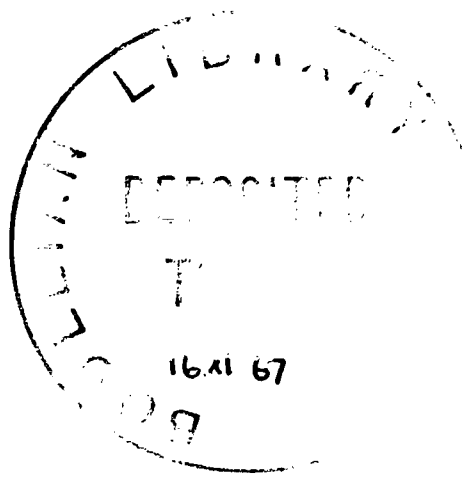



# STUDIES IN ORGANIC PHOTOCHEMISTRY

Being a Thesis submitted to the

Board of the Faculty of Physical Sciences

in the

University of Oxford

for the degree of Doctor of Philosophy

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# CHAPTER I

## INTRODUCTION

Until the last decade the study of photochemistry was largely the province of the physical chemist, who was interested in the gas-phase reactions of simple molecules. Despite the efforts of some early pioneers, notably Ciamician and Silber, there was little research into organic photochemistry, mainly because of the difficulties in resolving the complex mixtures often formed in photochemical reactions. The present interest in organic photochemistry has been aided by the advances in new techniques for the isolation and identification of organic compounds. Furthermore, spectroscopy has provided an increasing volume of information as to the nature of the excited state, with the result that the chemical reactions of the excited state have been approached more urgently. In consequence, there has recently been a great quantity of published work relating to electronic spectra, to energy transfer between molecules and between excited states, and to organic photochemistry. Several recent books [1-7] and review articles [8-20] on these topics have appeared, and it is not therefore proposed to review these subjects here.

It should be noted however that from something of a curiosity, organic photochemistry has advanced to the stage where photochemical

reactions are being used in the syntheses of a corrin,[21] of ±caryophyllene,[22] of ±thujopsene,[23] and of compounds related to naturally occurring alkaloids.[24-26] As a result of the current interest in photochemistry Woodward and Hoffman[27-29] have advanced a new theory to explain the orientation of the products in cyclic reactions proceeding by concerted movements of electrons. These principles pertain equally to thermal reactions, and the familiar Diels-Alder reaction is one to which they may be applied.[30]

A particularly promising aspect of organic photochemistry has been the synthesis of highly strained systems, which are inaccessible by ordinary chemical means. Photochemical steps have been used in the synthesis of cubane[31-32] and of bicyclobutane.[33] Other novel compounds prepared photochemically include the photo-isomerisation products of hexa-, 1, 5-diene (i)[34] and cyclo-octa-1, 5-diene (ii);[35] the tetracyclic compounds formed by irradiation of bicyclo-(2, 2, 1)-heptadienes (iii)[36, 37] and the "cage" compounds formed from the photodimers of benzoquinone (iv)[38] and 2, 3-dimethylbenzoquinone (v).[39]

Both novel and highly strained are the recently discovered valence tautomers of benzene and its derivatives. "Dewar" (vi) benzenes have recently been prepared photochemically,[40] and thermally,[41, 42] and it has been postulated that the photo-isomer-

isation reactions of alkyl benzenes, in which the alkyl groups become differently disposed about the ring, proceed by way of Ladenburg benzene, or prismane (vii).[40a, 42-46] According to the conditions of the photolysis, benzene may give rise to benzvalene (viii), or to fulvene (ix).[47-52] The aromatic sextet of benzene is destroyed also in photochemical addition reactions; adducts of benzene with maleic anhydride (x),[53] acetylenes (xi),[54, 55] olefins (xii-xv),[56-58] alcohols (xvi, xvii),[59] and acids (xviii)[60] have been isolated and characterised. These diverse photoreactions of benzene have been explained by reference to the nature of the excited states involved in their formation.[61, 62]

