m)}{(M_1 - m)}$$

and so, by adding a known weight of compound (2) to a known total weight of reaction mixture, the weights of the components of that mixture can be determined from a knowledge of the peak areas.

(iii) A Varian Aerograph 1520B chromatograph using nitrogen as carrier gas, with both density balance and flame ionisation detectors, was used qualitatively and for the isolation of compounds. Columns used were  $\frac{1}{8}$ " o.d. and 2 metres long.

(iv) For preparative work on Aerograph Autoprep Model A-700 with  $\frac{3}{8}$ " o.d. columns, nitrogen carrier gas and flame ionisation detector was used.

Abbreviations for columns used are:

PEGA	polyethylene glycol adipate (an 100-120 mesh celite)	
SIL	silicone oil	"
NPGS	neopentyl glycol succinate	"
CARB	carbowax	"
BDS	butanediol succinate	"
APL	apiezon "L" grease	(an 100-120 mesh silocell)

Melting points were determined on Koffler heating stage apparatus.

Microanalyses were carried out by Bernhardt of Mulheim, Germany and Weiler and Strauss, Oxford.

## 2. PREPARATION AND PURIFICATION OF MATERIALS.

For column chromatography, silica used was Whatman's Column Chromedia SG31 and alumina was Spence and Sons, Type H, 100/200's mesh. For thin layer chromatography, silica used was MN-Silica Gel G (Macherey, Nagel and Co.) and alumina was Merck's Aluminiumoxid G. Unless otherwise stated silica was used for thin layer chromatography. Plates were developed with iodine, but in the detection of 1,2,3,4-tetraphenyl~~naphthalene~~ they were first sprayed with 2,6-dichlorofluorescein and then observed under ultra violet illumination.

a) Solvents.

Benzene, ether and petroleum ether were distilled and dried over sodium. Methylene dichloride, bromobenzene and iodobenzene were distilled (distilling iodobenzene was protected from light) and dried over calcium chloride, with the purity of the latter two being checked by G.L.C. Pyridine (B.D.H., Analar) was dried over potassium hydroxide pellets and distilled immediately before use. Furan was distilled and dried over molecular sieve, Type 4A, 1/16" pellets (B.D.H.), Tetrahydrofuran was dried over potassium hydroxide pellets for five days and then distilled from lithium aluminium hydride immediately before use.

b) Di-aryl Peroxides.i) Dibenzoyl peroxide.

Wet dibenzoyl peroxide (B.D.H.) was dissolved in warm chloroform, the aqueous layer separated and the chloroform solution filtered. On addition of methanol to the stirred chloroform solution the peroxide was precipitated as a white crystalline solid which was filtered off and dried in vacuo. The melting point was 105° and was not changed on further precipitations.

(ii) The preparations of di-p-cyano-, di-m-bromo-, di-p-bromo-, di-p-chloro- and di-p-iodobenzoyl peroxides were similar and are exemplified by the following preparation of di-p-iodobenzoyl peroxide.

p-Iodobenzoic acid (20 g., 0.086 mol.) was boiled under reflux

with thionyl chloride (40 ml., 0.51 mol.) for 15 hours with the reaction protected from the atmosphere with a calcium chloride drying tube. The remaining thionyl chloride was removed by distillation under reduced pressure (20 mm.), the last traces of thionyl chloride being removed as the azeotrope with benzene. The remaining p-iodobenzoyl chloride was then distilled (80-86°/0.1 mms.), dissolved in chloroform (25 ml.), and added, over a period of 30 minutes, to a magnetically stirred solution maintained at less than 5°, made up from "20 vol." hydrogen peroxide (40 ml.) and a 25% solution of sodium hydroxide in water (15 ml.). Stirring was continued for a further hour, and on adding methanol (50 ml.) a pink-tinted white crystalline product was obtained which was filtered off, left under methanol for 36 hours and filtered again. The white solid was dissolved in warm chloroform and precipitated by the addition of methanol, filtered, dried between filter papers and then under vacuum to yield the peroxide (17.2 g.; 85%; m.p. 152°, decomp., lit.<sup>124</sup> 157°).

The yields and melting points of other peroxides prepared in this way are tabulated overleaf:

Peroxide	Yield (based on acid)	Melting Point
di- <u>p</u> -cyano-	48%	166° d., lit. <sup>124</sup> 165°
di- <u>m</u> -bromo-	35% (based on acid chloride)	127° d., lit. <sup>125</sup> 132°
di- <u>p</u> -bromo-	74%	141° d., lit. <sup>126</sup> 142°
di- <u>p</u> -chloro-	65%	140° d., lit. <sup>36</sup> 140-141°

Di-o-bromo-, di-p-methyl- and di-p-nitrobenzoyl peroxides were prepared by P.G. Hibbert and had melting points, 107° d., lit.<sup>124</sup> 108°; 136.5° d., lit.<sup>36</sup> 136-137° d. and 158° d., lit.<sup>36</sup> 153° d respectively.

c) Phenylazotriphenylmethane.

A solution of triphenylmethylchloride (9.7 g., 0.035 mol.) in anhydrous ether was added to a solution of freshly distilled phenylhydrazine (7.6 g., 0.07 mol., b.p. 135-140°/2 cms.) in anhydrous ether at room temperature to give a white precipitate. The mixture was boiled under reflux (1.5 hr.), allowed to stand for twelve hours at room temperature, filtered, and the filtrate added to a solution of potassium ferricyanide in water (54 g. in 200 ml.). After this solution had been cooled to 0°C an aqueous solution of sodium hydroxide (5.5 g. in 70 ml.) was added, with stirring, over a period of thirty minutes with the temperature being maintained at 0°C. Stirring was continued for an hour, ether was added to give 500 ml. of ethereal solution which was then washed with water (4 x 500 ml.) and dried over

anhydrous magnesium sulphate. Ether was distilled off under reduced pressure at room temperature and the residual yellow solid was dissolved in chloroform (30 ml.) and precipitated by the addition of methanol (250 ml.) to give phenylazotriphenylmethane (6.3 g.; 52%; m.p. 109-110°, lit.<sup>127</sup> 111°).

d) Acylarylnitrosamines.

Acylarylnitrosamines were prepared by a modification of the procedure of France, Heilbron and Hey.<sup>128</sup>

Nitrosyl chloride was prepared as described in "Inorganic Syntheses"<sup>129</sup> by allowing an aqueous solution of sodium nitrite to react with concentrated hydrochloric acid. Nitrosyl chloride was kept at 0°C as a 25% solution in acetic anhydride.

The preparations of the various substituted N-nitrosoacetanilides were similar and are illustrated by the preparation of o-iodo-N-nitrosoacetanilide.

o-Iodoaniline (15 g., 0.068 mol.), acetic anhydride (15 ccs.) and water (150 ccs.) were shaken for two minutes in a flask and the white solid which was precipitated was filtered off, recrystallised from aqueous ethanol and dried under vacuum. The resulting o-iodoacetanilide (14.6 g.; 0.056 mol.; m.p. 107-108°, lit.<sup>130</sup> 109-110°) with fused potassium acetate (14.6 g., 0.15 mol.) and phosphorus pentoxide (1.4 g.) in acetic acid (100 ml.) and acetic anhydride (7 ml.)

was magnetically stirred and cooled to 0°C in a flask protected from the atmosphere by a calcium chloride drying tube, Nitrosyl chloride (8.5 g., 0.13 mol.) as a 25% solution in acetic anhydride was added over 15 min. and stirring was continued for a further 30 min. The product was poured into ice water (ca. 500 g.), left for 30 min. when the yellow crystalline solid was filtered off and washed with water. The product was dried between filter paper and then over phosphorus pentoxide at 0.05 mms. for two hours to give o-iodo-N-nitrosoacetanilide (11.9 g.; 73%; m.p. 44-45°, decomp.). The I.R. spectrum of this compound showed no N-H absorption.

Data for other N-nitrosoacetanilides prepared similarly is given below.

<u>N</u> -Nitrosoacetanilide	Yield (%)	Melting Point (°)
unsubstituted	80-95	50-51, lit. <sup>128</sup> 50
<u>o</u> -methyl-	-	oil <sup>31</sup>
<u>o</u> -carbethoxy-	55 (based on ethyl anthrilate)	72-73.5, lit. <sup>128</sup> oil
<u>o</u> -chloro-	84	46-47, lit. <sup>132</sup> 59
<u>p</u> -chloro-	84	75, lit. <sup>133</sup> 83-84
<u>o</u> -phenyl-	-	unstable solid
<u>o</u> -iodo-	73	44-45
<u>m</u> -iodo-	90	70
<u>p</u> -iodo-	90	75-76
<u>o</u> -bromo-	89	53-56
<u>m</u> -bromo-	79	48-49
<u>p</u> -bromo-	89	81, lit. <sup>65c</sup> 84-35
<u>p</u> -nitro-	82	72, lit. <sup>128</sup> 75

e) Iodo Compounds.i) From amino compounds. -

The preparation of o-di-iodobenzene from o-iodoaniline is typical of this synthetic route.

o-Iodoaniline (3 g., 0.04 mol.) was heated on a water bath with concentrated hydrochloric acid (3.5 ml.) and water (5 ml.), cooled to 0°C and diazotisation effected by the gradual addition of an aqueous solution of sodium nitrite (1.5 g., 0.022 mol. in 5 ml.). After a further 30 min., an aqueous solution of potassium iodide (3 g., 0.018 mol. in 5 ml.) was added over 15 min., stirring was continued for a further 2 hrs. when the solution was extracted with light petroleum (b.p. 40-60°). The organic extract was washed with water (2 x 30 ml.), 3% sodium hydroxide (2 x 20 ml.), 5% sodium thiosulphate (2 x 20 ml.), water (2 x 20 ml.) and dried over magnesium sulphate. Light petroleum was distilled off and o-di-iodobenzene was distilled, protected from the light, as a pale red-brown liquid (2.9 g.; 64%; b.p. 74-76°/0.2 mms., lit.<sup>130</sup> 286-287°). The purity of the product was checked by G.L.C. and N.M.R. (AA'BB' spectrum, absorptions at  $\tau$  2.93 and  $\tau$  2.10).

The following compounds were similarly prepared.

Compound	Yield (%)	m.p. or b.p. (°)
<u>p</u> -di-iodobenzene	31	m.p. 128-129, lit. <sup>130</sup> 129.4
<u>m</u> -di-iodobenzene	40	m.p. 39, lit. <sup>130</sup> 40
2-iodobiphenyl	67	b.p. 114-116/0.04 mms., lit. <sup>130</sup> 140/3-4 mms.
<u>p</u> -iodonitrobenzene	63	m.p. 170.5-171, lit. <sup>130</sup> 174
<u>o</u> -bromiodobenzene	44	b.p. 53-55/0.1 mms., lit. <sup>130</sup> 257/754 mms.
<u>m</u> -bromiodobenzene	33.5	b.p. 65-66/0.1 mms., lit. <sup>130</sup> 120/18 mms.
<u>p</u> -iodotoluene	47	m.p. 35.5, lit. <sup>130</sup> 36-37

An isomeric mixture of the 4-chloro-, 2'-, 3'-, and 4'-iodobiphenyls (4.6 g., 0.23 m/m., b.p. 120-130°/0.2 mms.) was obtained by allowing di-p-chlorobenzoyl peroxide (20 g., 0.064 mol.) to decompose in nitrobenzene (142.2 g., 1.15 mol.) and then following the procedure of Woods et al.<sup>134</sup>

(ii) From halobenzenes.-

The method of Datta and Chatterjee<sup>135</sup> was used to prepare p-chloro- and p-bromo-iodobenzene.

Chlorobenzene (22 ml., 0.22 mol.) and iodine (25 g., 0.20 mol.) were gently boiled under reflux, while concentrated nitric acid (10 ml.) was added over 30 min. and the solution was gently boiled under reflux

for a further  $3\frac{1}{2}$  hrs. On cooling, the solution was extracted with ether (50 ml.) and the ether extract washed with 5% sodium hydroxide until there was a colour change from violet to yellow, washed with water (2 x 100 ml.) and dried over magnesium sulphate. The ether was distilled off, the residual solid was distilled at 0.05 mms., pressed between filter papers and recrystallised from ethanol to give p-chloriodobenzene (5.66 g.; 11.1%; m.p.  $54-54.5^{\circ}$ , lit.<sup>130</sup>  $57^{\circ}$ ).

Similarly p-bromiodobenzene was prepared in 22% yield with m.p.  $90.5-91^{\circ}$ , lit.<sup>130</sup>  $92^{\circ}$ .

(iii) Preparation of phenyl iodoso-di-p-nitrobenzoate.-

Iodoso benzene was prepared as described by Mann and Saunders,<sup>136</sup> and converted into the iodoso benzoate by a method based on that of Hey, Stirling and Williams.<sup>43</sup>

p-Nitrobenzoic acid (1.9 g., 0.011 mol.) dissolved in chloroform (70 ml.) and ethanol (10 ml.) was magnetically stirred at room temperature and iodoso benzene (1.2 g., 0.005 mol.) was added and dissolved in 5 min. After a further ten minutes white crystals began to precipitate, stirring was continued for 2 hrs. and the precipitate was filtered off, washed with chloroform (100 ml.), ethanol (50 ml.) and dried under vacuum over phosphorus pentoxide to give phenyl iodoso-di-p-nitrobenzoate (0.92 g.; 42%; m.p.  $209-211^{\circ}$ . Found: C, 45.1; H, 2.5%.  $C_{20}H_{13}N_2O_3I$ , requires C, 44.8; H, 2.4%).

f) Miscellaneous Compounds..i) 2,3,4,5-tetraphenylcyclopentadienone.-

Benzil (20 g., 0.095 mol.) and dibenzyl ketone (20 g., 0.095 mol.) were dissolved in ethanol (400 ml.) to which was added an ethanolic solution of potassium hydroxide (2 g. in 10 ml.) and the solution was boiled under reflux for 20 min. After cooling, the black crystals precipitated were filtered off, recrystallised from ethanol/benzene and dried under vacuum over phosphorus pentoxide to yield 2,3,4,5-tetraphenylcyclopentadienone (30.5 g.; 83%; m.p. 218-219<sup>o</sup>, <sup>138</sup>lit. 218<sup>o</sup>).

.ii) Phenyl acetates.-

Phenols were acetylated by heating in at the least, a twofold excess of acetic anhydride at 50-60<sup>o</sup> with a trace of concentrated sulphuric acid as catalyst for 30 min., and the resulting acetates were purified by distillation or recrystallisation, and had physical properties which were in agreement with literature values.

.iii) m-Bromobenzenediazonium fluoroborate.-

m-Bromoaniline (15 g., 0.087 mol.) was warmed to 50-60<sup>o</sup> with concentrated hydrochloric acid (27 ml.) and water (25 ml.), then cooled to 0<sup>o</sup>C and, with stirring, an aqueous solution of sodium nitrite (6.5 g. in 18 ml.) was added dropwise. An aqueous solution of sodium borofluoride (15 g. in 45 ml.) was added to the filtered diazonium solution which was maintained at 0<sup>o</sup> and stirred for a further

30 min. after which time the precipitated solid was filtered off, washed with methanol and ether, recrystallised from acetone/ether and dried under vacuum over phosphorus pentoxide to give m-bromobenzenediazonium fluoroborate (19.1 g.; 32%; m.p. 137-138<sup>o</sup>, lit.<sup>137</sup> 141, 145<sup>o</sup>).

### 3. DECOMPOSITIONS OF SUBSTITUTED N-NITROSOACETANILIDES IN BENZENE.

#### (a) o-Methyl-N-nitrosoacetanilide.

o-Methylacetanilide (10 g., 0.067 mol.) was nitrosated in a solution of acetic anhydride (20 ml.) and acetic acid (30 ml.), the products of the nitrosation reaction were poured into ice/water (100 g.) and left for 2 hrs. and this mixture was then shaken with benzene (65 ml.). The organic layer was separated, washed with water, left to stand for 1 hr. at 0<sup>o</sup> with methanol (10 ccs.), washed with water (3 x 100 ccs.) and stood over calcium chloride for 3 hrs. at 0<sup>o</sup>. The solution was filtered, benzene (120 ml.) added, and the solution was maintained at 40-45<sup>o</sup> for 8 hrs. and then boiled under reflux for 1 hr. On cooling, the solution was extracted with 2 N hydrochloric acid (30 ml.) and 5 N hydrochloric acid (3 x 10 ml.), the combined acid extract was made just alkaline with ammonia and extracted with chloroform (3 x 30 ml.). On evaporating the chloroform an oily solid (ca. 50 mg.) remained.

After the acid extraction the benzene solution was water washed, dried over calcium chloride and distilled to give (i) o-tolyl acetate

(0.5205 g.; 5.2%; b.p.  $76^{\circ}/0.7$  mms; lit.<sup>130</sup> b.p.  $208^{\circ}$ ) [identified by its I.R. spectrum and G.L.C. (10% PEGA at  $140^{\circ}$ )], (ii) An oil (3.52 g.;  $82-84^{\circ}/0.7$  mms.) which was then eluted through a silica column (100 g.) with benzene. A yellow oil passed through the column first and was followed by a pale yellow crystalline substance (2.3 g.; m.p.  $39-41^{\circ}$ ) with a musty smell identified as 1-acetyl indazole (21%) (Found: C, 67.5%; H, 5.25%. Calc. for  $C_9H_8N_2O$ , C, 67.5% H, 5.0%). The molecular weight was determined to be 154 (calc. value is 160) and the I.R. spectrum provided further confirmation of the structure.

All the distillation fractions were examined by G.L.C. for m- and p-~~acetates~~<sup>tolyl</sup> acetates which were found to be absent. The o-, m-, and p-~~acetates~~<sup>tolyl</sup> acetates were shown to be stable to 5N hydrochloric acid.

A high boiling residue (3.1 g.) remained in the distillation flask.

b) o-Carbethoxy-N-nitrosoacetanilide.

The nitrosamide (9.266 g., 0.039 mol.), in benzene (200 ml., 2.26 mol.) was left for 3 days at room temperature, boiled under reflux for 4 hours, most of the benzene distilled off and the residual dark coloured solution distilled to give a distillate (4.108 g., b.p.  $30-101^{\circ}/0.2$  mms.) and leaving a high boiling residue (1.83 g.).

The distillate was examined by G.L.C., whereupon o- and m-carbethoxy phenyl acetates were found to be present (1½% NPGS at 200° and 7% APL on bentonite at 220°) and the p-isomer was found to be absent, Ethyl diphenyl-2-carboxylate (authentic sample gifted by Professor D.H. Hey, F.R.S.) was confirmed as the major product of the reaction (7% APL on bentone at 208°).

By quantitative G.L.C. (7% APL on bentone at 208° with p-carbethoxy phenyl acetate as internal standard) the amount of ethyl diphenyl-2-carboxylate was determined to be 6.82 g. (75%) and of the o- and m-acetates to be 0.268 g. (3.3%) and 0.174 g. (2.1%) respectively.

c) o-Chloro-N-nitrosoacetanilide.

o-Chloro-N-nitrosoacetanilide (32.6 g., 0.16 mol.) in benzene (650 ml., 7.33 mol.) was left at room temperature for 24 hrs., maintained at 50-70° for 5 hrs. and boiled under reflux for 4 hrs. No o- or m-chlorophenyl acetates could be detected by G.L.C. By distillation and column chromatography 2-chlorobiphenyl (11.22 g.; 36%; m.p. 31.5-32°, mixed m.p. 31-31.5°, lit.<sup>130</sup> 32°) was isolated.

d) o-Phenyl-N-nitrosoacetanilide.

2-Acetamidobiphenyl (0.9 g., 0.0043 mol.) was nitrosated, the oily nitroso compound extracted with benzene (20 ml.) and the benzene solution was washed with water (3 x 40 ml.), dried over magnesium sulphate, filtered and the residue washed with benzene (5 ml.). The combined benzene solution (25 ml., 0.28 mol.) under nitrogen was

left at room temperature for 1 hr. and then boiled under reflux for 5 hrs. After cooling the solution was examined by G.L.C. The presence of o-terphenyl and biphenyl was demonstrated on 10% APL at 220° and on 1½% NPGS at 200° while the presence of o- and m- and the absence of p-acetoxybiphenyls was confirmed on 2% NPGS at 200° and on APL capillary at 170°.

With 2% NPGS at 163° and 2-chlorobiphenyl as internal standard the following quantitative data was computed.

Biphenyl	0.086 g.	13%
<u>o</u> -terphenyl	0.206 g.	21%
<u>o</u> -acetoxybiphenyl	0.057 g.	6.3%
<u>m</u> -acetoxybiphenyl	0.0405 g.	4.5%

e) Bromo-N-nitrosoacetanilides.

i) o-Bromo-N-nitrosoacetanilide.- The nitrosamide (1.17 g., 0.0048 mol.) in benzene (20 ml., 0.225 mol.), under nitrogen, was left at room temperature for 15 min. and boiled under reflux for ten hours.

In the products of reaction, o-dibromobenzene was detected (APL capillary at 120° and NPGS capillary at 140°) and it was also demonstrated by G.L.C. that 2-bromobiphenyl was the major product (5% bentone + 5% CARB at 165°). Similarly, o-, m- and p-bromophenyl acetates were shown to be absent.

On 2% NPGS at 148° with biphenyl as internal standard the following data was obtained:

<u>o</u> -dibromobenzene	0.058 g.	5.1%
2-bromobiphenyl	0.664 g.	59.2%

ii) m-Bromo-N-nitrosoacetanilide. - The nitrosamide (2.7 g., 0.011 mol.) in benzene (50 ml., 0.56 mol.) was allowed to decompose as in (i). The products of reaction were examined by G.L.C. (2% NPGS at 148°) whereby the presence of 3-bromobiphenyl (1.277 g., 49.3%) was confirmed using biphenyl as an internal standard. With the same column no m-dibromobenzene was found (0.1% would have been detected).

iii) p-Bromo-N-nitrosoacetanilide. - The nitrosamide (3 g., 0.012 mol.) was allowed to decompose in benzene (55 ml., 0.62 mol.) as described for the o-isomer. That p-dibromobenzene was a product was demonstrated by G.L.C. (2% NPGS at 148°; 10% PEGA at 120°) and the presence of 4-bromobiphenyl as the major product was similarly confirmed (2% NPGS at 148°). With the latter column at 148° and with biphenyl as internal standard the yield of p-dibromobenzene and 4-bromobiphenyl were found to be 1.3 and 47.4% respectively.

Table 1. The decomposition of bromo-N-nitrosoacetanilides  
in benzene

<u>N-Nitrosoacetanilide</u>	<u>Dibromobenzene (%)</u>	<u>Bromobiphenyl (%)</u>
<u>o</u> -Bromo-	5.1	59.2
<u>m</u> -Bromo-	-	49.3
<u>p</u> -Bromo-	1.32	47.4

4. THE ATTEMPTED DETECTION OF BENZYNOID INTERMEDIATES IN THE  
DECOMPOSITIONS OF ARYL RADICAL SOURCES IN SOLUTION.

a) Decomposition of N-Nitrosoacetanilides .

i) Decomposition of N-nitrosoacetanilide in benzene. - N-Nitroso-  
acetanilide (4 g., 0.024 mol.) in benzene (100 ml., 1.16 mol.)  
protected by a calcium chloride tube was left for 12 hours at room  
temperature and then boiled under reflux for one hour. Benzene  
was distilled off at atmospheric pressure and the residue was distilled  
(60-65°/0.05 mms.) giving a pale yellow solid which was dissolved in  
light petroleum (b.p. 40-60°) and passed through a column containing  
alumina (60 g.) to give biphenyl (1.5 g.; 39.5%; m.p. 69-70° and  
mixed m.p. with authentic sample 69-71°).

(ii) Decomposition of N-nitrosoacetanilide in benzene in the presence  
of 2,3,4,5-tetraphenylcyclopentadienone. - A solution of  
N-nitrosoacetanilide (2 g., 0.012 mol.) and 2,3,4,5-tetraphenylcyclo-  
pentadienone (10 g.; 0.026 mol.) in benzene (20 g.; 0.26 mol.),  
under nitrogen, was left for ten hours at room temperature and then

boiled under reflux for eight hours. When cool, 2,3,4,5-tetraphenylcyclopentadienone (5.9 g., after recrystallisation, with m.p. and mixed m.p. 217-219° and correct I.R. spectrum) was filtered off.

Preliminary T.L.C. examination [4% ether and 96% light petroleum (b.p. 40-60°)] indicated the presence of 1,2,3,4-tetraphenylnaphthalene. The filtrate was passed through an alumina column (500 g.) with ether (2.5 l.) and the solvent was removed from the eluate which was then dissolved in the minimum of benzene and passed through a second alumina column (500 g.). The first column was then eluted with methanol (2.5 l.) to give brown tarry material (1.7 g.) which had strong infra-red absorption at 1700 and 1750 cm.<sup>-1</sup> (carbonyl) and T.L.C. indicated that it consisted of at least seven components.

Elution of the second column with solvent ranging from light petroleum (b.p. 40-60°) to 30% benzene with 70% light petroleum (b.p. 40-60°) gave a yellow solid (1.34 g.) which was dissolved in benzene and the amount of biphenyl present was determined to be 0.0035 g. (0.02%) by G.L.C. (2% NPGS at 130° with 2-chlorobiphenyl as internal standard). Benzene was distilled off and the residual pale yellow solid was magnetically stirred with acetic acid (10 ml.) for 30 mins. to dissolve biphenyl. The solid was filtered off, recrystallised from boiling acetic acid and dried under vacuum to give 1,2,3,4-tetraphenylnaphthalene (1.3 g., 24.7%) identified by I.R. spectrum and m.p. and mixed m.p., 198-199°, lit.<sup>130</sup> 204-204.5°.

Further elution of the second column with solvent changing progressively from 30% benzene with 70% light petroleum (b.p. 40-60°) to benzene gave 2,3,4,5-tetraphenylcyclopentadienone (1.8 g. after recrystallisation, identified by I.R. and m.p.)

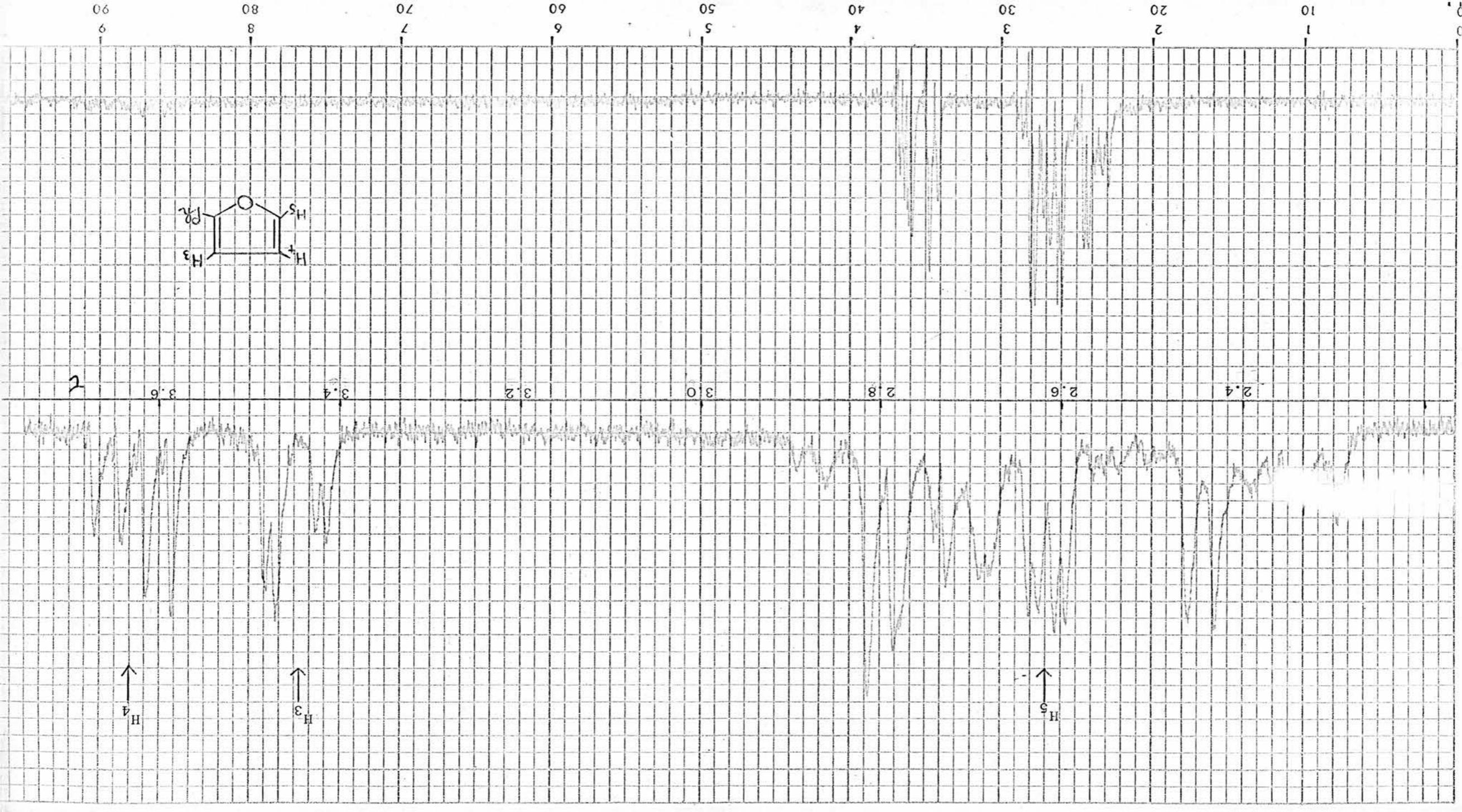
Finally, an elution with ether, a brown oil (0.35 g.) was obtained.

.iii) Competition reaction of 2,3,4,5-tetraphenylcyclopentadienone and furan with benzyne. - To a boiling, stirred, solution of amyl nitrite (3 g., 0.026 mol.), furan (1.96 g., 0.03 mol.) and 2,3,4,5-tetraphenylcyclopentadienone (11.2 g., 0.029 mol.) in benzene (22.8 g., 0.29 mol.) was added, over 40 min., a solution of anthranilic acid (2 g., 0.015 mol.) in acetone (10 ml.). The reaction mixture was boiled under reflux for a further 3 hours.

Preliminary examination of the reaction products on T.L.C., [5% ether and 95% light petroleum (b.p. 40-60°)], indicated the presence of 1,2,3,4-tetraphenylnaphthalene, while G.L.C., (2% NPGS at 120°), showed the absence of 1,4-dihydronaphthalene-1,4-endoxide. By chromatography on alumina (400 g.) using light petroleum (b.p. 60-80°) as eluant and subsequent recrystallisation from acetic acid 1,2,3,4-tetraphenylnaphthalene was isolated (5.2 g.; 32.4% based on anthranilic acid) and identified by m.p. 198-200°, mixed m.p. 197-200° and I.R. spectrum.

iv) Decomposition of N-nitrosoacetanilide in furan in the presence of 2,3,4,5-tetraphenylcyclopentadienone. -

N-Nitrosoacetanilide ( 2 g., 0.012 mol.), freshly redistilled furan (17.5 g., 0.26 mol.) and 2,3,4,5-tetraphenylcyclopentadienone (9.5 g., 0.025 mol.) were left, under nitrogen, at room temperature for 6 hours and the mixture was then boiled under reflux for 4 hours. When cool the reaction mixture was examined by G.L.C. (2% NPGS at 130°) whereupon biphenyl and 1,4-dihydronaphthalene-1,4-endoxide were found to be absent but there was a large unassignable peak with 4/7 of the retention time of biphenyl. 1,2,3,4-tetraphenylnaphthalene was not detected as one of the products of reaction by T.L.C. [4% ether and 96% light petroleum (b.p. 40-60°)]. The reaction mixture was filtered giving a filtrate (22.45 g.) and 2,3,4,5-tetraphenylcyclopentadienone (6.1 g.) identified by I.R. and m.p. and mixed m.p. (221-223°). At this stage the area of the unidentified G.L.C. peak was calibrated ( 2% NPGS at 120° using biphenyl as internal standard ) and this necessitated the use of a portion of the filtrate (2.27 g.). With another portion of the filtrate (9.32 g.), the compound giving rise to the unidentified peak was isolated by preparative G.L.C. on the Aerograph Autoprep machine, ( 20% SIL, 2 m. column at 200°, with injector at 210°, detector at 230-240° and collector at 165° ). A brown liquid (0.120 g.) was collected, which was taken up in ether (1.5 ml.) and distilled from a sublimation block in a side-arm tube



at 85-90° at 7-8 mms., after removal of the ether by distillation. The N.M.R. spectrum of the distillate, a pale yellow liquid (Found: C, 83.5; H, 5.8%. Calc. for C<sub>10</sub>H<sub>8</sub>O, C, 83.3; H, 5.55%), in carbon tetrachloride (15% solution) showed absorptions at  $\tau$  3.62 (H<sub>4</sub>),  $\tau$  3.45 (H<sub>3</sub>) and  $\tau$  2.62 (H<sub>5</sub>) [ $J_{H_3-H_4}$  3.4 c/s,  $J_{H_4-H_5}$  1.3 c/s,  $J_{H_3-H_5}$  0.8 c/s] and a complex multiplet at  $\tau$  2.28-2.90 (5H) for phenyl protons. Chemical shifts for furan are  $\alpha$  protons at ca.  $\tau$  = 2.7 and  $\beta$  protons at  $\tau$  = 3.75<sup>139</sup>. In 2-phenylfuran H<sub>3</sub> should be deshielded by a phenyl ring, causing the chemical shift to be ca. 0.2  $\tau$  lower than that for H<sub>4</sub>. Average values for  $J_{H_3-H_4}$ ,  $J_{H_4-H_5}$  and  $J_{H_3-H_5}$  are 3.2-3.8 c/s, 1.8-2.0 c/s and ca. 0.7 c/s respectively.<sup>140</sup> This would indicate that the compound is 2- rather than 3-phenylfuran.

Quantitative G.L.C. gave the yield (28%) of 2-phenylfuran.

The remaining reaction mixture filtrate (10.36 g.) was passed through an alumina column (400 g.). On elution with light petroleum (b.p. 40-60°) in decreasing admixture with benzene, no 1,2,3,4-tetraphenyl~~naphthalene~~ was obtained but 2-phenylfuran was isolated (0.21 g.) and 2,3,4,5-tetraphenylcyclopentadienone (0.8 g., m.p. and mixed m.p. 222-224° and I.R. spectrum) was obtained on elution with benzene. Elution with anaesthetic ether gave a yellow compound (0.41 g.) which was shown to consist of at least five components by T.L.C. [25% ether + 25% light petroleum

(b.p.  $40-60^{\circ}$ ) and had multiple I.R. absorption in the region  $1740-1730\text{ cm}^{-1}$ . Some brown tarry material remained on the column and did not move on elution with methanol.

Reactions of 1,4-dihydronaphthalene-1,4-endoxide. - 1,4-Dihydronaphthalene-1,4-endoxide (0.1144 g., 0.0003 mol.), benzene (1.53 g., 0.02 mol.) and acetic acid (0.0535 g., 0.0009 mol.) were boiled under reflux for 4 hours. Subsequent G.L.C. examination (10% PEGA at  $110^{\circ}$ ) showed that the 1,4-dihydronaphthalene-1,4-endoxide was unaffected by this treatment.

1,4-Dihydronaphthalene-1,4-endoxide (0.0034 g., 0.00006 mol.), furan (0.57 g., 0.0034 mol.) and N-nitrosoacetanilide (0.062 g., 0.00033 mol.) were gently boiled under reflux for 11 hours. G.L.C. analysis (2% NPGS at  $120^{\circ}$ ) showed that 1,4-dihydronaphthalene-1,4-endoxide was unchanged.

v) Decomposition of N-nitrosoacetanilide in benzene in the presence of anthracene. - N-Nitrosoacetanilide (5 g., 0.030 mol.), anthracene (10 g., 0.056 mol.) in benzene (40 gms., 0.51 mol.), under nitrogen, was stirred at room temperature for 10 hours and then boiled under reflux for 3 hours. Preliminary examination of the reaction products by G.L.C. (2% APL at  $210^{\circ}$ ) indicated the absence of triptycene.

Benzene was distilled off and replaced by xylene (100 ml.), maleic anhydride (3 g., 0.08 mol.) was added, the mixture was boiled under

reflux for 30 min., left for 14 hours and filtered. The filtrate was diluted (2 x) with dichloromethane, washed with water (400 ml.), with 15% potassium hydroxide (3 x 50 ml.), with water (2 x 400 ml.) and dried over sodium sulphate.

No triptycene was isolated on passing the solution through an alumina column (300 g.) with light petroleum (b.p. 40-60°) and benzene.

vi) Decomposition of N-nitrosoacetanilide in pyridine in the presence of 2,3,4,5-tetraphenylcyclopentadienone. - N-Nitrosoacetanilide (3 g., 0.018 mol.) and 2,3,4,5-tetraphenylcyclopentadienone (15 g., 0.039 mol.) in pyridine (30 g., 0.38 mol.), under nitrogen, was stirred at room temperature for 10 hours and then boiled under reflux for 8 hours.

Preliminary examination of the reaction products by T.L.C. [5% ether + 95% light petroleum (b.p. 40-60°)] indicated the absence of 1,2,3,4-tetraphenylnaphthalene and G.L.C. examination (2% NPGS at 120° and 10% PEGA at 170°) revealed the absence of phenylpyridines as products of reaction. Filtration yielded, after recrystallisation, 2,3,4,5-tetraphenylcyclopentadienone (9.2 g.) by I.R. spectrum and m.p. and mixed m.p. 216-217°.

The filtrate was passed through an alumina column (600 g.) with ether (3.5 l.), the column was then eluted with methanol (2.5 l.) to give tarry material (2.6 g.) which was shown to have at least nine components by T.L.C. After methanol elution the column was heavily

streaked with tarry material which did not move on methanol elution. Ether was distilled off the first fraction and the residual solution was passed through a second alumina column (600 g.). No 1,2,3,4-tetraphenyl~~naphthalene~~ was obtained on elution with light petroleum (b.p. 40-60°) and benzene, 2,3,4,5-tetraphenylcyclopentadienone (2.8 g.), after recrystallisation, identified by I.R. spectrum and m.p. and mixed m.p. 216-218°, was isolated on elution with benzene. On further elution with ether an oily solid (1 g.) was obtained which was shown by T.L.C. to have at least five components

vii) The decomposition of N-nitrosoacetanilide in tetrahydrofuran in the presence of 2,3,4,5-tetraphenylcyclopentadienone. -

N-Nitrosoacetanilide (2 g., 0.012 mol.) and 2,3,4,5-tetraphenylcyclopentadienone (10 g., 0.026 mol.) in tetrahydrofuran (13.3 g., 0.25 mol.), under nitrogen, was left at room temperature for 90 mins. and then boiled under reflux for 6 hours. Preliminary investigation of the reaction products by T.L.C. [4% ether and 96% light petroleum (b.p. 40-60°)] indicated the presence of 1,2,3,4-tetraphenyl~~naphthalene~~. Tetrahydrofuran was distilled off and replaced by benzene (25 ml.), the solution was filtered giving, after recrystallisation, 2,3,4,5-tetraphenylcyclopentadienone (1.6 g.), identified by I.R. spectrum and m.p. and mixed m.p. 217-219°. The filtrate was passed through an alumina column (500 g.). On elution with a mixture of 10% benzene and 90% light petroleum (b.p. 40-60°) a pale yellow solid

was isolated which was recrystallised from acetic acid to give 1,2,3,4-tetraphenylnaphthalene (1.25 g.; 23.8%; m.p. and mixed m.p. 198-199°). The I.R. spectrum of this compound was verified. 2,3,4,5-Tetraphenylcyclopentadienone (6.25 g.), obtained after elution with benzene and recrystallisation, was identified by its I.R. spectrum and m.p. and mixed m.p. (217-218°). Further elution with ether and methanol gave a multi component brown solid (3.6 g.).

viii) The decomposition of N-nitrosoacetanilide in benzene in the presence of 1,3-diphenylisobenzofuran. - N-Nitrosoacetanilide (0.5 g., 0.003 mol.) and 1,3-diphenylisobenzofuran (1.65 g., 0.006 mol.) in benzene (9.5 g., 0.125 mol.), under nitrogen, was left at room temperature for 10 hours and then boiled under reflux for 6 hours. On cooling, powdered zinc (3 g., 0.12 mol.) and acetic acid (20 ml., 0.35 mol.) were added and the solution was stirred for 8 hours at 85°, filtered, then the volatile components of the filtrate distilled off and benzene (10 ml.) added to the residue. This solution was then examined by T.L.C. [light petroleum (b.p. 40-60°)] and the presence of 9,10-diphenylanthracene was indicated. On elution through an alumina column (350 g.) with a mixture of 10% benzene and 90% light petroleum (b.p. 40-60°) and subsequent recrystallisation from acetic acid, 9,10-diphenylanthracene (0.1371 g.; 14%; m.p. and mixed m.p. 246-248°, lit.<sup>98</sup> 246-247°, and identical I.R. spectrum with an authentic specimen) was isolated.

ix) Decomposition of o-iodo-N-nitrosoacetanilide in benzene in the presence of 2,3,4,5-tetraphenylcyclopentadienone. - A mixture of 2,3,4,5-tetraphenylcyclopentadienone (12 g., 0.031 mol.) with o-iodo-N-nitrosoacetanilide (5.5 g., 0.019 mol.) in benzene (29 g., 0.37 mol.), under nitrogen, was maintained at 50-60° for 4 hours and then boiled under reflux for 3 hours. Examination of the reaction products by T.L.C. [4% ether and 96% light petroleum (b.p. 40-60°)] indicated the presence of 1,2,3,4-tetraphenylnaphthalene. On cooling, the solution was filtered and the filtrate passed through an alumina column (220 g.) with light petroleum (b.p. 60-80°). All the fractions coming off the column before the purple band of 2,3,4,5-tetraphenylcyclopentadienone were collected, the solvent was distilled off and the residual solid was dissolved in the minimum of benzene and run on 1 mm. thick silica T.L.C. plates with 4% ether and 96% light petroleum (b.p. 40-60°) as solvent. On spraying the plates with 2,6-dichlorofluorescein, a strongly fluorescent band was observed on ultra violet illumination and this band was removed, stirred with benzene (400 ml.) for 1 hour, filtered, benzene distilled off and the residual solid was recrystallised from acetic acid to yield 1,2,3,4-tetraphenylnaphthalene (0.0293 g.; 0.23%; m.p. 194.5-195.5 and mixed m.p. 195-196° and correct I.R. spectrum).

x) Decomposition of o-iodo-N-nitrosoacetanilide in furan and benzene. - The nitrosamide (5.5 g., 0.019 mol.) in benzene (29 g., 0.37 mol.) with freshly redistilled furan (4 g., 0.06 mol.), under nitrogen, was maintained at 50-60° for 4 hours and boiled under reflux for 3 hours.

No 1,4-dihydronaphthalene-1,4-endoxide was detected by G.L.C. on a 10% PEGA column at 110°.

xi) The reaction of o-di-iodo benzene with 2,3,4,5-tetraphenylcyclopentadienone in benzene. - Freshly prepared o-di-iodobenzene (3 g., 0.0091 mol.), 2,3,4,5-tetraphenylcyclopentadienone (4 g., 0.01 mol.) and benzene (22 g., 0.28 mol.) were boiled under reflux for 4 hours under nitrogen.

From a T.L.C. run from 4% ether and 96% light petroleum it was observed that no 1,2,3,4-tetraphenylnaphthalene had been formed.

xii) The reaction of dibenzoyl peroxide with o-di-iodobenzene in the presence of 2,3,4,5-tetraphenylcyclopentadienone. - Freshly prepared o-di-iodobenzene (1 g., 0.003 mol.), dibenzoyl peroxide (1.5 g., 0.006 mol.), 2,3,4,5-tetraphenylcyclopentadienone (2.3 g., 0.006 mol.) and benzene (5 g., 0.064 mol.) were boiled under reflux for 72 hours under nitrogen.

From a T.L.C. run from carbon tetrachloride it was observed that no 1,2,3,4-tetraphenylnaphthalene had been formed.

b) Decomposition of Dibenzoyl Peroxide in Benzene in the presence of 2,3,4,5-Tetraphenylcyclopentadienone.

Dibenzoyl peroxide (2 g., 0.0083 mol.) and 2,3,4,5-tetraphenylcyclopentadienone (6.35 g., 0.016 mol.) in benzene (12.6 g., 0.16 mol.), under nitrogen, was boiled under reflux for 72 hours. A preliminary examination of the reaction products by T.L.C. [4% ether and 96% light petroleum (b.p. 40-60°)] indicated the absence of 1,2,3,4-tetraphenylnaphthalene. The reaction mixture was diluted with benzene (100 ml.), extracted with 10% potassium bicarbonate solution and on acidification of the alkaline extract there was no precipitation of solid. The reaction mixture was concentrated and separated into its components by column chromatography on alumina. No 1,2,3,4-tetraphenylnaphthalene was isolated on elution with benzene/light petroleum (b.p. 40-60°) mixtures, but 2,3,4,5-tetraphenylcyclopentadienone (3.25 g.), identified by I.R. spectrum and m.p. and mixed m.p. 217-218° was isolated. Further elution with benzene produced a violet coloured glass-like solid (0.5 g.) which was shown by T.L.C. to have at least five components. On elution with ether, a purple-white solid (3.8 g.) was isolated which was recrystallised from carbon tetrachloride to yield a pure white crystalline compound (2.3 g., m.p. 200-201°) which was found to be soluble in benzene and acetone and insoluble in ether and light petroleum. The compound was analysed (C, 80.0%; H, 4.7%) and its molecular weight determined (M.W., 553).