Other work has been published concerning the photochemistry of benzenes bearing other than alkyl groups. Anisole has been shewn to fission into a phenoxy radical and a methyl radical.[63] Other aromatic ethers split up similarly to give o- and p-alkylated phenols in a rearrangement which has been called the photo-Fries reaction.[64-68] Zimmermann has shewn that the ring substituted methoxy benzyl acetates give rise to a benzyl cation, or a benzyl radical according to the position of the methoxyl group.[69] Iodobenzene splits up on irradiation to give an iodine atom and a phenyl radical.[70] In this reaction the products are biphenyl and iodobiphenyls; Kharasch has developed this as a method of obtaining substituted biphenyls in good

yield;[71-73] a similar reaction is observed with chlorobenzene.[74]

The work described in this thesis falls into two separate although related parts, and they are divided as such. The first part concerns the photonucleophilic substitution reactions of aromatic compounds and is a continuation of work described in an earlier thesis.[75] During the course of this investigation it was found that under some conditions nitrobenzene is photochemically reduced, the products being dependent upon the reaction conditions. A study of this phenomenon was therefore made and the results of this study form the second part of this thesis.

# CHAPTER II

## Photonucleophilic Substitution in Monosubstituted Benzenoid Compounds

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### Introduction

Although there are several reports in the literature concerning the photochemical substitution reactions of disubstituted benzenes (and these are to be discussed below in Chapter III), most photoreactions of monosubstituted benzenes studied to date have concerned their reactions in the absence of other substrates.

However, there are isolated reports of the photochemical substitution reactions of these compounds. Aside from the well-known photochemical halogenations of aromatic compounds,[76] it has been found that in the presence of light, bromobenzene reacts with chlorine in a radical chain process to yield chlorobenzene and molecular bromine.[77, 78] Bromobenzene also reacts photochemically with liquid ammonia. The product is aniline, which is formed very slowly and in very low yield.[79]

Nitrobenzene has been subjected to both electrophilic and to nucleophilic photochemical attack. In 70% nitric acid[80] the products are m-dinitrobenzene, p-dinitrobenzene and picric acid, under conditions where no thermal reaction can be detected.[81] In liquid ammonia the products are o- and p-nitroaniline. In concentrated hydrochloric

acid 2, 4-dichloroaniline and 2, 4, 6-trichloroaniline were produced.[82] The reaction was shewn to exhibit first order kinetics and the rate depended only upon the concentration of chloride ion. The reaction mechanism is as yet unknown.

Interest in these laboratories in the substitution chemistry of monosubstituted benzenes was stimulated by the observation of Thomson,[83] that photolysis of anisole in the presence of piperidine leads to displacement of the methoxyl group by piperidine to yield N-phenylpiperidine (xix). It was the object of an earlier thesis by the present author[75] to determine the scope of this reaction.

Briefly, it was found that nucleophilic substitution of a substituent already present was favoured:

(i) If the substituent was a good leaving group in the context of nucleophilic substitution:

(ii) If the attacking reagent was a nucleophilic species, and particularly if the attacking reagent was a stronger nucleophile than the leaving group.

Typically it was found that the fluorine atom of fluorobenzene could be displaced by alcohols, alkoxides, and amines; the alkoxy group of phenyl alkyl ethers could be displaced by amines and sometimes by alkoxides, whereas substituents such as dialkylamino could not be displaced at all. The reaction was in all cases rather inefficient, the highest yield recorded being 10%; the starting material

unaccounted for was usually converted to a polymer. This had the effect of stopping the reaction after only low conversions of starting material, since it was deposited on that wall of the reaction vessel nearer to the light source.

When displacement reactions were carried out upon chlorobenzene, in addition to the expected products, there were obtained biphenyl and the isomeric monochlorobiphenyls. Their formation was explained by invoking an initial fission of chlorobenzene into a chlorine atom and a phenyl radical in a manner analogous to that observed for iodobenzene.[70]

With regard to the reaction mechanism, it was established by using filter solutions that the excited state of the aromatic component is involved, rather than that of the nucleophile. An ionic process of some kind was indicated by the nature of the attacking reagents used (amines, and alkoxides). The possibility that a benzyne intermediate might be involved was eliminated by a photolysis of p-fluorotoluene with piperidine, when the exclusive product was N-p-tolylpiperidine. A benzyne intermediate would lead, in addition to this product, to the meta isomer.

An initial scission of the aromatic compound into $C_6H_5^+$ and $X^-$ was also considered unlikely, for the phenyl cation is a very reactive and therefore very unselective species. It would thus be expected to react with any nucleophilic entity present, yet an irradiation of fluoro-

benzene in aqueous methanol gave anisole but no phenol.