The I.R. spectrum was found to be complex with strong absorptions at 1712, 1730 and 1778  $\text{cm.}^{-1}$ ; the N.M.R. spectrum suggested the presence of benzoyl groups and the U.V. spectrum was very similar to that of cis-stilbene. Further elution of the column with methanol resulted in the isolation of tarry material (0.4 g.).

c) Decomposition of Phenylazotriphenylmethane in Benzene in the Presence of 2,3,4,5-Tetraphenylcyclopentadienone.

Phenylazotriphenylmethane (6 g., 0.017 mol.),  
2,3,4,5-tetraphenylcyclopentadienone (13.2 g., 0.034 mol.) in benzene (26.9 g., 0.34 mol.), under nitrogen, was maintained at 60-80° for 30 min. and then boiled under reflux for 2½ hours.

A preliminary examination of the reaction products by T.L.C. [3% ether with 97% light petroleum (b.p. 40-60°)] indicated that 1,2,3,4-tetraphenylnaphthalene was not a product of the reaction. The reaction mixture was concentrated and chromatographed on alumina (500 g.). Elution with light petroleum (b.p. 40-60°) gave a pale yellow solid (3.06 g.). G.L.C. analysis (2% NPGS at 160°) using 2-chlorobiphenyl as internal standard, showed the presence of biphenyl (0.0405 g., 0.015 m/m.). The solid was further investigated by chromatography on an alumina column (100 g.) and preparative T.L.C. whereupon no 1,2,3,4-tetraphenylnaphthalene was detected.

Further elution of the reaction mixture with benzene/light petroleum (b.p. 40-60°) gave a red oil (0.183 g.), benzene, alone,

gave 2,3,4,5-tetraphenylcyclopentadienone (after recrystallisation, 12.3 g., identified by I.R. spectrum and m.p. and mixed m.p. 217-219°), benzene/ether (50-50) gave a yellow oil (seven components by T.L.C.), and finally methanol gave a yellow solid (1.108 g.) containing at the least seven components (T.L.C.).

d) Aniline and Amyl Nitrite.

- i) The reaction of aniline, with amyl nitrite and 2,3,4,5-tetraphenylcyclopentadienone in benzene. - Freshly distilled aniline (2 g., 0.022 mol.) in benzene (9 g., 0.11 mol.) was added over a period of 20 min. to a stirred solution of amyl nitrite (4 g., 0.034 mol.) and 2,3,4,5-tetraphenylcyclopentadienone (8.4 g., 0.022 mol.) in benzene (9 g., 0.12 mol.) which was boiling under reflux. The solution was boiled under reflux for a further 3 hours. On cooling, a preliminary examination of the reaction products by T.L.C. [4% ether and 96% light petroleum (b.p. 40-60°)] indicated the absence of 1,2,3,4-tetraphenyl~~naphthalene~~. This was verified by column chromatography on an alumina column (550 g.). The products of the reaction were very complex and no products were isolated.
- ii) The reaction of aniline, with amyl nitrite, and 2,3,4,5-tetraphenylcyclopentadienone in dichloromethane. - The procedure and quantities were as in i) apart from the fact that aniline was dissolved in dichloromethane (10 g., 0.012 mol.) and that in the initial solution boiling under reflux benzene was replaced by

dichloromethane (23 g., 0.33 mol.). Investigation of the products of the reaction by T.L.C. [4% ether and 96% light petroleum (b.p. 40-60°)] was inconclusive as regards the presence of 1,2,3,4-tetraphenylnaphthalene, and the reaction mixture was passed through an alumina column (500 g.). On elution with petroleum ether (b.p. 40-60°) a solid (0.1 g.) was obtained, from which was isolated by preparative T.L.C., on 1 mm. thick plates with carbon tetrachloride as solvent, 1,2,3,4-tetraphenylnaphthalene (0.01 g., 0.12%; m.p. and mixed m.p. 197-199° and correct I.R. spectrum, after recrystallisation from acetic acid). As with the reaction in benzene the products of reaction were highly complex.

iii) The reaction of aniline with amyl nitrite and 2,3,4,5-tetraphenylcyclopentadienone in benzene in the presence of anhydrous magnesium sulphate. - To vigorously stirred amyl nitrite (4.0 g., 0.034 mol.), 2,3,4,5-tetraphenylcyclopentadienone (8.4 g., 0.022 mol.) and anhydrous magnesium sulphate (3 g., 0.06 mol.) in benzene (25 g., 0.30 mol.) being boiled under reflux, freshly distilled aniline (2 g., 0.022 mol.) in benzene (9 g., 0.11 mol.) was added over a period of 20 min. and boiling was continued for 3 hours.

T.L.C. examination of the products of reaction [4% ether with 96% light petroleum (b.p. 40-60°)] indicated the absence of 1,2,3,4-tetraphenylnaphthalene.

iv) The reaction of aniline with amyl nitrite, acetic acid and 2,3,4,5-tetraphenylcyclopentadienone in benzene in the presence of anhydrous magnesium sulphate. - This reaction was conducted exactly as described above (iii) with the exception that acetic acid (1.3 g., 0.022 mol.) was added to the reaction mixture before the addition of aniline.

By T.L.C. [4% ether with 96% light petroleum (b.p. 40-60°)] it was shown that 1,2,3,4-tetraphenylnaphthalene was not a product of the reaction.

e) The Gomberg Reaction.

Freshly distilled aniline (2 g., 0.022 mol.) in concentrated hydrochloric acid (6 ml.) and water (6 ml.) was heated, then cooled to 0° and, with stirring, an aqueous solution of sodium nitrite (2 g., 0.03 mol. in 5 ml.) was slowly added. Stirring was continued for 30 min., the solution was filtered and divided into two equal fractions. A solution of benzenediazonium chloride (from 1 g. aniline) was vigorously stirred with benzene (20 ml., 0.23 mol.) and 2,3,4,5-tetraphenylcyclopentadienone (8 g., 0.021 mol.), maintained at 0°C, while an aqueous solution of sodium hydroxide (1.8 g., 0.045 mol. in 3 ml.) was added over a period of 15 mins. The reaction mixture was surrounded by an ice bath for a further 4 hours and then left stirring at room temperature for a further 56 hours.

An identical diazonium solution was treated in a similar fashion with the exception that sodium hydroxide was replaced by sodium acetate (4.2 g., 0.44 mol.).

The products of both reactions were investigated by T.L.C. [4% ether with 96% light petroleum (b.p. 40-60°)] but 1,2,3,4-tetraphenylnaphthalene was not detected in either case.

f) Reaction of Benzenediazonium Fluoroborates with Strong Bases

i) The reaction of m-bromobenzenediazonium fluoroborate with sodium methoxide in the presence of 2,3,4,5-tetraphenylcyclopentadienone in benzene. - m-Bromobenzenediazonium fluoroborate (5.3 g., 0.02 mol.) and 2,3,4,5-tetraphenylcyclopentadienone (15 g., 0.04 mol.) was stirred in benzene (40 g., 0.51 mol.) at 0° while sodium methoxide (1.15 g., 0.021 mol.) was slowly added. There was no visible reaction so the ice bath was removed and the reaction was stirred at room temperature for a further 12 hours.

Investigation of the reaction products by T.L.C. [4% ether with 96% light petroleum (b.p. 40-60°)] indicated the absence of 5-bromo-1,2,3,4-tetraphenylnaphthalene.

ii) The reaction of benzenediazonium fluoroborate with n-butyl lithium in benzene in the presence of 2,3,4,5-tetraphenylcyclopentadienone. - Benzenediazonium fluoroborate (1.5 g., 0.0078 mol.), 2,3,4,5-tetraphenylcyclopentadienone (3 g., 0.0078 mol.) and benzene (12 g., 0.15 mol.) were vigorously stirred and n-butyl lithium (0.5 g., 0.008 mol.) in 15% solution in hexane (Foote Mineral Co.)

was added as rapidly as possible with a hypodermic syringe. The solution, protected from the atmosphere by a calcium chloride drying tube, was stirred for a further 4 hours. No 1,2,3,4-tetraphenylnaphthalene was detected by T.L.C. [4% ether with 96% light petroleum (b.p. 40-60°)].

iii) The reaction of benzenediazonium fluoroborate with n-butyl lithium in furan. - Benzenediazonium fluoroborate (1.5 g., 0.0078 mol.) was vigorously stirred in furan (12 g., 0.18 mol.) and n-butyl lithium (0.5 g., 0.008 mol.) in 15% solution in hexane was rapidly added with a hypodermic syringe and the reaction left stirring for 4 hours protected from the atmosphere by a calcium chloride drying tube. T.L.C. examination of the products of reaction [4% ether with 96% light petroleum (b.p. 40-60°)] indicated the absence of 1,4-dihydronaphthalene-1,4-endoxide.

5) THE ABSTRACTION OF IODINE FROM AROMATIC IODIDES BY ARYL RADICALS.

a) The Decomposition of o-Iodo-N-nitrosoacetanilide in Benzene.

i) o-Iodoacetanilide (14 g., 0.054 mol.) was nitrosated, the resulting nitroso compound was an oil and was extracted with benzene (70 ml.), washed with water (2 x 80 ml.), left to stand for 1 hour with methanol (10 ml.), washed with water (3 x 100 ml.) and dried over magnesium sulphate at 0°. The solution was filtered and benzene (130 ml.) was added to the filtrate, the total amount of benzene being (200 ml., 2.26 mol.). The solution was maintained

at 50-60° for 8 hours, boiled under reflux for 4 hours, distilled under vacuum and on examining the distillate by G.L.C. (10% SIL at 195 and 7% APL on bentonite at 180°) o- and m-iodophenylacetates were seen to be absent, 2-iodobiphenyl was confirmed to be present and a large unassignable peak with a retention time comparable to that of biphenyl was observed. Using 1/5 of the distillate, a sample of the unknown compound (0.53 g.) was isolated by preparative G.L.C. using the Aerograph Autoprep instrument (20% SIL, 2 m. column at 200°, with collector at 228°, detector at 245° and injector at 230°). A Lassaigne test gave a positive result for iodine and the I.R., U.V. and N.M.R. spectra of the isolated compound were seen to be identical with the spectra of freshly prepared o-diiodobenzene. A sample of 2-iodobiphenyl was also separated and its identity confirmed by comparison of its I.R. spectrum with that of an authentic sample.

On further examination of the remainder of the filtrate by G.L.C. (APL capillary at 220° and 2% NPGS at 190°) o-terphenyl was identified.

ii) o-Iodo-N-nitrosoacetanilide (8.2 g., 0.028 mol.) was dissolved in benzene (44 g., 0.56 mol.) and, under nitrogen and protected from light, was boiled under reflux for 11 hours. Subsequent G.L.C. analysis (2% NPGS at 150° with biphenyl as internal standard) gave the following data: o-diiodobenzene (2.146 g., 0.1924 m/m.),

2-iodobiphenyl (1.904 g., 0.2012 m/m.) and o-terphenyl (0.042 g., 0.028 m/m. based on o-di-iodobenzene. Using a portion of the reaction mixture, a potassium bromide disc was prepared by collection of the effluent gases, corresponding to elution of o-terphenyl and o-iodoacetanilide, from a Varian Aerograph 1520B G.L.C. (10% QF1 at 150°). The I.R. spectrum obtained was identical with a spectrum obtained from a mixture of the authentic compounds. A portion of the reaction mixture was distilled from an oil bath at 250° at 0.4 mms. and, on correction, the total high boiling residue for the reaction amounted to 1.74 g.

b) The Decomposition of m-Iodo-N-nitrosoacetanilide in Benzene.

m-Iodo-N-nitrosoacetanilide (2.08 g., 0.0072 mol.) in benzene (11 g., 0.14 mol.), under nitrogen and protected from the light, was boiled under reflux for 11 hours. G.L.C. analysis of the products of the reaction confirmed the presence of m-di-iodobenzene (10% SIL at 200° and 10% PEGA at 190°), 3-iodobiphenyl (7% APL on bentone and 2% NPGS at 150°) and m-terphenyl (APL capillary at 220° and 2% NPGS at 210°). By G.L.C. (2% NPGS column 150°) with biphenyl as internal standard, the following yields were calculated: m-di-iodobenzene (0.433 g., 0.183 m/m.), 3-iodobiphenyl (0.709 g., 0.3528 m/m.) and m-terphenyl (0.0545 g., 0.1806 m/m based on m-di-iodobenzene). On distillation at 0.4 mms. from an oil bath at 240°, the high boiling residue was 0.71 g. for the reaction.

c) The Decomposition of p-Iodo-N-nitrosoacetanilide in Benzene. -  
p-Iodo-N-nitrosoacetanilide (1.65 g., 0.0057 mol.) in benzene  
 (9 g., 0.115 mol.), under nitrogen and protected from the light,  
 was boiled under reflux for 11 hours. By G.L.C. analysis of the  
 reaction products, p-di-iodobenzene and 4-iodobiphenyl (10% PEGA  
 at 200° and 10% APL at 275°), and p-terphenyl (3% APL at 235° and  
 2% NPGS at 210°) were identified. With biphenyl as internal  
 standard and with a 2% NPGS column at 150° the following yields  
 were calculated: p-di-iodobenzene (0.410 g., 0.2181 m/m.),  
 4-iodobiphenyl (0.577 g., 0.3621 m/m.) and p-terphenyl (0.073 g.,  
 0.255 m/m. based on p-di-iodobenzene). On distillation at 0.3 mms.  
 from an oil bath at 240° the high boiling residue produced in the  
 reaction weighed 0.66 g.

Table 2. The decomposition of iodo-N-nitrosoacetanilides  
in benzene.

<u>N-nitrosoacetanilide</u>	<u>Products (m/m. Iodo-N-nitrosoanilide)</u>	
	<u>di-Iodobenzene</u>	<u>Iodobiphenyl</u>
<u>o</u> -Iodo-	0.1924	0.2012
<u>m</u> -Iodo-	0.183	0.3528
<u>p</u> -Iodo-	0.2181	0.3621

d) The Decomposition of di-p-Chlorobenzoyl Peroxide in Iodobenzene.

- i) Di-p-chlorobenzoyl peroxide (2 g., 0.0064 mol.) was warmed with iodobenzene (28.6 g., 0.14 mol.) to dissolve the peroxide and then left, under nitrogen in a thermostated oil tank at 80° for 72 hours. When cool, the solution was filtered, the white crystals thus obtained were washed with benzene and identified by I.R. and m.p. and mixed m.p. 240-242°, lit.<sup>130</sup> 243° as p-chlorobenzoic acid (0.91 g., 0.91 m/m.). Alkali extraction of the filtrate gave no more acid. On G.L.C. analysis of the filtrate, p-chloriodobenzene (1½% NPGS at 100° and 10% APL at 185°) and 2-, 3-, and 4-iodobiphenyl (10% APL at 245° and 10% PEGA at 180°) were identified. With p-dibromobenzene as internal standard (10% PEGA at 158° and 2% NPGS at 142°) the following yields were calculated: p-chloriodobenzene (1.288 g., 0.82 m/m.) and 2-, 3-, and 4-iodobiphenyls (1.044 g.; molar yield based on p-chloriodobenzene, 0.69; isomer ratios: 56% 2-, 26% 3- and 18% 4-iodobiphenyl). 4-Chloro-2'-, 3'- and 4'-iodobiphenyls were sought by G.L.C. (2% NPGS column at 190°) and were found to constitute a yield of less than 0.03 m/m.
- ii) Di-p-chlorobenzoyl peroxide (4 g., 0.0128 mol.) was allowed to decompose in iodobenzene (57.2 g., 0.28 mol.) as described above (i). After distillation there was a high boiling residue (0.82 g.)

e) The Decomposition of Di-*p*-bromobenzoyl Peroxide in Iodobenzene.

p-Bromobenzoyl peroxide (3 g., 0.0075 mol.) was allowed to decompose in iodobenzene (29.8 g., 0.146 mol.) as described above (d). On filtration, p-bromobenzoic acid was isolated (1.45 g., 0.95 m/m., m.p. and mixed m.p. 250-253°, lit.<sup>130</sup> 251-253°, and correct I.R. spectrum) and no more acid was obtained on alkali extraction of the filtrate. The filtrate was examined by G.L.C. and p-bromiodobenzene (10% PEGA at 185° and 10% APL at 190°) and 2-, 3- and 4-iodobiphenyl (10% PEGA at 185° and 10% APL at 245°) were shown to be present. With 2-chlorobiphenyl as internal standard (10% PEGA at 170°) the following yields were calculated: p-bromiodobenzene (1.601 g.; 0.76 m/m.) and 2-, 3- and 4-iodobiphenyls (0.745 g.; molar yield based on p-bromiodobenzene, 0.48; isomer ratios: 57% 2-, 26% 3- and 17% 4-iodobiphenyl).

4-Bromobiphenyl was sought by G.L.C. as a product of the reaction (2% NPGS column at 130°) but was not detected.

Using the Aerograph Autoprep instrument (20% APL, 8 ft. column at 275°, collector and detector at 330° and injector at 325°) two fractions were separated from the reaction mixture. The first fraction was a viscous pale yellow liquid, which had the odour of 2-iodobiphenyl and was identified as such by comparison of its I.R. and N.M.R. spectra with those of an authentic sample. The second fraction was a solid which was identified as a mixture of 3- and 4-iodobiphenyls by comparison of its I.R. spectrum with that of an authentic mixture.

f) The Decomposition of Di-*p*-chlorobenzoyl Peroxide in Bromobenzene.

As described above (d), di-*p*-chlorobenzoyl peroxide (6.19 g., 0.02 mol.) was allowed to decompose in bromobenzene (70 g., 0.45 mol.) and the products were worked up in the usual manner. Subsequent G.L.C. examination (10% PEGA at 130°) revealed that if *p*-chlorobromobenzene were a product of the reaction it was present to the extent of less than 0.01 m/m.

g) The Decomposition of Di-*p*-bromobenzoyl Peroxide in Bromobenzene.

Similarly, di-*p*-bromobenzoyl peroxide (3 g., 0.0075 mol.) was allowed to decompose in bromobenzene (26 g., 0.16 mol.). Subsequent G.L.C. examination (10% PEGA at 130°) revealed that if *p*-dibromobenzene were a product of the reaction it was present to an extent less than 0.017 m/m.

h) The Decomposition of Di-*p*-chlorobenzoyl Peroxide in 2-Iodobiphenyl.

As described above (d), di-*p*-chlorobenzoyl peroxide (2.1 g., 0.0068 mol.) was allowed to decompose in 2-iodobiphenyl (30.1 g., 0.107 mol.). Subsequent G.L.C. analysis indicated the absence of biphenylene as a product of the reaction (authentic sample gifted by Mr. D. Lloyd). By the use of biphenyl as internal standard (2% NPGS at 120°) the amount of *p*-chloriodobenzene, after confirming its presence (10% SIL at 165° and 10% PEGA at 190°), was calculated to be 1.16 g., (0.72 m/m.).

i) The Decomposition of Di-p-iodobenzoyl Peroxide in Benzene.

Following the usual procedure (d), di-p-iodobenzoyl peroxide (8 g., 0.016 mol.) was allowed to decompose in benzene (25 g., 0.31 mol.).

On filtration, a solid (1.9 gms.) was obtained which was stirred overnight with a 5% solution of sodium hydroxide, some insoluble material (0.25 g.) was filtered off and acidification of the filtrate gave p-iodobenzoic acid (1.6 g., m.p. and mixed m.p. 270-272°, lit.<sup>130</sup> 270°, and correct I.R. spectrum). On G.L.C. examination of the filtrate from the reaction mixture, p-di-iodobenzene (3% APL at 180° and 1½% NPGS at 140°), iodobenzene (10% PEGA and 10% APL at 143°), biphenyl (10% PEGA at 180°), p-terphenyl and 4-iodobiphenyl (APL capillary at 240° and 2% NPGS at 220°) were confirmed to be present. With 2-chlorobiphenyl as internal standard (2% NPGS column at 150°) the following yields are computed: biphenyl (0.0365 g., 0.00025 m/m.), p-di-iodobenzene (1.793 g., 0.3355 m/m.), 4-iodobiphenyl (0.796 g., 0.1754 m/m.); with the column at 210°, p-terphenyl (0.027 g., molar yield based on p-di-iodobenzene, 0.022) and with the column at 125°, iodobenzene (0.207 g., 0.03547 m/m.). On extraction of the filtrate from the reaction mixture with a 5% sodium hydroxide solution there was an immediate precipitation of a solid (1.8 g.) which was identical with the previously obtained alkali insoluble material. This substance did not melt below 330°.

Acidification of the alkaline solution yielded p-iodobenzoic acid

(0.21 g., m.p. and mixed m.p. 271-274° and correct I.R. spectrum).

The total recovery of p-iodobenzoic acid is 1.81 g. (0.45 m/m.).

By distillation under vacuum there was found to be a high boiling residue of 0.91 g.

j) The Decomposition of Di-m- and Di-o-bromobenzoyl Peroxides and Di-p-methylbenzoyl Peroxide in Iodobenzene.

Following the procedure described under (d) the above peroxides (1 mol.) were allowed to decompose in iodobenzene (20 mol.) and the results in Table 3 were obtained by qualitative and quantitative G.L.C.: m-bromiodobenzene (10% PEGA at 142° with p-dibromobenzene as internal standard), o-bromiodobenzene (2% NPGS at 140° with 2-chlorobiphenyl as internal standard), p-iodotoluene (10% PEGA at 154° with p-dibromobenzene as internal standard) and 2-, 3- and 4-iodobiphenyls (2% NPGS at 140-148° with the same internal standards as used for the respective iodides).

Table 3

Dibenzoyl Peroxide	Acid (m/m.)	Products	
		Aryl iodide (m/m)	Iodobiphenyls (molar yield based on aryl iodide; isomer ratios)
<u>m</u> -Bromo-	0.91	0.6	0.55; (2-, 57%; 3-, 24.5%; 4-, 18.5%)
<u>o</u> -Bromo-	0.74	0.71	0.44; (2-, 56%; 3-, 23%; 4-, 21%)
<u>p</u> -Methyl-	0.72	0.82	0.28; (2-, 48.5%; 3-, 29.5%; 4-, 22%)

k) The Decomposition of Di-*o*-bromobenzoyl Peroxide in a Mixture of Benzene and Iodobenzene.

By the usual procedure, di-*o*-bromobenzoyl peroxide (3 g., 0.0075 mol.) was allowed to decompose in a mixture of benzene (23.4 g., 0.3 mol.) and iodobenzene (3.1 g., 0.015 mol.).

By filtration and extraction of the filtrate with a 5% sodium hydroxide solution *o*-bromobenzoic acid (0.79 g.; 0.53 m/m.); m.p. 146-148° and mixed m.p. 149-150°, lit.<sup>130</sup> 150°; correct I.R. spectrum) was isolated. By G.L.C. (MBM capillary at 150° and APL capillary at 130°) bromobenzene, iodobenzene, biphenyl and *o*-bromiodobenzene were shown to be present as the products of the reaction. 2-Bromobiphenyl was also shown to be present (10% APL at 195° and 8% BDS at 162°). With *p*-dibromobenzene as internal standard (2% NPGS at 120°) the following yields were calculated: *o*-bromiodobenzene (0.436 g., 0.21 m/m.), 2-bromobiphenyl (0.402 g., 0.23 m/m.), and biphenyl (0.0975., molar yield based on *o*-bromiodobenzene 0.412). There was (10% PEGGA with chlorobenzene as internal standard) calculated to be 0.107 g. (0.03 m/m.) of bromobenzene.

l) The Decompositions of Di-*m*- and Di-*p*-bromobenzoyl Peroxides in Mixtures of Benzene and Iodobenzene.