Unfortunately, in the earlier study it was not possible to reach a final conclusion regarding the mechanism of the reaction. Whilst it was possible to exclude benzyne and the phenyl cation as intermediates, the evidence thus far obtained was insufficient to differentiate between two alternative modes of nucleophilic attack, and the radical displacement reaction observed for bromobenzene.[7] The way in which these three mechanisms were distinguished is described below.

## Discussion

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The earlier investigation of photonucleophilic substitution in the monosubstituted benzene series was incomplete, both because of the failure to establish definitely the mechanism of the reaction, and because only a limited range of attacking reagents and leaving groups was used.

A first series of experiments concerned the effect of concentration in the anisole-diethylamine system. Having earlier established that the photo-excitation involves the aromatic component rather than the attacking reagent, the photolysis was repeated using solutions increasingly dilute in anisole in the hope that, as dilution progressed, the yield of N,N-diethylaniline would increase by virtue of the greater concentration of diethylamine molecules in the vicinity of an excited anisole molecule. Table 1 shews that this was indeed the case, for on dilution by stages from equimolar (55%) to 1% in anisole, the yield of purified N,N-diethylaniline increased from 9% to about 30%.

Furthermore, the quantity of polymer decreased, indicating perhaps that the aromatic component unaccounted for is consumed by an unknown process involving other aromatic molecules. This suggestion is consistent with the fact that the amorphous brown polymer produced from anisole shews i-r absorptions due to phenyl groups and

Table 1

Concentration Effects in the Anisole/Diethylamine System

| Anisole (g.) | Recovered Anisole (g.) | Diethylamine (ml.) | N, N-Diethylaniline (mg.) | Yield % |
|---|---|---|---|---|
| 9.0 | 6.0 | 10 | 390 | 9 |
| 5.0 | 1.3 | 75 | 360 | 17 |
| 2.0 | 0.52 | 100 | 630 | 31 |
| 1.0 | 0.29 | 100 | 300 | 30 |

ether linkages; very little else may be discerned. Dilution consequently reduced polymer formation, and increases the yield of the normal product, by increasing the chance that reaction with the attacking reagent will occur before the excited species encounters another aromatic molecule.

In order to extend the range of possible attacking reagents, anisole was irradiated with cyanide ion, from which benzonitrile was produced. An irradiation with glacial acetic acid was carried out in the hope of replacing the methoxyl group to give phenyl acetate or its possible photolysis product, phenol. The interest in this reaction was that it might be a useful method of cleaving aromatic ethers under relatively mild conditions. However, no replacement occurred; an increase of the nucleophilic power of the solvent by an irradiation with sodium acetate in acetic acid met with no more success, neither did an attempt to render the methoxyl group a better leaving group by protonation, in an irradiation with hydrogen chloride in acetic acid.

Other possible leaving groups were now investigated. Thioanisole was found to react photochemically with diethylamine, but a large number of products in addition to diethylaniline was obtained, and the latter could not be freed completely from sulphur-containing material. Presumably, the thiomethoxy group, being like chlorine a substituent

with a rather low bond energy, splits off to give radicals, [74] and this is the origin of the other products.

It was decided to examine the effect of an electron-withdrawing substituent, in order to determine whether substitution could still occur, or whether other modes of reaction would be preferred. In the case of benzontrile, an irradiation in the presence of diethylamine led to little change; the only product was a very small quantity of material inferred to be N, N-diethylbenzamide from its g.l.c. retention characteristics, and from the carbonyl stretching frequency of the i-r spectrum of the small impure sample obtained. This product is presumed to arise by nucleophilic attack of diethylamine on the cyano group, followed by hydrolysis during the work-up of the resultant amidine (xx).

Nitrobenzene, however, gave a considerable quantity of basic material on irradiation in diethylamine. Both g.l.c. and t.l.c. indicated that this was not diethylaniline, but a more polar material. The i-r spectrum indicated the presence of an N-H group, and preparation of the acetyl and benzoyl derivatives shewed them to be identical to those prepared from aniline. As diethylaniline had not previously been observed to lose ethyl groups to any significant extent, [75] it was concluded that the nitrobenzene must have been reduced by the diethylamine. This view was confirmed on examination of the neutral

material produced in the irradiation for, after repeated crystallization from methanol, there were obtained red needles, the mass spectrum of which showed a molecular ion at $m^+/e$ 198 and a cracking pattern consistent with the compound being a monohydroxyazobenzene. The n. m. r. spectrum, apart from aromatic protons, had a singlet below 0 p. p. m., indicative of a hydrogen-bonded hydroxyl group. The m. p. was the same as that recorded for 2-hydroxyazobenzene (xxi), a known photolysis product of azoxybenzene.[84] Other experiments relating to this observation are described in Chapter IV.