Following the procedure described above (k), di-*m*-bromobenzoyl peroxide (1 mol.) was allowed to decompose in a mixture of benzene (40 mol.) and iodobenzene (2 mol.) and di-*p*-bromobenzoyl peroxide (1 mol.) was allowed to decompose in solutions of benzene (40 mol.) with

iodobenzene (2 mol.) and benzene (81 mol.) with iodobenzene (2 mol.).

The results obtained are given in Table 4 along with the results from (k).

TABLE 4.

Peroxide	Molar ratio of benzene to iodobenzene	(m/m.)				Biphenyl (molar yield based on aryl iodide).
		Aryl iodide	Bromobiphenyl	Bromobenzene	Acid	
di- <u>o</u> -Bromo-	20:1	0.21	0.23	0.08	0.53	0.41
di- <u>m</u> -Bromo-	20:1	0.31	0.36	0.05	0.54	0.38
di- <u>p</u> -Bromo-	20:1	0.35	0.17	0.05	0.54	0.37
di- <u>p</u> -Bromo-	405:1	0.38	0.28	0.05	0.47	0.38

m) The Decomposition of p-Chloro-N-nitrosoacetanilide in Iodobenzene, Iodobenzene with Benzene and Benzene.

i) p-Chloro-N-nitrosoacetanilide (2.5 g., 0.013 mol.) in iodobenzene (52 g., 0.25 mol.), under nitrogen, protected from light, was left at room temperature for 24 hours, maintained at 70-80° for four hours and at 100° for 3 hours. By G.L.C. examination of the reaction products, p-chloriodobenzene (2% NPGS at 145° and 10% APL at 175°) and 2-, 3- and 4-iodobiphenyl (2% NPGS at 142° and 10% PEGA at 190°) were confirmed to be present. By quantitative G.L.C., with p-bromiodobenzene as internal standard (2% NPGS column) the following yields were calculated: at a column temperature of 115°, p-chloriodobenzene (1.619 g., 0.54 m/m) and at 142°, 2-, 3- and 4-iodobiphenyls (0.898 g.; molar yield based on p-chloriodobenzene, 0.4724; isomer ratios: 2-, 58%; 3-, 23% and 4-, 19%). There was seen to be less than a 1% yield of the 4-chloro-2'-, 3'- and 4'-iodobiphenyls produced in the reaction [by G.L.C. examination (2% NPGS column at 190°)].

ii) Similarly, p-chloro-N-nitrosoacetanilide (3 g., 0.015 mol.) was allowed to decompose in benzene (30 ml., 0.34 mol.).

iii) Similarly, p-chloro-N-nitrosoacetanilide (2.61 g., 0.013 mol.) was allowed to decompose in a mixture of benzene (30 ml., 0.34 mol.) and iodobenzene (2.863 g., 0.014 mol.).

The results of experiments m i), m ii) and m iii) are summarised in Table 5.

TABLE 5.

Reaction	(m/m.)			(Molar yield based on <u>p</u> -chloriodobenzene)	
	<u>p</u> -Chloriodobenzene	4-Chlorobiphenyl	Chlorobenzene	Biphenyl	Iodobiphenyls
m i)	0.54	-	-	-	0.4724
m ii)	-	0.488	0.014	-	-
m iii)	0.36	0.171	-	0.4793	-

n) The Decomposition of Di-p-nitrobenzoyl Peroxide in Iodobenzene

Di-p-nitrobenzoyl peroxide (2 g., 0.006 mol.) was allowed to decompose in iodobenzene (32.2 g., 0.16 mol.) as described above (d). The reaction mixture was filtered giving a solid (A), and by G.L.C. analysis of the filtrate p-nitroiodobenzene and 2-, 3- and 4-iodobiphenyl (10% APL 245° and 10% PEGA 200°C) were shown to be present. By G.L.C. (2% NPGS at 142° and o-dinitrobenzene as internal standard) the following yields were calculated: p-nitroiodobenzene (0.436 g.; 0.30 m/m.) and 2-, 3- and 4-iodobiphenyls (0.305 g.; molar yield based on p-nitroiodobenzene, 0.62; isomer ratios: 57% 2-, 25% 3- and 18% 4-iodobiphenyl). The reaction mixture filtrate was extracted with 5% sodium hydroxide solution, washed with water, dried over magnesium sulphate and distilled to give a high boiling residue (0.34 g.). From acidification of both the alkaline extract and the alkaline (5% sodium hydroxide) solution with which the solid (A) was stirred with for 30 min., p-nitrobenzoic acid (0.48 g., 0.48 m/m., m.p. and mixed m.p. 239-240°, lit.<sup>130</sup> 241-5°) was isolated. The solid remaining after (A) had been stirred with alkali was washed with water and benzene and dried in vacuo to give a pale yellow solid (1.4 g., m.p. 209-210°). This solid was insoluble in 20% sulphuric acid and all common organic solvents except warm acetic acid and warm dimethyl sulphoxide. In both of these solvents, the solid decomposed, producing in the case of acetic acid iodobenzene which was detected by G.L.C.

On sublimation p-nitrobenzoic acid was isolated. The I.R. spectrum of the solid had a strong carbonyl absorption at  $1660\text{ cm.}^{-1}$ ,  $30\text{ cm.}^{-1}$  greater than the carbonyl absorption frequency for p-nitrobenzoic acid and the solid oxidised potassium iodide in acetic acid. The solid was identified as phenyl iodoso-di-p-nitrobenzoate on comparison (m.p. and mixed m.p.  $209-211^{\circ}$  and correct I.R. spectrum) with the authentic compound.

#### Summary of results

p-nitrobenzoic acid (0.48 m/m.)

p-nitroiodobenzene (0.30 m/m.)

phenyl iodoso-di-p-nitrobenzoate (0.43 m/m.)

2-,3- and 4-iodobiphenyl (molar yield based on p-nitroiodobenzene, 0.62).

#### o) The Decomposition of Di-p-cyanobenzoyl Peroxide in Iodobenzene.

Di-p-cyanobenzoyl peroxide (2 g., 0.0068 mol.) was allowed to decompose in iodobenzene (28 g., 0.14 mol.) following the procedure described in (d). On filtration of the dark mixture, a solid was obtained which was stirred for 1 hour in ethanol/acetone leaving insoluble material (0.047 g.). p-Cyanobenzoic acid (1.35 g.; 1.35 m/m.; m.p. and mixed m.p.  $218-219^{\circ}$ , lit.<sup>130</sup>  $219^{\circ}$  and correct infrared spectrum) was recovered from the solvent. The reaction mixture filtrate was extracted with 5% sodium hydroxide, yielding no acid, and was then washed with water and dried over magnesium sulphate. By G.L.C., with biphenyl as internal standard (2% NPGS column at  $140^{\circ}$ ), the yield of p-cyanoiodobenzene was calculated to

be 0.243 g., (0.1552 m/m.). A test for the presence of oxidising agents in the solution, with potassium iodide in acetic acid, was negative. On distillation of the solution under vacuum a high boiling residue of black tarry material (0.42 g.) was isolated.

6) THE RATE OF DECOMPOSITION OF DIBENZOYL PEROXIDE IN IODOBENZENE.

a) Development of Experimental Technique.

Normally the concentration of dibenzoyl peroxide in organic solvents is determined iodometrically, but this technique was found to be unsatisfactory when the solvent was iodobenzene.<sup>149</sup> Consequently, it was decided to attempt to follow the decomposition of dibenzoyl peroxide in iodobenzene, and in bromobenzene, by estimation of the amount of triethyl phosphate produced after an excess of triethyl phosphite had been added to the peroxide solution.<sup>141</sup>



The amount of triethyl phosphate was to be estimated by G.L.C. using an internal standard.

A 10% PEGA column operating at 155°, using biphenyl as internal standard, was found to be the most suitable method of analysis for triethyl phosphate in solution of bromobenzene and iodobenzene, and this technique was used throughout the investigation. It was found that a constant value for the amount of triethyl phosphate was obtained 90 min. after the addition of an excess of triethyl phosphite to stirred solutions of dibenzoyl peroxide (ca. 0.10 moles litre<sup>-1</sup>) in

bromobenzene and iodobenzene. Consequently all estimations of dibenzoyl peroxide were made at 90 min. and 120 min. after the addition of triethyl phosphite.

Calibration curves were constructed for both bromobenzene and iodobenzene, for solutions of known dibenzoyl peroxide concentration, the ratio  $\frac{\text{mass of dibenzoyl peroxide}}{\text{mass of biphenyl (internal standard)}}$ , being plotted against that of  $\frac{\text{area of triethyl phosphate peak}}{\text{area of biphenyl peak}}$  for a range of concentrations of dibenzoyl peroxide from ca. 0.12 to ca. 0.005 moles litre<sup>-1</sup>. The same quantity of triethyl phosphite (0.2921 g., 0.00176 mol.) was added to each peroxide solution (3.3 ml. in the case of bromobenzene and 3.5 ml. in the case of iodobenzene) after the addition of biphenyl, and the solution was then magnetically stirred in a vessel protected from the light, prior to G.L.C. analysis. The calibration curves obtained are reproduced (Fig. 1 and 2).

b) The Rate of the Decomposition of Dibenzoyl Peroxide in Bromobenzene.

Dibenzoyl peroxide (1.1663 g., 0.0048 mol.) was dissolved in bromobenzene to give a solution (39.5 ml.) and into each of nine thick walled glass tubes fitted with a ground glass joint was run a portion (3.3 ml.) of the solution. The solutions were then degassed by freeze-thaw cycles on a vacuum line, operating at a pressure of less than one micron, and sealed off under vacuum. The reaction tubes were placed in an oil bath, maintained at 80°, for

different periods of time, then kept in liquid nitrogen. Analysis for dibenzoyl peroxide remaining was carried out as follows: the contents of each tube were transferred to a vessel containing a weighed amount of biphenyl, triethyl phosphite (0.2 ml.) was added with stirring which was continued (the reaction mixture was protected against the light) until G.L.C. analysis was effected as described previously (p. 91). The results obtained are tabulated (Table 6).

In Fig. 3, the concentration of dibenzoyl peroxide is plotted against time and in Fig. 4,  $\ln$  (concentration of dibenzoyl peroxide) is plotted against time. From measurement of the gradient of the straight line obtained in Fig. 4 it was calculated that  $k_1(\text{obs.}) = 4.57 \times 10^{-5} \text{ sec.}^{-1}$  (where  $k_1(\text{obs.})$  is the apparent first order rate constant).

c) The Rate of the Decomposition of Dibenzoyl Peroxide in Iodobenzene

Dibenzoyl peroxide (1.3871 g., 0.057 mol.) was dissolved in iodobenzene and the solution made up to 49 ml. and into each of nine tubes was transferred a portion (3.5 ml.) of this solution. The experimental procedure is as described previously (p. 91) and the results obtained are tabulated (Table 7).

In Fig. 3, the concentration of dibenzoyl peroxide is plotted against time and in Fig. 5,  $\ln$  (concentration of dibenzoyl peroxide) is plotted against time. From measurement of the gradient of the straight line obtained in Fig. 5, it was calculated that  $k_1(\text{obs.}) = 3.7 \times 10^{-5} \text{ sec.}^{-1}$

TABLE 6

Tube	Time (hrs.) at 80°	$\frac{\text{Area of triethyl phosphate peak}}{\text{Area of biphenyl peak}}$	Biphenyl (g.)	(g.)	$\frac{\text{Dibenzoyl peroxide remaining}}{(\text{moles litre}^{-1})}$	$(\ln. \text{ moles litre}^{-1})$
1	0	0.4051	0.2054	0.0785	0.09833	-2.3195
2	1	0.3567	0.2012	0.0638	0.0798	-2.6454
3	2	0.2332	0.1960	0.0464	0.0582	-2.8439
4	4	0.2261	0.2086	0.0348	0.0436	-3.1327
5	7	0.1601	0.1988	0.0189	0.0267	-3.6231
6	10	0.1319	0.2014	0.0131	0.0164	-4.1105
7	14	0.0959	0.1937	0.0636	0.0080	-4.8284
8	19	0.1155	0.2045	-	-	-
9	24.033	0.1023	0.1824	-	-	-

TABLE 7

Tube	Time (hrs.) at 80°	$\frac{\text{Area of triethyl phosphate peak}}{\text{Area of biphenyl peak}}$	Biphenyl (g.)	Dibenzoyl peroxide remaining		
				(g.)	(moles litre <sup>-1</sup> )	(ln moles litre <sup>-1</sup> )
1	0	0.3664	0.1910	0.0940	0.1096	-2.2107
2	1	0.2943	0.2139	0.0904	0.1054	-2.2500
3	2	0.2510	0.1865	0.0681	0.0794	-2.5333
4	3.93	0.2401	0.1833	0.0642	0.0749	-2.5916
5	7	0.1503	0.2024	0.0415	0.0484	-3.0283
6	10	0.1145	0.1874	0.0272	0.03171	-3.4512
7	13.75	0.0704	0.1977	0.0138	0.0162	-4.1228
8	19	0.0564	0.1912	0.0088	0.0103	-4.5756
9	24	0.0250	0.1972	-	-	-

Fig. 1. Calibration curve for iodobenzene.

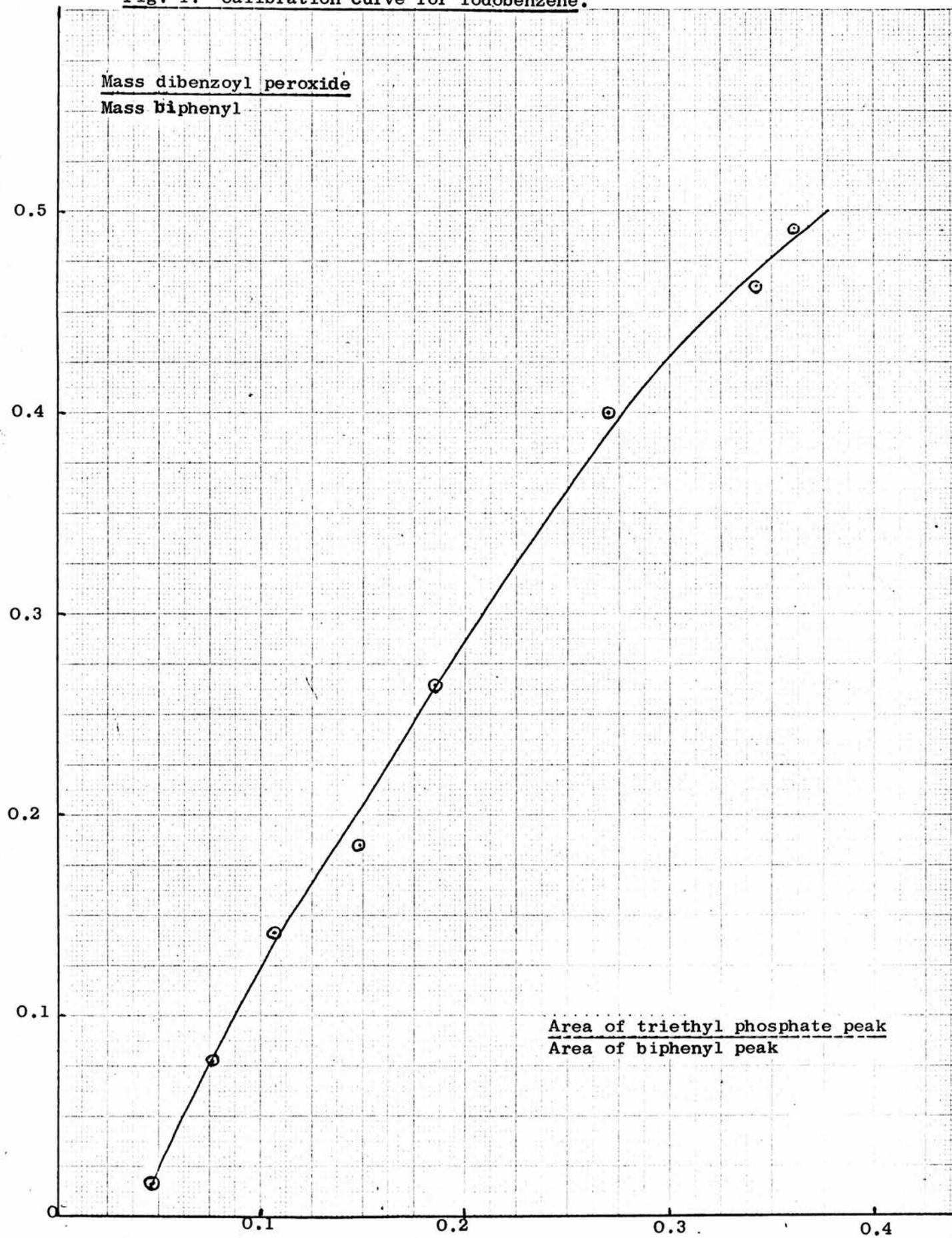


Fig. 2. Calibration curve for bromobenzene.

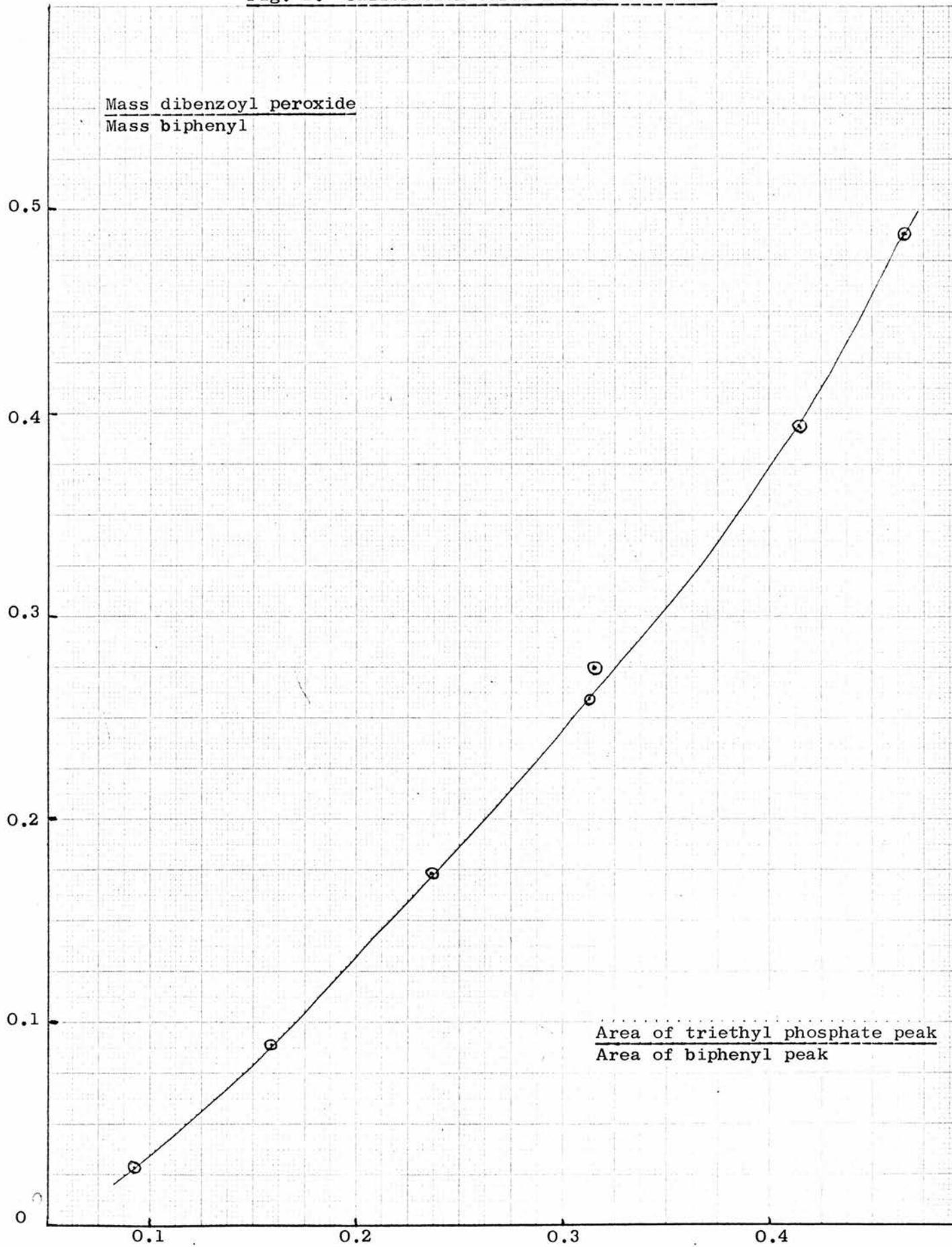


Fig. 3. The change in concentration of dibenzoyl peroxide with time at 80°

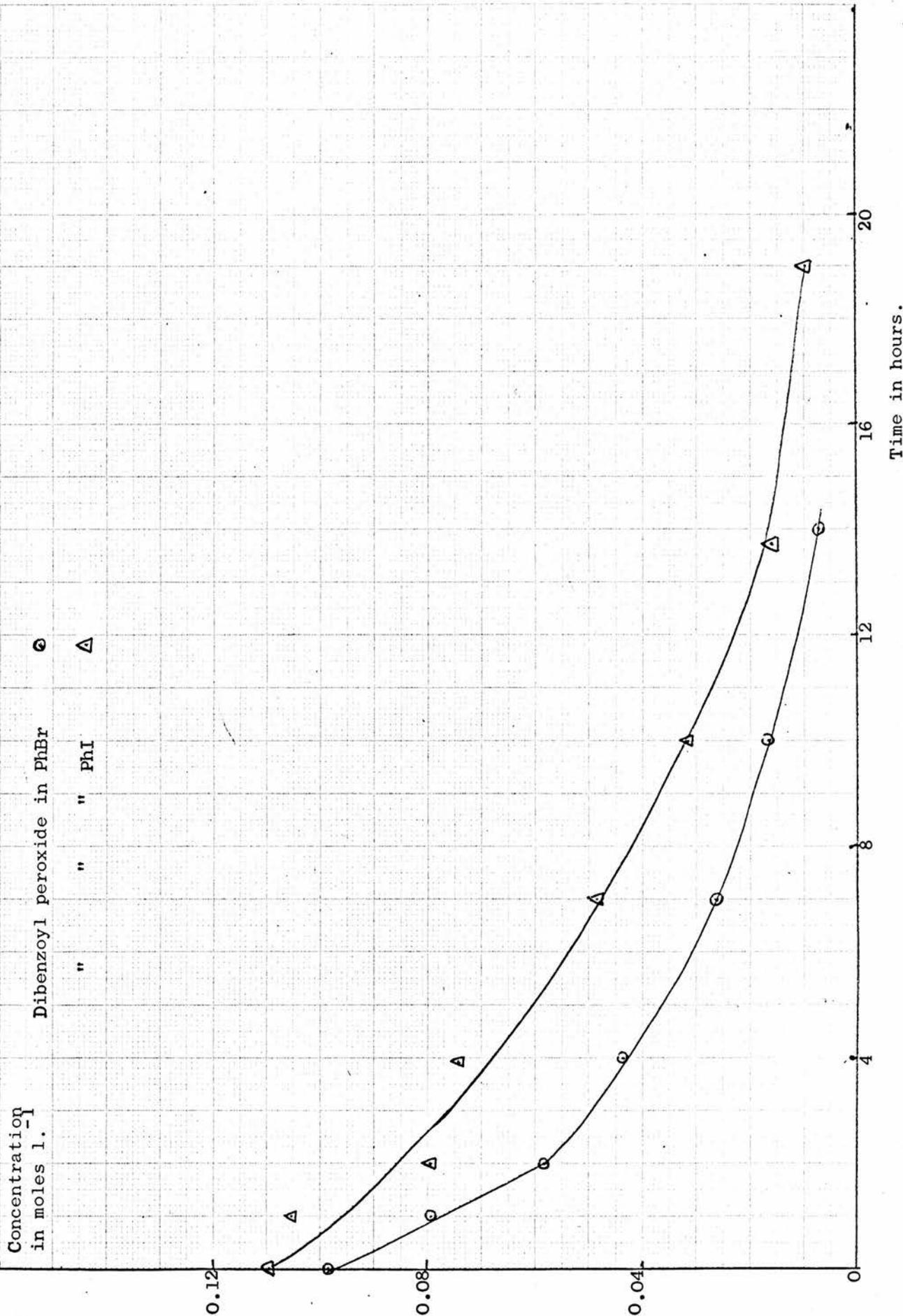


Fig. 4

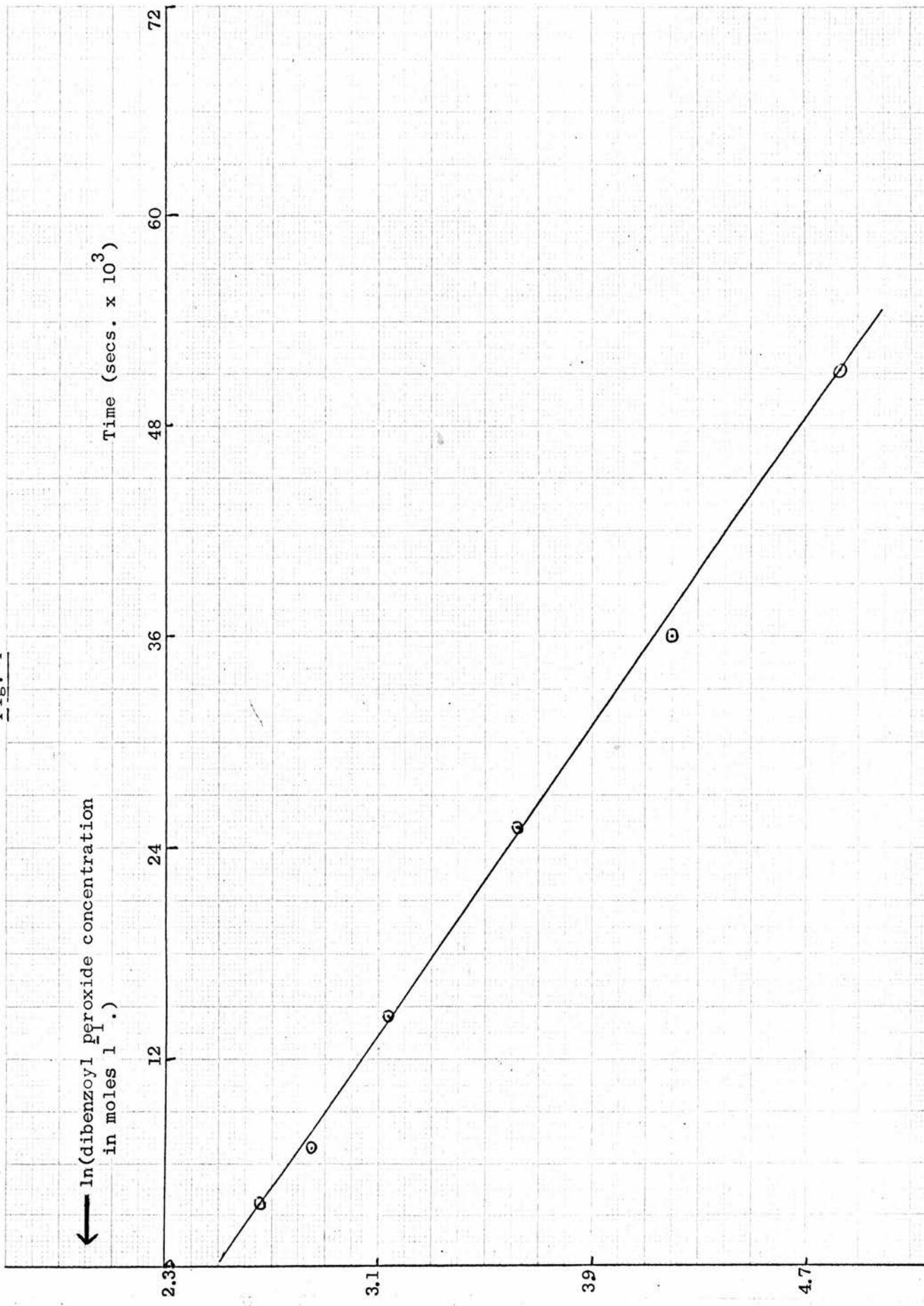
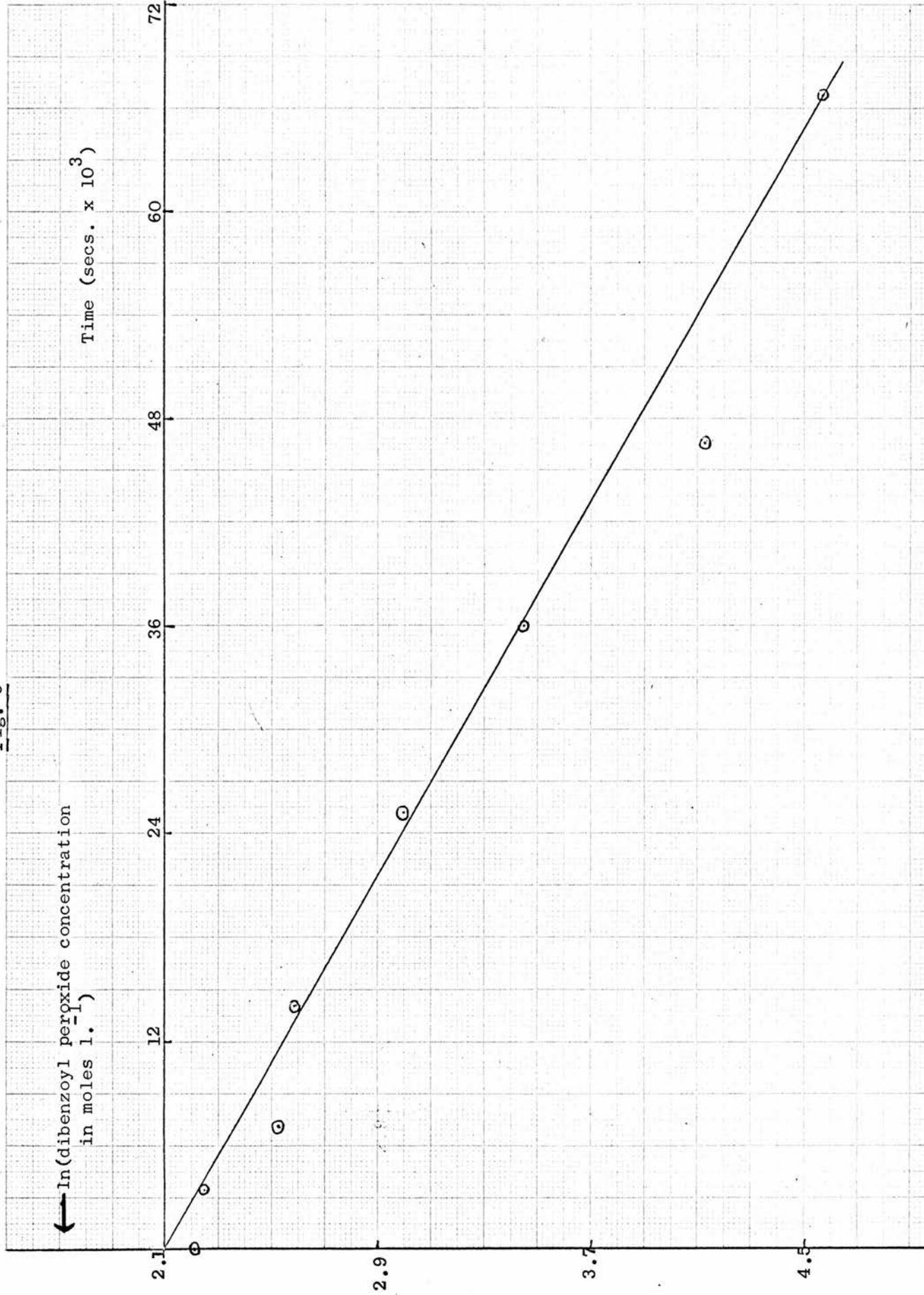


Fig. 5

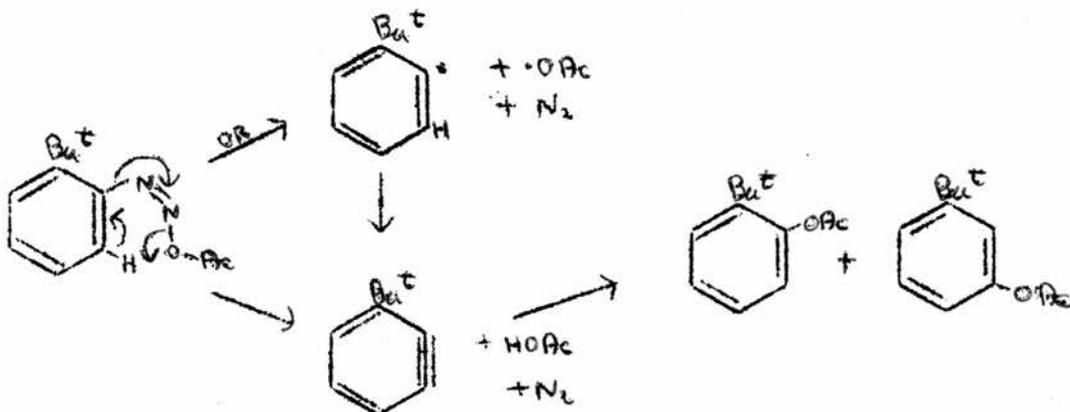


DISCUSSION

	Page
1) <u>THE DECOMPOSITION OF SUBSTITUTED N-NITROSOACETANILIDES IN BENZENE.</u>	96
2) <u>THE ATTEMPTED DETECTION OF BENZYNOID INTERMEDIATES IN THE DECOMPOSITION OF ARYL RADICAL SOURCES IN SOLUTION.</u>	106
3) <u>THE ABSTRACTION OF IODINE FROM AROMATIC IODIDES BY ARYL RADICALS.</u>	117
a) Product Analysis.	117
b) The Rate of Decomposition of Dibenzoyl Peroxide in Iodobenzene.	125
c) The Mechanism of the Abstraction of Iodine from Aromatic Iodides by Aryl Radicals.	127

1) THE DECOMPOSITION OF SUBSTITUTED N-NITROSOACETANILIDES  
IN BENZENE.

In 1964, Cadogan and Hibbert<sup>78</sup> reported that the decomposition of o-t-butyl-N-nitrosoacetanilide in benzene was anomalous in that the major products were o- and m-t-butylphenyl acetates (total yield 46%) in the ratio 2:1, instead of the expected o-t-butylbiphenyl. Also, when the nitrosamide was allowed to decompose in the presence of anthracene in benzene, 2-t-butyl-triptycene (9%) was isolated, the yield of o- and m-t-butylphenyl acetates was found to have dropped to 20% and the relative proportion of the o-isomer had increased. Consequently, the intermediacy of 3-t-butylbenzyne was postulated and the following reaction scheme was suggested in which the bulky o-t-butyl group was assumed to lead to rearrangement of the nitrosoamide to the cis-diazotate.



This postulate involves a hitherto unexpected steric effect in the rearrangement of N-nitrosoacylarylamines. Accordingly, a number of o-substituted N-nitrosoacetanilides were allowed to decompose in benzene and the products were investigated. The results of this work is summarised in Table 8.

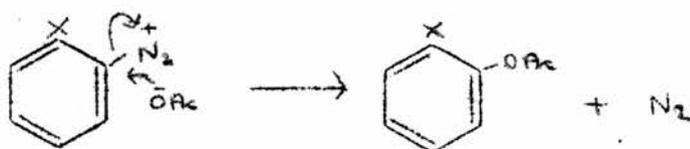
In two cases (o-carbethoxy- and o-phenyl-N-nitrosoacetanilide) both o- and m-substituted phenyl acetates were detected in low yield (5.4% and 10.3%) with a preponderance of the o-isomer, and in the decomposition of o-methyl-N-nitrosoacetanilide o-tolyl acetate (5.2%) was isolated and m-tolyl acetate was shown to be absent (G.L.C.). In all three cases no p-substituted phenyl acetate was found. Both carbethoxy- and phenyl- are much less bulky groups than t-butyl- and, on the basis of Cadogan and Hibbert's<sup>78</sup> postulates, it is to be expected that acetates, if produced at all, would be formed in much lower yield than in the case of the decomposition of o-t-butyl-N-nitrosoacetanilide. Carbethoxy- is a strong electron withdrawing group in contrast to t-butyl- which is electron donating and so the anomalous decompositions of o-substituted N-nitrosoacetanilides appear to be primarily a function of the bulk of the substituted group.

TABLE 8

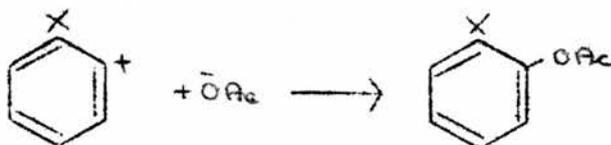
The decomposition of o-substituted N-nitrosoacetanilides in benzene

<u>N</u> -Nitrosoacetanilide [Ar·N(NO)·CO·CH <sub>3</sub> ]	Substituted phenyl acetates [Ar·O·CO·CH <sub>3</sub> ]			Major Products (%)	Other Products (%)	Accountancy of Ar (%)
	<u>o</u> -isomer (%)	<u>m</u> -isomer (%)	<u>p</u> -isomer (%)			
<u>o</u> -Carbethoxy-	3.3	2.1	0	Ethyl biphenyl-2- carboxylate (75)	-	80.4
<u>o</u> -Phenyl-	6.3	4.5	0	<u>o</u> -Terphenyl (21)	Biphenyl (13)	44.8
<u>o</u> -Methyl-	5.2	0	0	1-Acetyl indazole (21)	-	26.2
<u>o</u> -Chloro-	0	0	0	2-Chlorobiphenyl (36)	-	36
<u>o</u> -Bromo-	0	0	0	2-Bromobiphenyl (59)	<u>o</u> -Dibromo- benzene (5.1)	64.3
<u>o</u> -Iodo-	0	0	0	2-Iodobiphenyl (20)	<u>o</u> -Di-iodo- benzene (19) <u>o</u> -Terphenyl (0.5)	39

It was suspected<sup>78</sup> that some of the o-*t*-butylphenyl acetate was formed otherwise than by addition of acetic acid to 3-*t*-butylbenzyne, and it is of interest that in the decomposition of o-methyl-N-nitrosoacetanilide only one acetate, o-tolyl acetate, was found. This formation of the o- acetates may be due to elimination of nitrogen from the intermediate aryldiazonium cation<sup>67</sup> by acetate anion attack,



or by attack of acetate anion on a possible carbonium ion<sup>157</sup> intermediate.



As well as o-terphenyl (21%), the decomposition of o-phenyl-N-nitrosoacetanilide in benzene gave biphenyl (13%), presumably formed by hydrogen abstraction by the intermediate 2-biphenyl radical. Hydrogen abstraction may be more than usually favoured in this case since arylation of the solvent is sterically hindered. (This may also be the reason for the formation of *t*-butylbenzene (14%) in the decomposition of

o-t-butyl-N-nitrosoacetanilide in benzene). Low yields of the corresponding terphenyl are reported by De Tar and Howard<sup>144</sup> on generating the 2'-methyl-6'-nitro-2-biphenyl radical in benzene and Chan and Huang<sup>143</sup> found that on the decomposition of 1-(o-biphenyl)-3,3-dimethyltriazene in benzene, by the action of acetic acid, biphenyl was a product but no o-terphenyl was isolated.

Thus, there is a similarity between the decomposition of o-t-butyl- and o-phenyl-N-nitrosoacetanilide in that both give o- and m- substituted phenyl acetates and the hydrogen abstraction product of the resultant aryl radical, and it is clear that further investigation of these phenomena is desirable.

1-Acetyl indazole (21%) was isolated from the decomposition of o-methyl-N-nitrosoacetanilide, but no indazole, which Huisgen and Nakaten<sup>131</sup> reported to be formed in 54-62% yield, was obtained. The reaction mixture was very tarry and a large amount of high boiling residue was obtained. It is also noteworthy that on one occasion a sample of o-methyl-N-nitrosoacetanilide spontaneously exploded with considerable violence.

From the decomposition of o-chloro-N-nitrosoacetanilide (m.p. 46-47°) 2-chlorobiphenyl (36%) was isolated. Haworth and Hey<sup>132</sup> did not obtain any 2-chlorobiphenyl from o-chloro-N-nitrosoacetanilide (reported m.p. 59°) prepared by the action of

fumes on o-chloroacetanilide and it now seems doubtful that the compound prepared by these workers was in fact o-chloro-N-nitrosoacetanilide.

o-Dibromobenzene (5.1%) was identified as a product of the decomposition of o-bromo-N-nitrosoacetanilide, as well as the anticipated 2-bromobiphenyl (59%). The isolation of this unexpected product led to the investigation of the decomposition of m- and p-bromo-N-nitrosoacetanilide under similar conditions. The results obtained are summarised in Table 1.

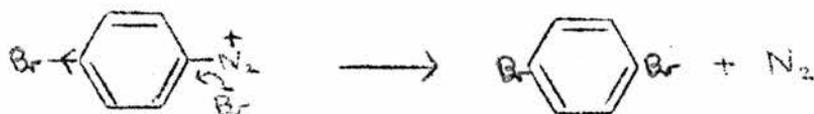
Table 1

The decomposition of bromo-N-nitrosoacetanilides in benzene

<u>N</u> -Nitrosoacetanilide	Dibromobenzene (%)	Bromobiphenyl (%)
<u>o</u> -Bromo-	5.1	59.2
<u>m</u> -Bromo-	0	49.3
<u>p</u> -Bromo-	1.3	47.4

The most obvious interpretation of the phenomenon of dibromobenzene formation in the o- and p- cases only, bearing in mind that aryl radicals have been shown to be incapable of abstracting bromine from aromatic bromides (Section (3), p. 123),

is that there is a nucleophilic displacement of nitrogen in o- and p-bromobenzenediazonium ions<sup>67,68</sup> by bromide ions generated in some process. Activation of the nitrogen bearing carbon atoms seems to be governed by the -I effect of the bromine atom; thus there is a lower yield of p-dibromobenzene than o-dibromobenzene and m-dibromobenzene is not formed. Thus, for p-bromo-N-nitrosoacetanilide we have:



How bromide ions are initially generated is unknown. However, they are not generated by displacement from p-bromobenzenediazonium cations by acetate anions (cf. Suschitzky et al.<sup>67,68</sup>), since no p-acetoxybiphenyl was detected (G.L.C.) in the products of reaction.

Hantzsch and Smythe<sup>143</sup> have reported that o- and p-bromo substituted benzenediazonium chlorides rearranged to the respective chlorobenzenediazonium bromides but that there was no rearrangement with the m-bromo isomer while Hey et al.<sup>22</sup> have reported that on passing hydrogen chloride through a solution of 1-p-bromophenyl-3,3-dimethyltriazene an exchange of chlorine for bromine occurred.

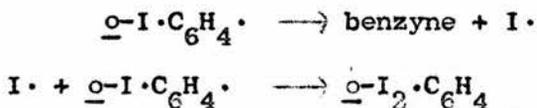
o-Di-iodobenzene (19%), again an unexpected product, was isolated from the decomposition of o-iodo-N-nitrosoacetanilide, as

well as the anticipated 2-iodobiphenyl (20%). As a result of experiments described later (Section 3) it is concluded that o-di-iodobenzene is formed as a result of abstraction of iodine from an aromatic iodide by an o-iodophenyl radical.

1,2,3,4-Tetraphenylnaphthalene (0.23%) was isolated from the decomposition of o-iodo-N-nitrosoacetanilide in benzene, in the presence of 2,3,4,5-tetraphenylcyclopentadienone, while no 1,4-dihydro-1,4-endoxide was detected among the products of the reaction in furan and benzene.

It was shown that o-di-iodobenzene did not react with 2,3,4,5-tetraphenylcyclopentadienone to form adduct and also that the decomposition of dibenzoyl peroxide in a mixture of o-di-iodobenzene and benzene in the presence of 2,3,4,5-tetraphenylcyclopentadienone gave no 1,2,3,4-tetraphenylnaphthalene. Thus it can be deduced that the formation of 1,2,3,4-tetraphenylnaphthalene is attributable neither to the reaction of iodophenyl radicals, nor to the reaction of o-di-iodobenzene, with 2,3,4,5-tetraphenylcyclopentadienone. The species reacting with 2,3,4,5-tetraphenylcyclopentadienone to form 1,2,3,4-tetraphenylnaphthalene is unlikely to be benzyne since no furan adduct was obtained, and can only be rationalised in terms of the reaction of some dipolar benzenoid intermediate with a polarisable cyclodiene.