A new approach to elucidating the reaction mechanism was now made. Although the attacking reagents and leaving groups used imply an ionic process of some kind, a radical reaction cannot be entirely excluded in view of the radical displacement of the bromine in bromobenzene by chlorine.[72] It would be surprising, though, if this were the case, for disubstituted benzenes should be found among the products, according to the reaction

$$C_6H_5X + Y^{\cdot} \longrightarrow X.C_6H_4.Y \text{ (o, m, and p)}$$

To date none such have been found, although in a study of the reactions of methyl radicals upon anisole,[85] the three isomers of cresyl methyl ether were detected but not toluene.

The first experiment concerned the possibility that photo-

excitation via the end-absorption by diethylamine might produce diethylamino radicals which might then displace the fluorine of fluorobenzene in a radical displacement reaction:

$$\text{i.e. } Et_2NH \xrightarrow{h\nu} Et_2N^{\cdot} + H^{\cdot} \quad \ldots\ldots (1)$$

$$Et_2N^{\cdot} + Ph\text{-}F \longrightarrow Ph\text{-}NEt_2 + F^{\cdot} \quad \ldots\ldots (2)$$

Diethylchloramine was prepared and was photolysed in the presence of fluorobenzene. This method is known to produce diethylamino radicals,[86] and these may then attack fluorobenzene. The reaction mixture was analysed by g.l.c. ; three peaks were detected and while the compounds were not isolated, they were presumed to be o-, m-, and p-fluoro-N,N-diethylaniline, but no peak of retention time corresponding to that of N,N-diethylaniline could be observed.

In order to eliminate the possibility that the fluorine atom was first abstracted from the fluorobenzene by a hydrogen atom produced by breakdown of the diethylamine (equation 1), an attempt to produce hydrogen atoms in situ was made. Di-imide, $N_2H_2$, is the analogue of azomethane; since the latter fissions on photolysis to give methyl radicals, it was hoped that di-imide might photolyse similarly to give hydrogen atoms.

Di-imide was produced in the reaction mixture by the thermal decomposition of p-toluenesulphonyl hydrazide.[87] The irradiation

was carried out in refluxing benzene and the reaction mixture was analysed by g.l.c. When di-imide was irradiated in the presence of cyclohexene, bicyclohexenyl was detected by g.l.c., but when the irradiation was carried out in the presence of fluorobenzene under conditions where no light was absorbed by fluorobenzene, no biphenyl was produced. It was therefore concluded that a radical mechanism could be excluded.

The U.V. absorption spectra of both fluorobenzene and anisole show red shifts on going from cyclohexane to ethanol, indicating that the lowest energy transition is $\pi,\pi^*$ in character.[88] Since excitation is to the singlet level, and since the singlet-triplet splitting is greater for $\pi,\pi^*$ than for $n,\pi^*$ states,[89] then whatever the multiplicity of the excited state it must be $\pi,\pi^*$ in nature. Zero-order H.M.O. calculations[90] on anisole indicate that in this state C(1) and C(4) are electron deficient. By contrast, in the $n,\pi^*$ state all nuclear positions are electron rich - See Table 2 and Appendix 1.

Table 2

Formal charges in the excited states of anisole

| Formal Charges | C(1) | C(2) | C(3) | C(4) |
|---|---|---|---|---|
| in $n,\pi^*$ state | -0.004 | -0.23 | -0.25 | -0.03 |
| in $\pi,\pi^*$ state | +0.23 | -0.16 | -o.20 | +0.24 |

Note h(O) = 2; k(C - O) = 1

Since in the $\pi, \pi^*$ state C(1) and C(4) are electron deficient, it might be expected that nucleophilic reagents would prefer to attack at these positions. Three possibilities therefore arise; and these are illustrated in Scheme 1, pathways 'A', 'B', and 'C'.