After our investigation was complete, Kampmeir and Rubin<sup>150</sup> reported that they had obtained o-di-iodobenzene (18%), 2-iodobiphenyl (40%) and 1,2,3,4-tetraphenylnaphthalene (7.7%) from the decomposition of N-(2-iodophenyl)-N-nitrosobenzamide in benzene, in the presence of 2,3,4,5-tetraphenylcyclopentadienone. These workers put forward the following scheme for the formation of o-di-iodobenzene and benzyne,

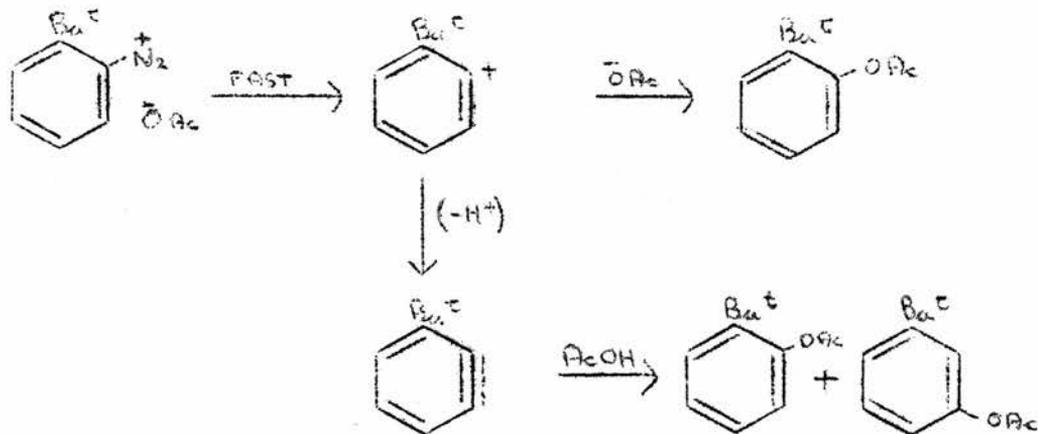


and argued that the formation of o-di-iodobenzene constituted circumstantial evidence for the elimination of an iodine atom from an iodophenyl radical to give benzyne.

Not only did Kampmeir and Rubin have insufficient evidence for the existence of benzyne, in that they only isolated one adduct, but also they did not realise that it is unnecessary to link the formation of benzyne with that of o-di-iodobenzene since the latter was undoubtedly formed by the abstraction of iodine from an aromatic iodide by a 2-iodophenyl radical (see Section [3]).

In conclusion, only two of the o-substituted N-nitrosoacetanilides investigated (o-phenyl- and o-carbethoxy-) paralleled the anomalous behaviour of o-t-butyl-N-nitrosoacetanilide in that they formed the respective o- and m-substituted phenyl acetates. More light has lately been cast on the problem by Franck and Yanagi<sup>157</sup> who

obtained 2,5-di-*t*-butylchlorobenzene (36%), 2,5-di-*t*-butylphenyl acetate (29%) and the furan adduct of 2,5-di-*t*-butylbenzynes (22%) on adding 2,5-di-*t*-butyl aniline with acetic acid in dichloromethane to a mixture of butyl nitrite, furan and dichloromethane boiling under reflux. Similar results were obtained using mesitoic and pivalic acid. These workers rationalised their results on the basis of an intermediate 2,5-di-*t*-butyl carbonium ion. The most acceptable explanation of the anomalous decomposition of *N*-nitrosoacetanilides with bulky *o*- groups is that the latter can cause rapid expulsion of nitrogen from the intermediate diazonium cation to yield a carbonium ion which can react as shown:



In support of the intermediacy of arynes in such systems, Cadogan and Harger<sup>158</sup> have isolated the furan adduct of

2,5-di-*t*-butylbenzyne from the decomposition of 2,5-di-*t*-butyl-N-nitrosoacetanilide.

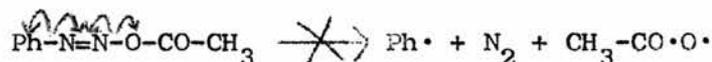
For the further elucidation of the mechanism of the anomalous decomposition of o-substituted N-nitrosoacetanilides it will be necessary to investigate the decompositions of a range of N-nitrosoacetanilides with large o-groups (in particular, o-trichloromethyl-, which is the same size as o-*t*-butyl- but has a different electronic effect in that it is electron attracting) in a variety of solvents.

Ideally, a physical method of detection of arynes should be developed with which it would be possible to investigate the decompositions, obviating the necessity of altering the reaction conditions by adding an arynophile to detect aryne intermediates. Further investigation of the decomposition of o-substituted N-nitrosoacetanilides is being carried out by Cadogan and Harger.

## 2) THE ATTEMPTED DETECTION OF BENZYNOID INTERMEDIATES IN THE DECOMPOSITIONS OF ARYL RADICAL SOURCES IN SOLUTION.

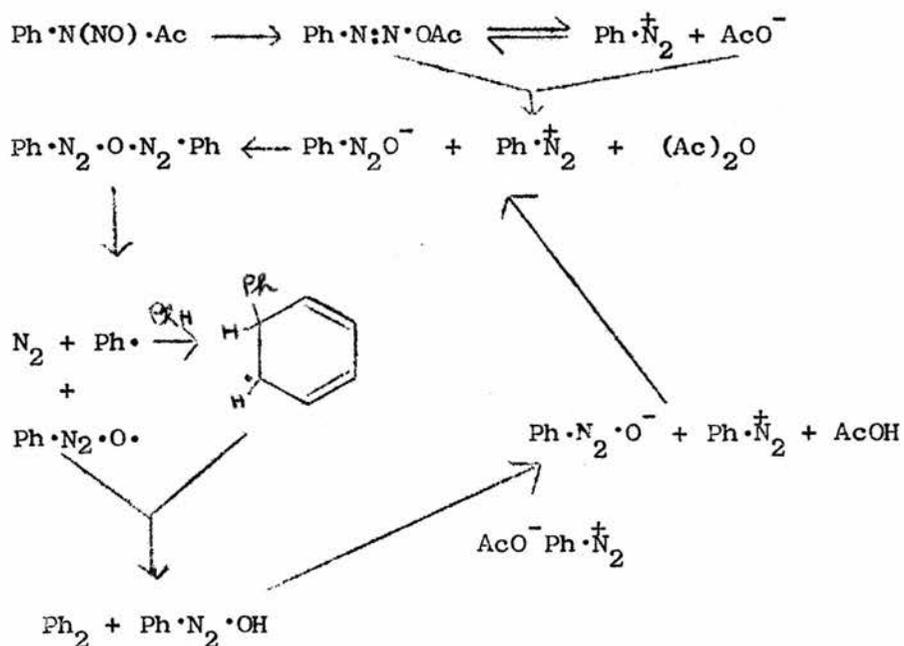
The mechanism of the decomposition of N-nitrosoacetanilides in aromatic solvents is one of the outstanding problems in the field of free radical chemistry. Work carried out before this investigation was begun is discussed in the Introduction (pp. 19-25) Significant differences are reported between the products obtained from the decomposition of N-nitrosoacetanilide and other aryl

radical sources in various solvents. Thus, Hey, Stirling and Williams<sup>44</sup> found that phenylation of pyridine with N-nitrosoacetanilide gave a mixture of phenylpyridines of isomeric composition different from that obtained by phenylation with such radical sources as dibenzoyl peroxide and phenylazotriphenylmethane. Hey and Peters<sup>146</sup> found that N-nitrosoacetanilide abstracted chlorine, as well as hydrogen, from chloroform, whereas dibenzoyl peroxide and phenylazotriphenylmethane abstracted only hydrogen. Hibbert<sup>159</sup> rationalised the formation of chlorobenzene by postulating the intermediacy of benzenediazonium chloride which decomposes to chlorobenzene. Similarly, the anomalous formation of p-dichlorobenzene, on allowing p-chloro-N-nitrosoacetanilide to decompose in bromotrichloromethane, was explained by the decomposition of p-chlorobenzenediazonium chloride, which was isolated from the reaction. Further, when N-nitrosoacetanilide is allowed to decompose in aromatic solvents high yields of acetic acid and low yields of both carbon dioxide and methyl radicals<sup>69,70,71</sup> are obtained. Thus the decomposition can not proceed by a homolysis of the intermediate diazo enter to give acetoxy



radicals, since acetoxy radicals are known to decompose rapidly to methyl radicals and carbon dioxide.<sup>118</sup> The most satisfactory explanation for the mechanism of the decomposition of N-nitroso-

acetanilide in aromatic solvents, before the work described in this thesis was carried out, was provided by Rüdhardt et al.<sup>74,75,76,77</sup> (see p. 24) who postulated the formation of the stable diazotate radical ( $\text{Ph-N=N-O}\cdot$ ) from homolytic breakdown of previously formed diazo anhydride ( $\text{Ph-N=N-O-N=N-Ph}$ ). However, Rüdhardt's scheme, reproduced again for convenience below, does not account for the anomalous ortho- cases described in (1),



and hence it was thought desirable to determine whether benzyne was a hitherto undetected intermediate in the decomposition of N-nitrosoacetanilide itself in benzene. This reaction was allowed to proceed in the presence of 2,3,4,5-tetraphenylcyclopentadienone, a good benzyne trap,<sup>97,98</sup> with the result that the yield of biphenyl

was found to have dropped from 39.5% (in the absence of 2,3,4,5-tetraphenylcyclopentadienone) to 0.02%, and 1,2,3,4-tetraphenylnaphthalene (24.7%), the benzyne adduct, was isolated. The results obtained on allowing N-nitrosoacetanilide to decompose in the presence of several known benzyne traps are summarised in Table 9.

Table 9

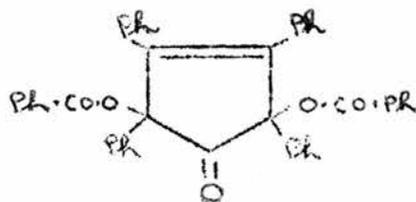
Solvent	Arynophile	Benzyne adduct	(% based on <u>N</u> -nitrosoacetanilide)
Benzene	2,3,4,5-Tetraphenylcyclopentadienone	1,2,3,4-Tetraphenylnaphthalene	(24.7)
Tetrahydrofuran	2,3,4,5-Tetraphenylcyclopentadienone	1,2,3,4-Tetraphenylnaphthalene	(23.8)
Pyridine	2,3,4,5-Tetraphenylcyclopentadienone	1,2,3,4-Tetraphenylnaphthalene	(0)
Benzene	1,3-Diphenylisobenzofuran <sup>98</sup>	9,10-Diphenylanthracene	(14) (obtained after reduction)
Benzene	Anthracene <sup>96, 97</sup>	Triptycene	(0)
-	Furan <sup>92</sup> + 2,3,4,5-Tetraphenylcyclopentadienone	1,2,3,4-Tetraphenylnaphthalene	(0)
		1,4-Dihydronaphthalene-1,4-endoxide	(0)

Since no adducts were obtained with furan or with 2,3,4,5-tetraphenylcyclopentadienone in pyridine as solvent, it was a possibility that in the presence of molecules with an available electron lone pair the formation of adduct was being inhibited. That the presence of a molecule with an available lone pair has no effect on adduct formation was demonstrated by the fact that a large yield of adduct (23.8%) was obtained from reaction in tetrahydrofuran in the presence of 2,3,4,5-tetraphenylcyclopentadienone. In the case of 2,3,4,5-tetraphenylcyclopentadienone in pyridine, the formation of phenylpyridines was completely suppressed and much tarry material was obtained. When N-nitrosoacetanilide was allowed to decompose in furan with added 2,3,4,5-tetraphenylcyclopentadienone, 2-phenylfuran (23%) was obtained and neither 1,4-dihydronaphthalene-1,4-endoxide nor 1,2,3,4-tetraphenylnaphthalene were detected. 1,4-Dihydronaphthalene-1,4-endoxide was shown to be stable under the experimental conditions. It was demonstrated, also, that 2,3,4,5-tetraphenylcyclopentadienone was a far stronger arynophile than furan, by the isolation of only 1,2,3,4-tetraphenylnaphthalene (82-4%) from a reaction in which authentic benzyne was generated, from anthranilic acid and amyl nitrite,<sup>100</sup> in benzene in the presence of an equimolar mixture of the two arynophiles. It should be borne in mind, however, that

in the absence of 2,3,4,5-tetraphenylcyclopentadienone, benzyne, produced in the latter fashion, readily reacts with furan to give an adduct.<sup>100</sup> However, it is puzzling that no 1,2,3,4-tetraphenyl-naphthalene was detected on allowing N-nitrosoacetanilide to decompose in furan with added 2,3,4,5-tetraphenylcyclopentadienone; it appears that in this case furan is more reactive as a substrate for phenylation than as an arynophile. There is also the possibility that the adduct forming intermediate produced in the decomposition of N-nitrosoacetanilide is not benzyne but is some highly reactive dipolar species which forms adducts only with highly polarisable substrates such as 2,3,4,5-tetraphenylcyclopentadienone, but not with compounds of low polarisability such as furan (see below). This theory is borne out by the fact that 9,10-diphenylanthracene (14%) was isolated from the decomposition of N-nitrosoacetanilide in benzene in the presence of 1,3-diphenylisobenzofuran, which is highly polarisable. No triptycene was detected when the decomposition was carried out in the presence of anthracene in benzene, but anthracene is both less polarisable and a weaker arynophile<sup>98</sup> than either 1,3-diphenylisobenzofuran or 2,3,4,5-tetraphenylcyclopentadienone.

When phenylazotriphenylmethane, an authentic source of phenyl radicals,<sup>47</sup> was allowed to decompose in benzene in the

presence of 2,3,4,5-tetraphenylcyclopentadienone, no adduct was detected and similarly no adduct was obtained with dibenzoyl peroxide. In the latter case, no benzoic acid was isolated but an unidentified white compound, which seems to be the result of reaction of benzoyloxy radicals with 2,3,4,5-tetraphenylcyclopentadienone, was obtained. The N.M.R., U.V. and I.R. spectra of the compound are consistent with the following structure:

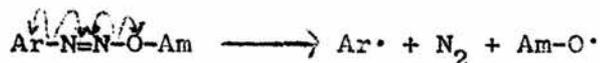


but analysis (Found: C, 30.0; H, 4.7. Calc. for  $C_{43}H_{30}O_5$ : C, 32.4; H, 4.7%) and molecular weight (Found: 553. Calc. for  $C_{43}H_{30}O_5$ : 626) are not in accordance.

No benzyne adduct was obtained when Gomberg reactions (benzenediazonium chloride with both sodium hydroxide and sodium acetate) were carried out in the presence of 2,3,4,5-tetraphenylcyclopentadienone. Since it was known that the presence of water inhibited the formation of 1,2,3,4-tetraphenylnaphthalene in the decompositions of acylarylnitrosamines<sup>147</sup> in the presence of 2,3,4,5-tetraphenylcyclopentadienone, no adduct formation was

anticipated with the ~~B~~omberg reactions.

No adduct was obtained on reaction of aryl nitrite with aniline in boiling benzene, both in the absence and presence of added anhydrous magnesium sulphate and acetic acid. This reaction is likely to proceed by way of a diazo ether

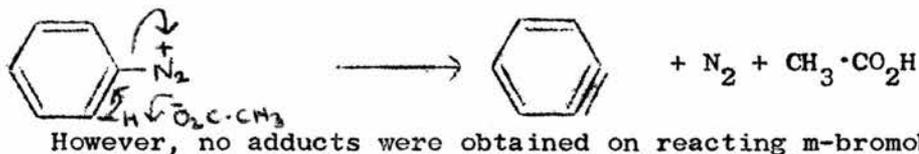


which closely resembles, in structure, the intermediate diazo ester formed in the N-nitrosoacetanilide decomposition. When aniline and aryl nitrite were allowed to decompose in dichloromethane with added 2,3,4,5-tetraphenylcyclopentadienone a trace of 1,2,3,4-tetraphenylnaphthalene (0.12%) was isolated. Presumably adduct formation is due to the use of a solvent of higher dielectric constant which favours the existence of some dipolar intermediate.

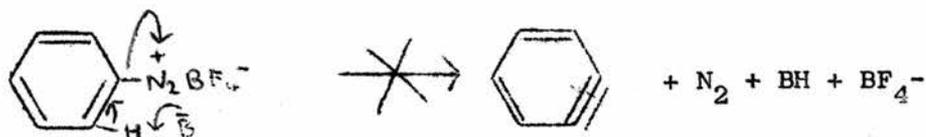
Thus, apart from the trace of adduct formed from the reaction of aniline and aryl nitrite in dichloromethane, it was shown that N-nitrosoacetanilide was the only aryl radical source investigated which gave benzyne adducts, and then only with the more polarisable and more arynophilic benzyne traps, 2,3,4,5-tetraphenylcyclopentadienone and 1,3-diphenylisobenzofuran, and that with these traps in benzene the yield of biphenyl was suppressed.

One explanation of these results is that an acetate anion

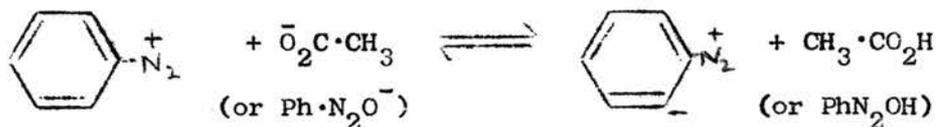
abstracts an ortho hydrogen atom from a benzenediazonium cation to give benzyne in an irreversible process.



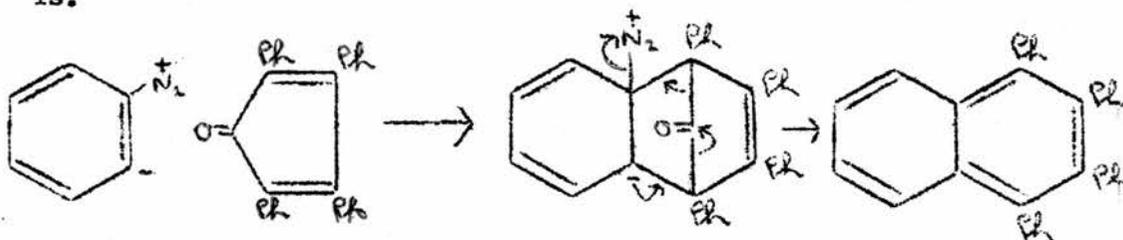
2,3,4,5-tetraphenylcyclopentadienone in benzene, or benzenediazonium fluoroborate with *n*-butyl lithium in furan.



Another point against this explanation is that the products and the course of the decomposition of N-nitrosoacetanilide in benzene in the absence of aryneophiles is adequately explained by Rüdhardt's reaction scheme (p.108). A possible, but not yet proven, interpretation of the experimental data obtained is that there is a dipolar intermediate, which gives a benzyne adduct with highly polarisable cyclic dienes, in equilibrium with a precursor of the phenyl radical, e.g.

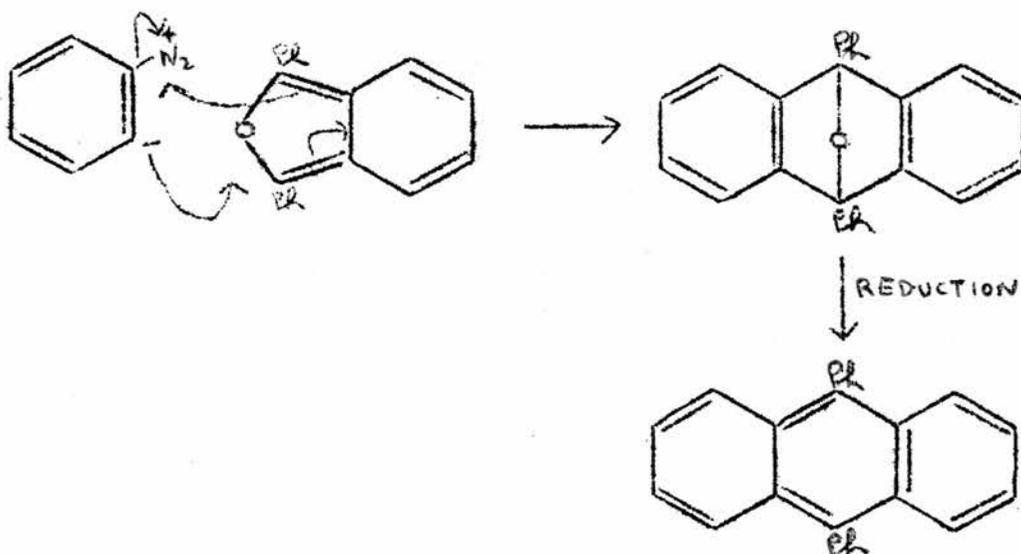


with the equilibrium lying far to the left. In the absence of highly polarisable cyclic dienes the dipolar species will be unobserved, but in their presence it will be rapidly removed to yield benzenoid adducts after loss of nitrogen. The proposed mechanism for reaction with 2,3,4,5-tetraphenylcyclopentadienone is:



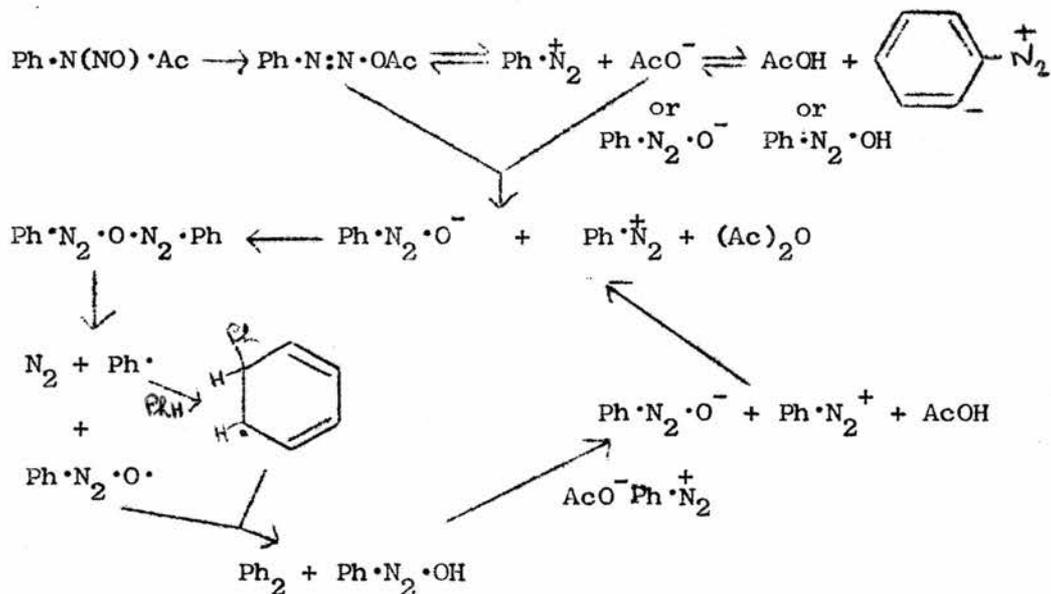
(a completely concerted process)

and for reaction with 1,3-diphenylisobenzofuran:



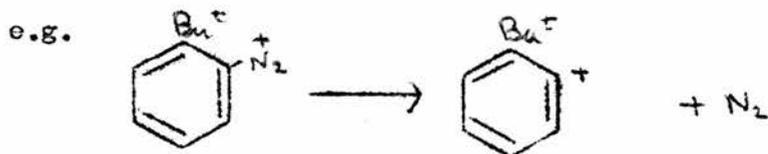
In conclusion it is suggested that Rüchardt's reaction scheme for the decomposition of N-nitrosoacetanilide in benzene be modified to include the equilibrium system described above.