Pathway 'B' is an unlikely process because it involves the loss of hydride ion from the intermediate (xxii) and the failure to observe any disubstituted products in the photolyses discussed above indicates that it occurs to a negligible extent.

An attempt was made to observe pathway 'C' by an irradiation of 2, 6-dimethylanisole in diethylamine. Attack at C(4) would give 3, 5-dimethyl-N, N-diethylaniline, but none was detected among the products. This is a particularly favourable case for observing pathway 'C', because of the steric hindrance by the two neighbouring methyl groups at C(1) reducing possible competition from process 'A'. Indeed, so great is the steric interaction that no reaction at all was observed, i.e. no 2, 6-dimethyl-N, N-diethylaniline could be detected either. By contrast, 3, 5-dimethylanisole reacted normally and the fact that the product was uniquely 3, 5-dimethyl-N, N-diethylaniline (xxiii) is further evidence against a benzyne mechanism. The homogenelty of the product was demonstrated both by g.l.c. analysis, and by the fact that the three isolated aromatic protons of the product were

observed as a singlet in the n. m. r. spectrum.

It is thus concluded that pathway 'A' represents the mechanism of the photosubstitution reaction. A simple kinetic treatment shews (Appendix 2) that if this mechanism be correct, then the rate of production of substituted material should ~~depend directly upon~~ be a function of the concentration of the nucleophile, and upon no other variable, assuming a constant light intensity. A plot of product formation against time should be linear provided that the conversion is sufficiently low that the effective concentrations of nucleophile and excited aromatic component are constant. This will be so if the nucleophile is in large excess of that required for the conversion involved, and if sufficient aromatic component is present that almost all the light is absorbed by it at all times, even when there is some product in solution.

For the kinetic experiments the above conditions were fulfilled. The lamp intensity was assumed to be constant, despite the results of Albone[91] who shewed that considerable variations may occur over short periods. However, over longer periods, and particularly after the initial period in which the lamp warms up, these variations are much less, and were minimized by using the same lamp for the whole series of experiments and by switching on the lamp about 30 min. before the beginning of a run. The samples were removed by means