Thus:

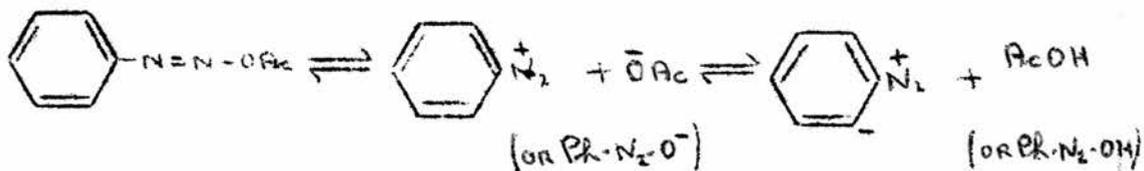


However, it should be stressed that neither Rüchardt's scheme nor the modification proposed above, explains the anomalous decomposition of N-nitrosoacetanilides having large o- groups e.g. the decomposition of 2,5-di-*t*-butyl-N-nitrosoacetanilide in benzene does not conform to Rüchardt's scheme, even in the absence of aryne traps, and in the presence of furan an aryne adduct is obtained, in contrast to N-nitrosoacetanilide from which no benzyne-furan adduct is obtained.

As discussed before, an acceptable explanation for the anomalous behaviour of N-nitrosoacetanilides with large o-groups is that nitrogen is rapidly expelled from the intermediate diazonium cation to give a carbonium ion,



whereas in N-nitrosoacetanilides with no big o- groups, in non polar solvents, the following equilibrium system is postulated.



### 3) THE ABSTRACTION OF IODINE FROM AROMATIC IODIDES BY ARYL RADICALS.

#### a) Product Analysis.

From the decomposition of o-iodo-N-nitrosoacetanilide (1 mol.) in benzene (20 mol.) the unexpected product o-di-iodobenzene (19%) was isolated. This observation prompted experiments with m- and p-iodo-N-nitrosoacetanilides and di-p-iodobenzoyl peroxide, the results of which are summarised in Table 10.

Clearly, the formation of di-iodobenzenes is independent of directive influences within the radical source, apart from the fact that there is a slightly lower yield in the case of o-di-iodobenzene; this could be attributable to steric hindrance

TABLE 10The decomposition of iodine containing radical sources (1 mol.) in benzene (20 mol.)

Radical source	Products (m/m radical source)					Accountance* of aryl fragments (%)
	di-Iodobenzene	Iodobiphenyl	Terphenyl	Acid Iodobenzene		
<u>o</u> -Iodo- <u>N</u> -nitrosoacetanilide	0.192	0.201	0.005	-	-	39.3
<u>m</u> -Iodo- <u>N</u> -nitrosoacetanilide	0.183	0.353	0.0324	-	-	53.6
<u>p</u> -Iodo- <u>N</u> -nitrosoacetanilide	0.213	0.362	0.054	-	-	53.0
Di- <u>p</u> -iobenzoyl peroxide	0.335	0.175	0.006	0.45	0.035	50.0

\* The remainder of the radical source was accounted for as tarry high boiling residue.

in having two bulky iodine atoms on adjacent carbon atoms. This independence of electronic directive influences, together with the isolation or detection of the corresponding terphenyls, points to the formation of di-iodobenzenes via a radical process. To test this, the next stage in the investigation was the decomposition of substituted dibenzoyl peroxides and N-nitrosoacetanilides in iodo-aromatic solvents. The results obtained are given in Table 11.

TABLE 11

The decomposition of substituted dibenzoyl peroxides and  
N-nitrosoacetanilides in iodobenzene and mixtures of iodobenzene and benzene

Radical source (1 mol.)	Solvent (mol.)		Products (m/m radical source)						Accountance of aryl fragments (%)
	PhH	PhI	ArPh	ArH	ArI	Ar'CO <sub>2</sub> H	Ph <sub>2</sub>	Iodobiphenyls*	
Di- <u>p</u> -chlorobenzoyl peroxide	0	20	0	0	0.82	0.91	0	0.56	86
Di- <u>o</u> -bromo-	0	20	0	0	0.71	0.74	0	0.31	72
Di- <u>m</u> -bromo-	0	20	0	0	0.6	0.91	0	0.33	75
Di- <u>p</u> -bromo-	0	20	0	0	0.76	0.95	0	0.36	85
Di- <u>p</u> -methyl-	0	20	0	0	0.82	0.72	0	0.23	77
Di- <u>o</u> -bromo-	40	2	0.23	0.08	0.21	0.53	0.086	0	52
Di- <u>m</u> -bromo-	40	2	0.36	0.05	0.31	0.54	0.118	0	63
Di- <u>p</u> -bromo-	40	2	0.17	0.05	0.35	0.54	0.129	0	55
Di- <u>p</u> -bromo-	81	2	0.28	0.05	0.33	0.47	0.144	0	59
<u>p</u> -Chloro- <u>N</u> -nitrosoacetanilide	0	20	0	0	0.54	0	0	0.25	54
"	20	0	0.49	0.014	0	0	0	0	50
"	26	1	0.17	0	0.37	0	0.177	0	54

\*See Table 12.

TABLE 12

The isomer ratios of iodobiphenyls obtained from  
the decomposition of aryl radical sources in  
iodobenzene.

Radical source	Iodobiphenyl (%)		
	2-	3-	4-
Di- <u>p</u> -chlorobenzoyl peroxide	56	26.1	17.9
Di- <u>o</u> -bromobenzoyl peroxide	56.3	23.6	21.1
Di- <u>m</u> -bromobenzoyl peroxide	56.6	26.5	17
Di- <u>p</u> -bromobenzoyl peroxide	57.2	25.8	17
Di- <u>p</u> -methylbenzoyl peroxide	49.4	31.4	19.2
Di- <u>p</u> -nitrobenzoyl peroxide	57	25.4	17.6
<u>p</u> -Chloro- <u>N</u> -nitrosoacetanilide	53	23	19

In the decompositions of p-chloro-N-nitrosoacetanilide (1 mol.) and di-p-chlorobenzoyl peroxide (1 mol.) in iodobenzene (20 mol.) the yield of 4-chloro-2'-, 3'- and 4'-iodobiphenyl was shown in both cases to be less than 0.03 m/m. The attempted synthesis of biphenylene by the decomposition of di-p-chlorobenzoyl peroxide (1 mol.) in 2-iodobiphenyl (16 mol.) did not succeed, but p-chloriodobenzene (0.72 m/m) was a product of the reaction.

From all the experimental data described above it can be seen that:

- 1) Aryl radicals, irrespective of whether they have substituents in the o-, m- or p- positions and irrespective of whether the substituents are electron attracting or electron repelling, abstract iodine from iodo-aromatic compounds to form aryl iodides.
- 2) In the abstraction of iodine from iodobenzene by aryl radicals there is evidence for the generation of phenyl radicals i.e. in iodobenzene, alone, 2-, 3-, and 4-iodobiphenyl are formed in relative amounts which are characteristic of free radical phenylation of iodobenzene. Thus, 56% 2-, 26% 3-, and 18% 4-iodobiphenyl was a typical isomer ratio found, which compares well with that obtained from the decomposition of dibenzoyl peroxide in iodobenzene (51.7% 2-, 31.6% 3-, and 16.7% 4-iodobiphenyl).<sup>145</sup> Also, the decomposition of substituted dibenzoyl peroxides in a mixture of iodobenzene (1 mol.) and benzene (20 mol.) led to phenylation of benzene to form biphenyl.

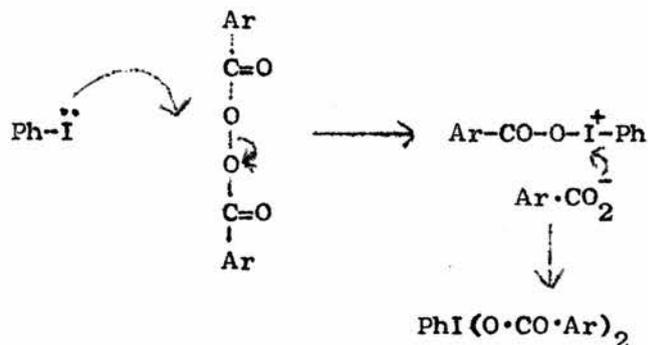
3) Aryl radicals have a high affinity for iodine in iodo-aromatic compounds. Thus, p-chlorophenyl radicals generated in iodobenzene react to give almost 30 times as much of the product of iodine abstraction compared with products of arylation of the solvent, while aryl radicals produced in a mixture of benzene (20 or 41 mol.) and iodobenzene (1 mol.) give as much as, or more of, the iodine abstraction product compared with the products of direct arylation of the solvent.

By allowing di-p-chloro- and di-p-bromobenzoyl peroxides to decompose in bromobenzene, it was demonstrated that abstraction of bromine by aryl radicals was insignificant, if it did in fact take place. The difference in behaviour of aryl iodides and aryl bromides towards aryl radicals is probably a function of two factors, namely the bond dissociation energies of the Ph-Br and the Ph-I bonds and the 'heavy atom' effect of the iodine atom. The bond dissociation energies of the Ph-Br and Ph-I bonds are  $71 \pm 2$  and  $61 \pm 1.3$  k.cals./mole,<sup>153</sup> but it may be that the difference in bond dissociation energy of 10 k. cal./mole is not alone responsible for the completely differing behaviour of aryl bromides and iodides. It is a possibility that the heavy atom effect of the iodine atom is one of the reasons for the ease of abstraction of iodine from aryl iodides by aryl radicals. The heavy atom effect is the enhancement of the probability of a process involving a change

in electron multiplicity, experienced by electrons which fall under the influence of the magnetic field due to the high nuclear charges of heavy atoms e.g. with ethyl iodide as a solvent, the otherwise weak and forbidden singlet-triplet absorption band of  $\alpha$ -chloronaphthalene is strengthened.<sup>154</sup> The weakness of the Ar-I bond, as compared to the Ar-Br bond, manifests itself in the photolyses of 4-iodobiphenyl and 4-bromobiphenyl,<sup>160</sup> in which, under the same conditions, the former was shown to have undergone almost complete (~ 98%) photolysis, whereas photolysis of the latter was only 70-80% complete. Similar experiments with 4-chloro- and 4-fluorobiphenyl resulted in only some 3% decomposition.

The reactions of di-p-nitrobenzoyl peroxide and di-p-cyano-benzoyl peroxide in iodobenzene were found to be anomalous. In the former case the yields of p-nitroiodobenzene and p-nitrobenzoic acid obtained were low (0.30 and 0.43 m/m peroxide), as was the yield of the isomeric mixture of iodobiphenyls (0.19 m/m). Further, an unexpected product, phenyl iodoso-di-p-nitrobenzoate (0.43 m/m), a hitherto unknown compound, was isolated. The reasons for the formation of this iodoso compound are not known, but are possibly related to the polarity of the peroxidic bond, induced by the presence of two nitro groups in the peroxide. Oxidation of the iodine atom of iodobenzene is effected and the following is

a suggested mechanism



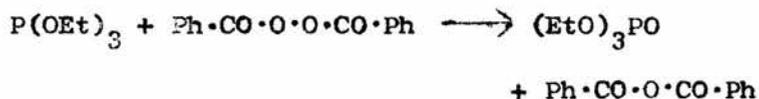
No iodoso compound was detected among the products of the decomposition of di-p-cyanobenzoyl peroxide in iodobenzene. This reaction gave a high yield of p-cyanobenzoic acid, a low yield of p-cyanoiodobenzene (1.35 and 0.1552 m/m peroxide, respectively) and a high yield of tars.

b) The Rate of Decomposition of Dibenzoyl Peroxide in Iodobenzene.

Although the rate of decomposition of dibenzoyl peroxide in benzene,<sup>32,33,34,35,36,37</sup> chlorobenzene and bromobenzene<sup>15c</sup> has been investigated in detail, there is no published work describing direct measurement of the rate of decomposition of dibenzoyl peroxide in iodobenzene. The concentration of dibenzoyl peroxide in solution is normally determined by an iodometric method but this technique was found to be unsatisfactory when iodobenzene was the solvent.<sup>149</sup> Since it was desirable to determine the rate of decomposition of dibenzoyl peroxide in iodobenzene, for the elucidation of the mechanism of the decomposition of aryl radical sources in that solvent,

a new method of analysis for dibenzoyl peroxide was developed.

Diaroyl peroxides react rapidly with triethyl phosphite<sup>141</sup> to give triethyl phosphate and diaroyl anhydrides as products



The basis of the method of peroxide estimation used was that the amount of triethyl phosphate produced, after addition of an excess of triethyl phosphite to the peroxide solutions, could be measured by gas liquid chromatography after suitable calibration. In this way, for both bromobenzene and iodobenzene as solvents, the concentrations of dibenzoyl peroxide in the kinetic experiments were calculated, and from measurement of the gradient of the best straight line obtained when  $\ln$  (concentration of dibenzoyl peroxide in moles litre<sup>-1</sup>) was plotted against the time of reaction at 80° in secs., a value was obtained for the apparent first order rate constant ( $k_1$  (obs.)).

In the case of bromobenzene, for an initial dibenzoyl peroxide concentration of 0.09833 moles litre<sup>-1</sup>,  $k_1$  (obs.) was calculated to be  $4.57 \times 10^{-5}$  sec.<sup>-1</sup>. For solutions of dibenzoyl peroxide in bromobenzene, of initial concentrations 0.1318 and 0.08749 moles litre<sup>-1</sup>, Gill and Williams<sup>156</sup> found that the apparent first order rate constants were  $8.12 \times 10^{-5}$  and  $8.10 \times 10^{-5}$  sec.<sup>-1</sup> respectively.

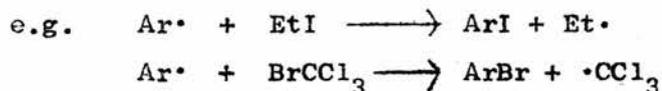
They allowed reaction to proceed at  $80.2^{\circ}$  under nitrogen and withdrew samples at time intervals for analysis of dibenzoyl peroxide concentration iodometrically. The difference between the value of  $k_1$  (obs.) determined and Gill and Williams' values may be due to the fact that reaction was carried out in sealed tubes under vacuum (less than one micron) whereas Gill and Williams allowed reaction to proceed under an atmosphere of nitrogen.

With an initial concentration of dibenzoyl peroxide in iodobenzene of 0.1096 moles litre<sup>-1</sup> the apparent first order rate constant was found to be  $3.7 \times 10^{-5}$  sec.<sup>-1</sup>

The apparent first order rate constants for the decomposition of dibenzoyl peroxide in bromobenzene and iodobenzene, as determined by the phosphite/phosphate method, were thus found to be very similar, and of the same order as that described by Gill and Williams for bromobenzene, demonstrating that the decomposition of dibenzoyl peroxide in iodobenzene does not occur by a very rapid induced decomposition process.

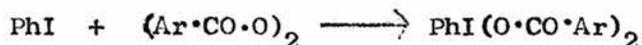
c) The Mechanism of the Abstraction of Iodine from Aromatic Iodides by Aryl Radicals.

Although abstraction of halogen atoms from alkyl polyhalides by free radicals is a well documented reaction,<sup>9,45,161</sup>



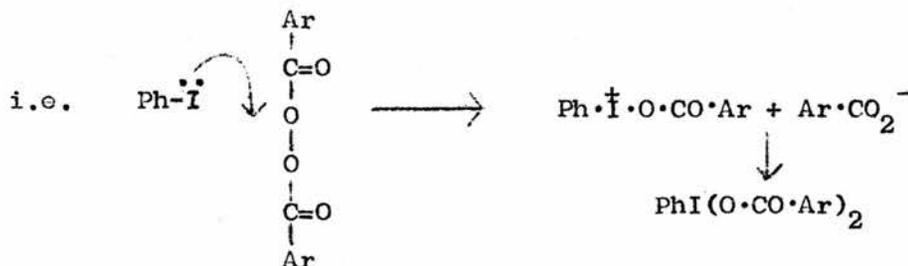
the abstraction of iodine from aromatic iodides, demonstrated in this investigation, is the first authenticated example of abstraction from an aromatic halide by aryl radicals.

The possibility of abstraction of iodine from aromatic iodides, in the decompositions of diaryl peroxides in aromatic iodides, proceeding via an iodoso intermediate



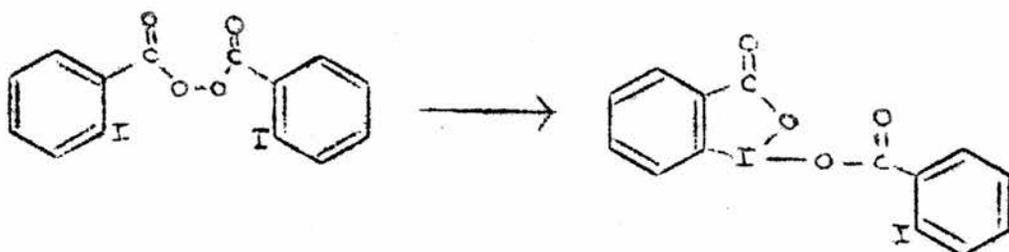
can be discounted because:

- 1) All reactions were carried out at 80°, and it was demonstrated<sup>79</sup> that only 5% of phenyl iododibenzoyl peroxide in 0.11M solution in benzene decomposed after the solution was boiled under reflux for 100 hours.
- 2) The rate of decomposition of dibenzoyl peroxide in iodobenzene ( $k_1$  (obs.) =  $3.7 \times 10^{-5}$  sec.<sup>-1</sup>) was very similar to the rate of decomposition in bromobenzene ( $k_1$  (obs.) =  $4.57 \times 10^{-5}$  sec.<sup>-1</sup>) and for formation of phenyl iodoso dibenzoyl peroxide, the rate of reaction would be expected to be much faster, due to additional induced decomposition of the peroxide.



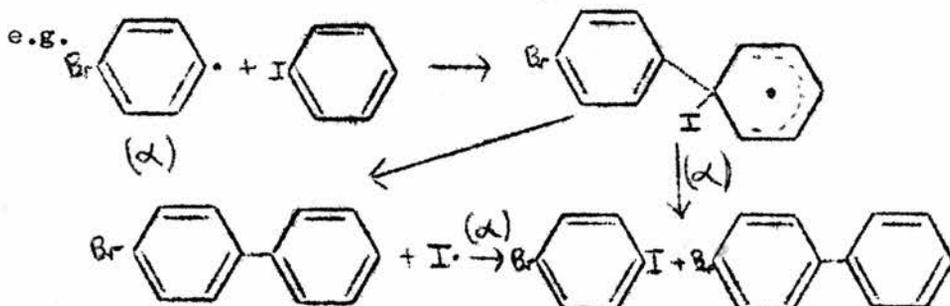
In this connection, it is noteworthy that Leffler et al.<sup>155</sup> have reported that di-o-iodobenzoyl peroxide, but not the para-isomer,

decomposes in chloroform several thousand times as quickly as other o-substituted diaryl peroxides decompose, to form a trivalent iodine compound.



3) The products of reaction can not be explained on the basis of a direct decomposition of an iodoso compound to an aryl iodide, because phenyl iodoso dibenzoates are known to decompose to aryloxy radicals<sup>43,79</sup> at elevated temperatures (120-160°). Also N-nitrosoacetanilides have been shown to abstract iodine, as well as diaryl peroxides.

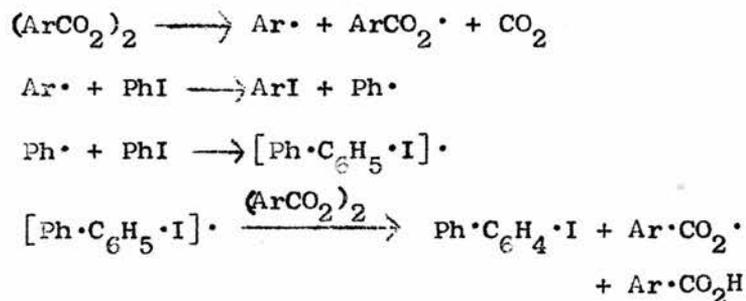
For the abstraction of iodine from an aromatic iodide by an aryl radical, it is conceivable that the aryl radical might attack the carbon atom bearing the iodine atom to form an intermediate aryliodocyclohexadienyl radical,



which would lose an iodine atom (which would then combine with an aryl radical) by spontaneous homolysis or, more probably, by abstraction by another aryl radical. In both cases aryl iodide is formed, as is the arylated benzene; however, no 4-bromobiphenyl was detected from the decomposition of di-p-bromobenzoyl peroxide in iodobenzene and so this mechanism may be discounted.

Alternatively aryl radicals may effect a direct abstraction of iodine, as described below, and the following reaction scheme largely accounts for the decomposition of dibenzoyl peroxides in iodobenzene.

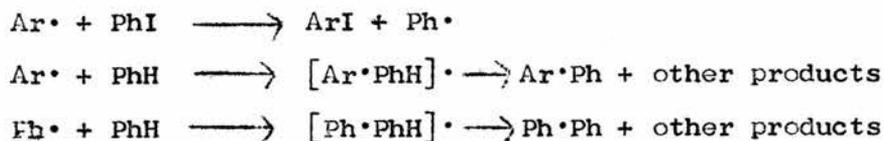
Scheme 1)



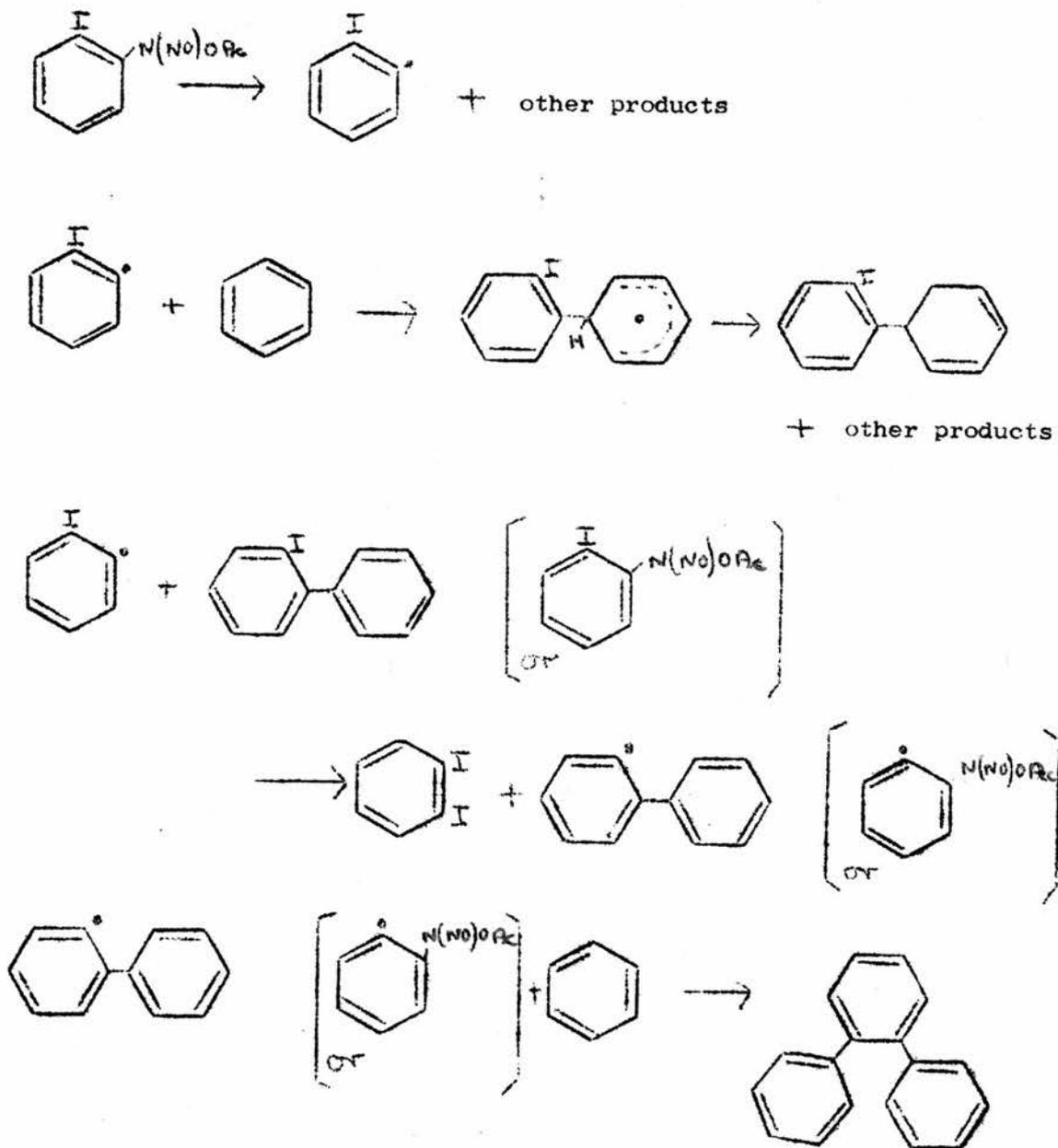
A similar reaction scheme will be operative for the decomposition of other aryl radical sources in iodobenzene.

The reaction of aryl radicals in a mixture of benzene and iodobenzene is accounted for by the following scheme.

Scheme 2)



Scheme 3)

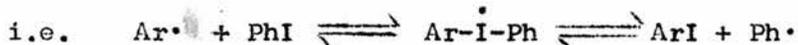


Scheme (3), for the decomposition of o-iodo-N-nitrosoacetanilide in benzene, can be modified to account for the mechanism of decomposition of m- and p-iodo-N-nitrosoacetanilide and di-p-iodo-benzoyl peroxide in benzene.

In conclusion, it has been shown that aryl radicals have a high affinity for iodine in aromatic iodides and that they effect abstraction of iodine from aromatic iodides by a homolytic process, involving direct aryl radical attack on the iodine atom in the aromatic iodide. Also, the presence of aromatic iodides does not have any marked effect on the rate of thermolytic decomposition of aryl radical sources.

After preliminary publication of the results<sup>113</sup> described above, Bunnett and Wamser<sup>142</sup> reported the abstraction of iodine from aromatic iodides by aryl radicals. However, they failed to observe the formation of 2-, 3- and 4-iodobiphenyls from the decomposition of di-p-chlorobenzoyl peroxide in iodobenzene and only reported the formation of two isomeric iodobiphenyls which were not further identified. The formation of 2-, 3- and 4-iodobiphenyls, in isomer ratios characteristic of free radical phenylation, is one of the vital arguments in favour of the iodine abstraction process occurring by a homolytic mechanism, and it is difficult to see how Bunnett and Wamser can justifiably propose a homolytic process for iodine abstraction on the basis of their experimental

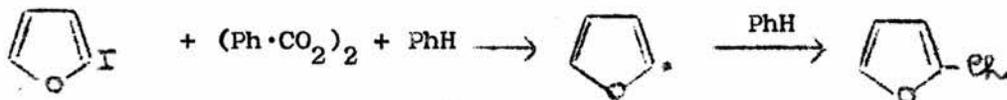
data. These workers indicated the possibility that abstraction of iodine might occur via a diaryliodine intermediate, in a two stage process.



While such a process is possible, it is no more than a refinement, lacking experimental support, of the mechanisms of Schemes 1-3 (above).

It should also be noted that one previous example of iodine abstraction by aryl radicals is recorded in the literature, although it was not recognised as such at the time. Harley-Mason and Mann,<sup>151</sup> in 1940, noted without details, that a Gomberg reaction of p-iodoaniline gave p-di-iodobenzene as a side product. Recently<sup>152</sup> p-di-iodobenzene was obtained as a product from the reaction of amyl nitrite with p-iodoaniline in benzene.

The abstraction of iodine from aromatic iodides by aryl radicals provides a convenient method of generating the radical derived from the iodide and thus, if the reaction is carried out in an aromatic solvent, arylation of the solvent will take place by the radical derived from the iodide. Potentially this is a process of considerable synthetic utility e.g. 2-phenylfuran could be synthesised by allowing dibenzoyl peroxide (2 mol.) to decompose in a mixture of benzene (20 mol.) and the readily obtained 2-iodofuran:



REFERENCES

1. M. Gomberg Ber., 1900, 33, 3150.
2. L.H. Cone and M. Gomberg, Ber., 1904, 37, 2033;  
1906, 39, 3274.
3. F. Paneth and W. Hofeditz, Ber., 1929, 62, 1335.
4. H.L.J. Backstrom, Z. phys. Chem. (Leipzig), 1934,  
25B, 99.
5. W.S.M. Grieve and D.H. Hey, J. Chem. Soc., 1934, 1797.
6. D.H. Hey, J. Chem. Soc., 1934, 1966.
7. M.S. Kharasch and F.R. Mayo, J. Amer. Chem. Soc.,  
1933, 55, 2468.
8. M.S. Kharasch, H. Engelmann, and F.R. Mayo,  
J. Org. Chem., 1937, 2, 288.
9. D.H. Hey and W.A. Waters, Chem. Rev., 1937, 21, 169.
10. C.K. Ingold, Trans. Faraday Soc., 1938, 34, 227.
11. D.F. De Tar and R.A.J. Long, J. Amer. Chem. Soc.,  
1958, 80, 4742.
12. D.H. Hey, M.J. Perkins, and G.H. Williams,  
J. Chem. Soc., 1963, 5604.
13. D.F. De Tar and A. Hlynsky, J. Amer. Chem. Soc., 1955,  
77, 4411.
14. E. Lippmann, Monatsh., 1886, 7, 521.
15. C. Brodie, J. Chem. Soc., 1864, 17, 266.
16. H. Gelissen and P.H. Hermans, Ber, 1925, 58, 285, 476,  
479, 764, 984, 2396; 1926, 59, 63, 662.
17. J. Boeseken and H. Gelissen, Rec. Trav. Chim., 1924,  
43, 869.

18. P.H. Hermans, Rec. Trav. Chim., 1935, 54, 760.
19. D.J. Brown, J. Amer. Chem. Soc., 1948, 70, 1208.
20. D.H. Hey, J. Chem. Soc., 1952, 1974.
21. D.R. Augood, D.H. Hey, and G.H. Williams, J. Chem. Soc., 1952, 2094.
22. D.H. Hey, A. Nechvatal, and T.S. Robinson, J. Chem. Soc., 1951, 2892.
23. D.R. Augood, D.H. Hey and G.H. Williams, J. Chem. Soc., 1953, 44.
24. D.H. Hey, M.J. Perkins, and G.H. Williams, J. Chem. Soc., 1963, 5604.
25. B.M. Lynch and K.H. Pausacker, Austral. J. Chem., 1957, 10, 165.
26. D.I. Davies, D.H. Hey, and G.H. Williams, J. Chem. Soc., 1961, 562.
27. J.H. Waters, Diss. Abs., 1961, 22, 432.
28. A.C. Cuthbertson, J.H. McLure and R.E. Robertson, Canad. J. Res., 1942, 20B, 103.
29. H. Wieland<sup>1</sup>, K. Heyman, T. Tsatsas, D. Juchum, G. Varvoglis, G. Labriola, O. Dobbelstein, and H.S. Boyd-Barrett, Annalen, 1934, 514, 145.
30. S.G. Cohen, J. Polymer Sci., 1947, 2, 511.
31. R. Huisgen and G. Horeld, Annalen, 1949, 562, 137.
32. W.E. Cass, J. Amer. Chem. Soc., 1946, 68, 1976.
33. W.E. Cass, J. Amer. Chem. Soc., 1947, 69, 500.
34. K. Nozaki and P.D. Bartlett, J. Amer. Chem. Soc., 1946, 68, 1636.
35. F.F. Rust, F.H. Seubold, and W.E. Vaughan, J. Amer. Chem. Soc., 1948, 70, 3258.

36. C.G. Swain, W.H. Stockmayer, and J.T. Clarke, J. Amer. Chem. Soc., 1950, 72, 5426.
37. G.B. Gill and G.H. Williams, J. Chem. Soc., 1965, 995.
38. D.R. Augood, Ph.D. Thesis, London 1951.
39. I.M. Roitt and W.A. Waters, J. Chem. Soc., 1952, 2695.
40. D.F. De Tar and J.C. Howard, J. Amer. Chem. Soc., 1955, 77, 4393.
41. D.H. Hey, M.J. Perkins, and G.H. Williams, Chem. and Ind., 1963, 83.
42. C.D. Hall, Chem. and Ind., 1965, 384.
43. D.H. Hey, C.J.M. Stirling, and G.H. Williams, J. Chem. Soc., 1954, 2747; 1956, 1475.
44. D.H. Hey, C.J.M. Stirling, and G.H. Williams, J. Chem. Soc., 1955, 3963.
45. C. Walling, "Free Radicals in Solution", John Wiley and Sons, Inc., New York, 1957, pp. 155 and 255.
46. M.G. Alder and J.E. Leffler, J. Amer. Chem. Soc., 1954, 76, 1425.
47. R. Huisgen and H. Nakaten, Annalen, 1954, 536, 70.
48. S.G. Cohen and Chi Hua Wang, J. Amer. Chem. Soc., 1953, 75, 5504.
49. E.L. Eliel, M. Eberhardt, and O. Simamura, Tetrahedron Letters, 1962, 749.
50. J.F. Garst and R.S. Cole, Tetrahedron Letters, 1963, 679.
51. G.A. Russell and R.F. Bridger, Tetrahedron Letters, 1963, 737.
52. D.H. Hey, M.J. Perkins, and G.H. Williams, J. Chem. Soc., 1965, 110.

53. W.E. Bachmann and R.A. Hoffmann, "Organic Reactions", John Wiley and Sons, Inc., New York, 1944, Vol. 2, p. 224.
54. O.C. Dermer and M.T. Edmiston, Chem. Rev., 1957, 57, 77.
55. J.I.G. Cadogan, J. Chem. Soc., 1962, 4257.
56. J.I.G. Cadogan, D.A. Roy, and D.M. Smith, J. Chem. Soc., (C), 1966, 1249
57. W.A. Waters, J. Chem. Soc., 1939, 864.
58. C.E. Waring and J.R. Abrams, J. Amer. Chem. Soc., 1941, 63, 2757.
59. M.R. Pettit and J.C. Tatlow, J. Chem. Soc., 1954, 1941
60. R.O.C. Norman and W.A. Waters, J. Chem. Soc., 1958, 167.
61. E. Bamberger, Ber., 1897, 30, 366.
62. E.C. Butterworth and D.H. Hey, J. Chem. Soc., 1938, 116.
63. R. Huisgen and G. Horeld, Annalen, 1949, 562, 137.
64. R. Huisgen, Angew. Chem., 1950, 62, 369; Annalen, 1951, 573, 163; 574, 184; R. Huisgen and H. Nakaten, ibid., 1951, 573, 181; R. Huisgen and L. Krause, ibid., 1951, 574, 157; R. Huisgen and J. Reinertshofer, ibid., 1952, 575, 174, 197.
65. D.H. Hey, J. Stuart-Webb, and G.H. Williams, Nature, 1951, 167, 725; Research, 1951, 4, 385; J. Chem. Soc., 1952, 4657.
66. D.F. De Tar, J. Amer. Chem. Soc., 1951, 73, 1446.
67. I.K. Barben and H. Suschitzky, J. Chem. Soc., 1960, 2735.
68. P. Miles and H. Suschitzky, Tetrahedron, 1962, 18, 1369.
70. D.H. Hey and J. Peters, J. Chem. Soc., 1960, 79.
71. D.F. De Tar and H.J. Schiefele, J. Amer. Chem. Soc., 1951, 73, 1442.

72. E.L. Eliel and J.G. Saha, J. Amer. Chem. Soc., 1964, 86, 3581.
73. D.B. Denney, N.E. Gershman, and A. Appelbaum, J. Amer. Chem. Soc., 1964, 86, 3180.
74. C. Rüchardt and E. Merz, Tetrahedron Letters, 1964, 2431.
75. C. Rüchardt and B. Freudenberg, Tetrahedron Letters, 1964, 3623.
76. G. Binsch and C. Rüchardt, J. Amer. Chem. Soc., 1966, 88, 173.
77. G. Binsch, E. Merz, and C. Rüchardt, Chem. Ber., 1967, 100, 247.
78. J.I.G. Cadogan and P.G. Hibbert, Proc. Chem. Soc., 1964, 338.
79. B.M. Lynch and K.H. Pausacker, Austral. J. Chem., 1957, 10, 329.
80. J.E. Leffler, W.J.M. Mitchell, and B.C. Meron, J. Org. Chem., 1966, 31, 1153.
81. G.A. Razuvaev and Yu. A. Ol'dekop, J. Gen. Chem. (U.S.S.R.), 1949, 19, 711, 1485; 1951, 21, 1225.
82. J.M. Blair, D. Bryce-Smith, and B.W. Pengilly, J. Chem. Soc., 1959, 3174.
83. P.A. Leighton and R.A. Mortensen, J. Amer. Chem. Soc., 1936, 58, 448.
84. D.H. Hey, D.A. Shingleton, and G.H. Williams, J. Chem. Soc., 1963, 5012.
85. W. Wolf and N. Kharasch, J. Org. Chem., 1965, 30, 2493.
86. N. Kharasch and R.K. Sharma, Chem. Comm., 1966, 106.
87. R. Stoermer and B. Kahlert, Ber., 1902, 35, 1633; W.E. Bachmann and H.T. Clarke, J. Amer. Chem. Soc., 1927, 49, 2089; K. Lüttringhaus and G.V. Saaf, Annalen, 1939, 542, 241; A.A. Morton, J.B. Davidson, and B.L. Hakan, J. Amer. Chem. Soc., 1942, 64, 2242.

88. G. Wittig, Naturwiss., 1942, 30, 696.
89. G. Wittig and H. Witt, Ber., 1941, 74, 1474;  
G. Wittig and G. Harborth, ibid., 1944, 77, 306, 315.
90. J.D. Roberts, H.E. Simmons jr., L.A. Carlsmith, and C.W. Vaughan, J. Amer. Chem. Soc., 1953, 75, 3290;  
J.D. Roberts, D.E. Semenow, H.E. Simmons jr., and L.A. Carlsmith, ibid., 1956, 78, 601.
91. R. Huisgen and H. Rist, Naturwiss., 1954, 41, 358;  
Annalen, 1955, 594, 137.
92. G. Wittig and L. Pohmer, Angew Chem., 1955, 67, 348;  
Chem. Ber., 1956, 89, 1334.
93. G. Wittig and W. Behnisch, Chem. Ber., 1953, 91, 2358;  
G. Wittig and B. Reichel, ibid., 1963, 96, 2851.
94. G. Wittig and E. Krauss, Chem. Ber., 1953, 91, 395.
95. E.M. Arnett, J. Org. Chem., 1960, 25, 324.
96. G. Wittig and H. Ludwig, Angew. Chem., 1956, 68, 40;  
G. Wittig, "Organic Syntheses", John Wiley and Sons, Inc., New York, 1959, Vol. 39, p. 75.
97. E. Le Goff, J. Amer. Chem. Soc., 1962, 84, 3756.
98. F.M. Beringer and J.J. Huang, J. Org. Chem., 1964, 29, 445.
99. M. Stiles and R.G. Miller, J. Amer. Chem. Soc., 1960, 82, 3802.
100. L. Friedman and F.M. Logullo, J. Amer. Chem. Soc., 1963, 85, 1549.
101. G. Wittig and R.W. Hoffmann, Chem. Ber., 1962, 95, 2718.
102. C.D. Campbell and C.W. Rees, Proc. Chem. Soc., 1964, 296.
103. T. Kauffmann, Angew. Chemie Internat.Eng. Ed., 1965, 4, 543.

104. G. Wittig and H.F. Ebel, Annalen., 1961, 650, 20.
105. R.S. Berry, G.N. Spokes, and R.M. Stiles, J. Amer. Chem. Soc., 1960, 82, 5240; 1962, 84, 3570.
106. R.S. Berry, J. Clardy, and M.E. Schafer, J. Amer. Chem. Soc., 1964, 86, 2738.
107. R.S. Berry, J. Clardy, and M.E. Schafer, Tetrahedron Letters, 1965, 1003, 1011.
108. I.P. Fisher and F.P. Lossing, J. Amer. Chem. Soc., 1963, 85, 1018.
109. C.A. Coulson, Chem. Soc. Special Publ., 1958, 12, 100.
110. R. Huisgen and J. Sauer, Angew. Chem., 1960, 72, 91.
111. G. Wittig, Angew. Chemie Internat. Eng. Ed., 1965, 4, 735.
112. J.P.N. Brewer and H. Heaney, Tetrahedron Letters, 1965, 4709; D.D. Callander, P.L. Coe, and J.C. Tatlow, Chem. Comm., 1966, 143.
113. D.L. Brydon and J.I.G. Cadogan, Chem. Comm., 1966, 744.
114. J.D. Roberts, C.W. Vaughan, L.A. Carlsmith, and D.A. Semenow, J. Amer. Chem. Soc., 1956, 78, 611.
115. G.B.R. de Graaf, H.J. Hertog, and W. Ch. Melger, Tetrahedron Letters, 1965, 963.
116. D.H. Hey, K.S.Y. Liang, and M.J. Perkins, Tetrahedron Letters, 1967, 1477.
117. G.L. Davies, D.H. Hey, and G.H. Williams, J. Chem. Soc., 1956, 4397.
118. F.G. Edwards and F.R. Mayo, J. Amer. Chem. Soc., 1950, 72, 1265.
119. C.J.M. Stirling, "Radicals in Organic Chemistry", Oldbourne Book Co. Ltd., London, 1965, p. 13.

120. J.A. Kampmeir and T.R. Evans, J. Amer. Chem. Soc., 1966, 88, 4096.
121. C.G. Overberger and J.G. Lombardino, J. Amer. Chem. Soc., 1958, 80, 2317.
122. J.I.G. Cadogan and E.G. Duell, J. Chem. Soc., 1962, 4154.
123. C.S.G. Phillips and P.L. Timms, J. Chromatog., 1961, 5, 131.
124. W. Cooper, J. Chem. Soc., 1951, 3107.
125. L. Vanino and E. Uhlfelder, Ber., 1900, 33, 1043.
126. Chang Shih, D.H. Hey, and G.H. Williams, J. Chem. Soc., 1958, 4403.
127. M. Gomberg, Ber., 1897, 30, 2043.
128. H. France, I.M. Heilbron, and D.H. Hey, J. Chem. Soc., 1940, 369.
129. J. R. Morton and H.W. Wilcox, "Inorganic Syntheses", McGraw-Hill Publishing Co. Ltd., London, 1953, Vol. 4, p. 48.
130. "Dictionary of Organic Compounds", Eyre and Spottiswoode Ltd., E. and F.N. Spon Ltd., London, 1965.
131. R. Huisgen and H. Nakaten, Annalen., 1954, 586, 84.
132. J.W. Haworth and D.H. Hey, J. Chem. Soc., 1940, 361.
133. W.S.M. Grieve and D.H. Hey, J. Chem. Soc., 1935, 691.
134. G.F. Woods, F.T. Reed, T.E. Arthur, and H. Ezekieli, J. Amer. Chem. Soc., 1951, 73, 3854.
135. R.L. Datta and N.R. Chatterjee, J. Amer. Chem. Soc., 1919, 41, 292.
136. F.G. Mann and B.C. Saunders, "Practical Organic Chemistry", Longmans, Green and Co. Ltd., London, 1938, p. 124

137. A. Roe, "Organic Reactions", John Wiley and Sons, Inc., New York, 1949, Vol. 5, p. 217.
138. "Chemistry of Carbon Compounds", Elsevier Publishing Co., London, 1951, Vol. 1, p. 98.
139. G.S. Reddy and J.H. Goldstein, J. Phys. Chem., 1961, 65, 1539.
140. J.W. Emsley, J. Feeney, and L.H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy", Pergamon Press, Oxford, 1966, p. 789.
141. A.J. Burn, J.I.G. Cadogan, and (in part) P.J. Bunyan, J. Chem. Soc., 1963, 1527.
142. J.F. Bunnett and C.C. Wamser, J. Amer. Chem. Soc., 1966, 88, 5534.
143. K.C. Chan and R.L. Huang, J. Chem. Soc., 1965, 2649.
144. D.F. De Tar and J.C. Howard, J. Amer. Chem. Soc., 1955, 77, 4393.
145. D.R. Augood, J.I.G. Cadogan, D.H. Hey, and G.H. Williams, J. Chem. Soc., 1953, 3412.
146. D.H. Hey and J. Peters, J. Chem. Soc., 1960, 79.
147. J.I.G. Cadogan and J.B. Thomson, private communication.
148. A. Hantzsch and J.S. Smythe, Ber., 1900, 33, 505.
149. G.B. Gill and G.H. Williams, private communication.
150. J.A. Kampmeir and A.B. Rubin, Tetrahedron Letters, 1966, 2853.
151. J. Harley-Mason and F.G. Mann, J. Chem. Soc., 1940, 1379.
152. J.I.G. Cadogan and D.M. Smith, private communication.
153. V.I. Vedeneyev, L.V. Gurrich, V.N. Kandrat'yev, V.A. Medvedev and Ye. L. Frankevich, "Bond Energies Ionization Potentials and Electron Affinities", Edward Arnold Ltd., London, 1966, p. 54.

154. M. Kasha, J. Chem. Phys., 1952, 20, 71.
155. J.E. Leffler, R.D. Faulkner and C.C. Petropoulos, J. Amer. Chem. Soc., 5435, 1958.
156. G.B. Gill and G.H. Williams, J. Chem. Soc., 1965, 7127.
157. R.W. Franck and K. Yanagi, Tetrahedron Letters, 1966, 2905.
158. J.I.G. Cadogan and M.J.P. Harger, private communication.
159. P.G. Hibbert, Ph.D. Thesis, London, 1963.
160. N. Kharasch, R.K. Sharma, and H.B. Lewis, Chem. Comm., 1966, 418.
161. J.I.G. Cadogan, D.H. Hey, and P.G. Hibbert, J. Chem. Soc., 1965, 3939.