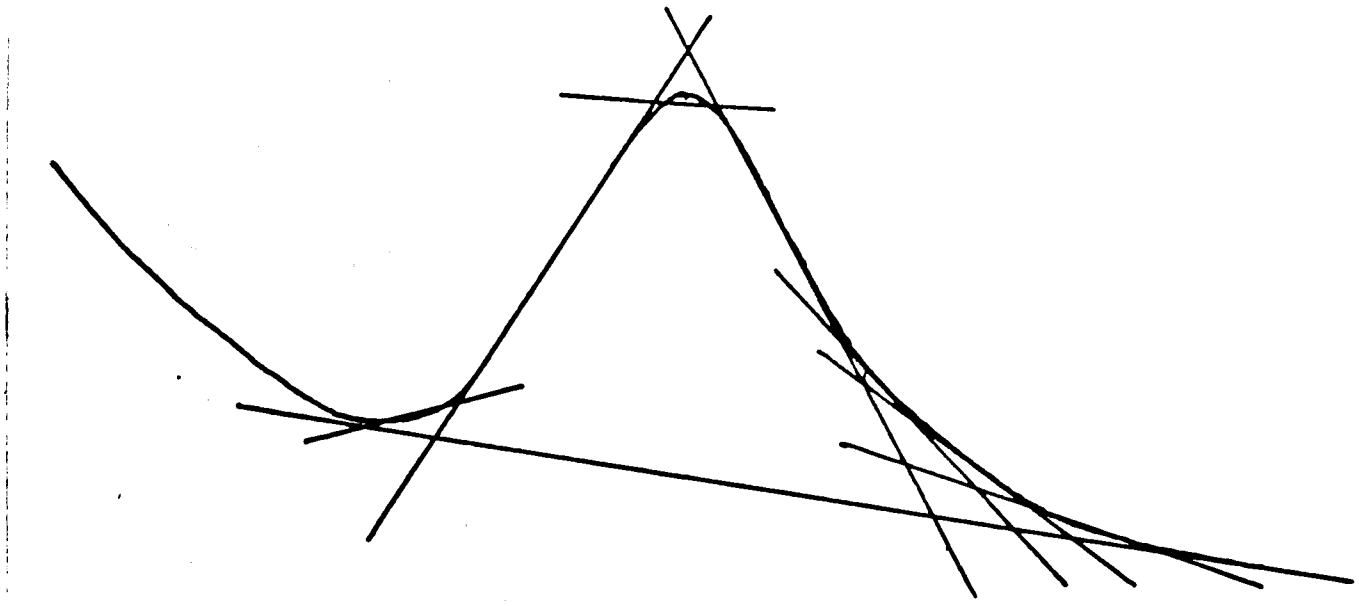


Fig. 1: Measurement by Triangulation of an Unsymmetrical Curve

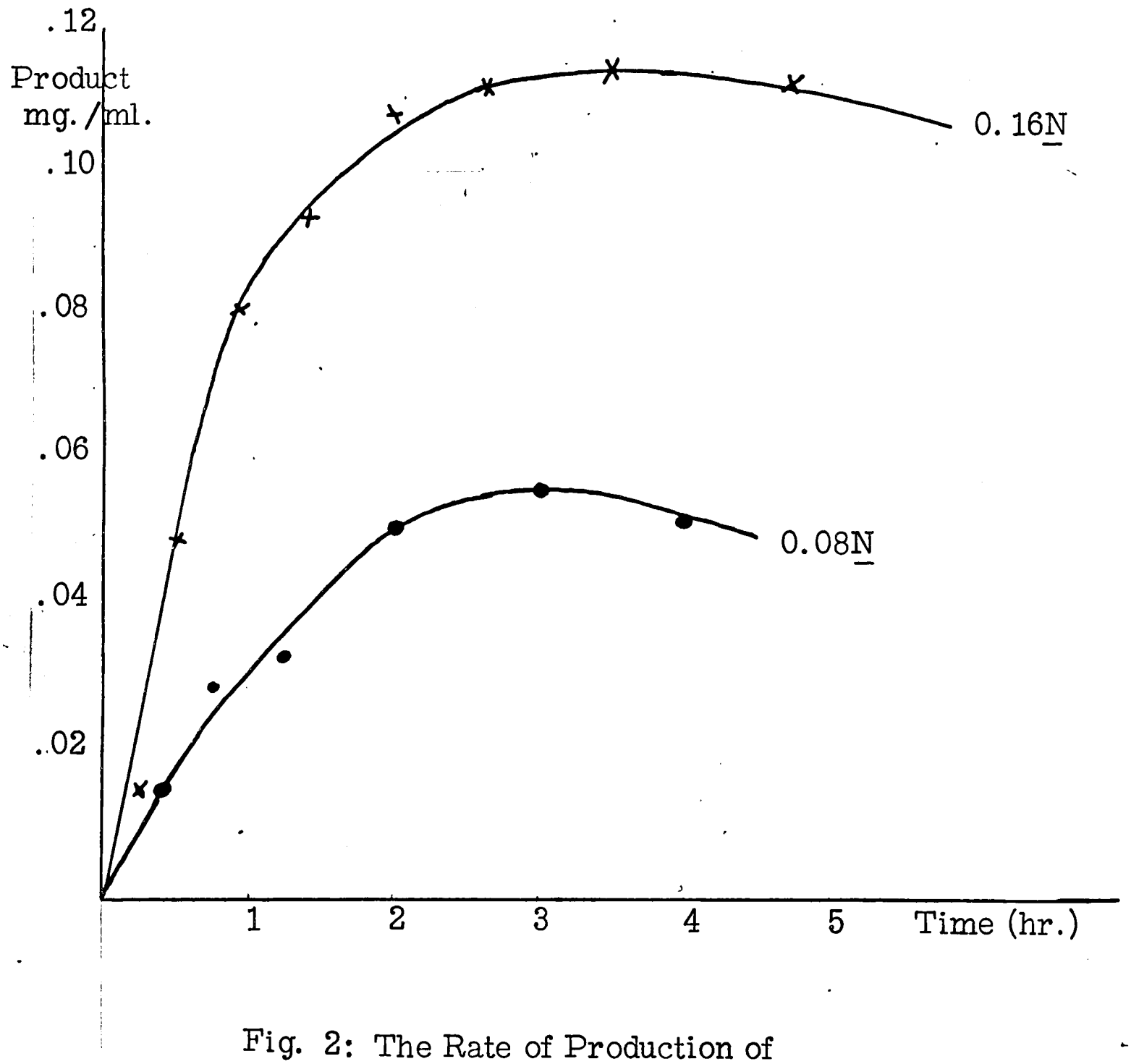



Fig. 2: The Rate of Production of Diethylaniline from Fluorobenzene

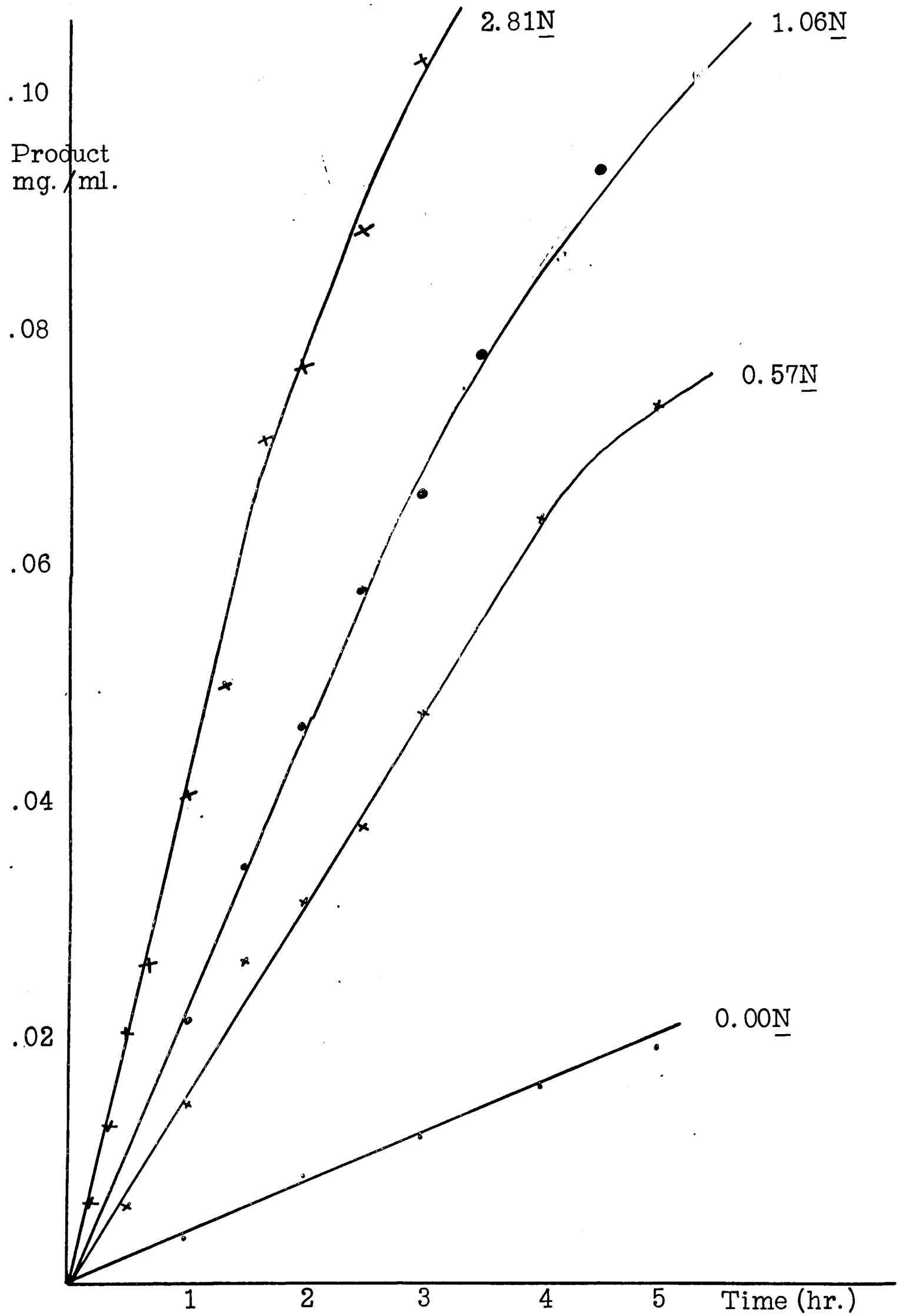



Fig. 3: The Rate of Production of Phenetole from Fluorobenzene at various concentrations of Ethoxide Ion

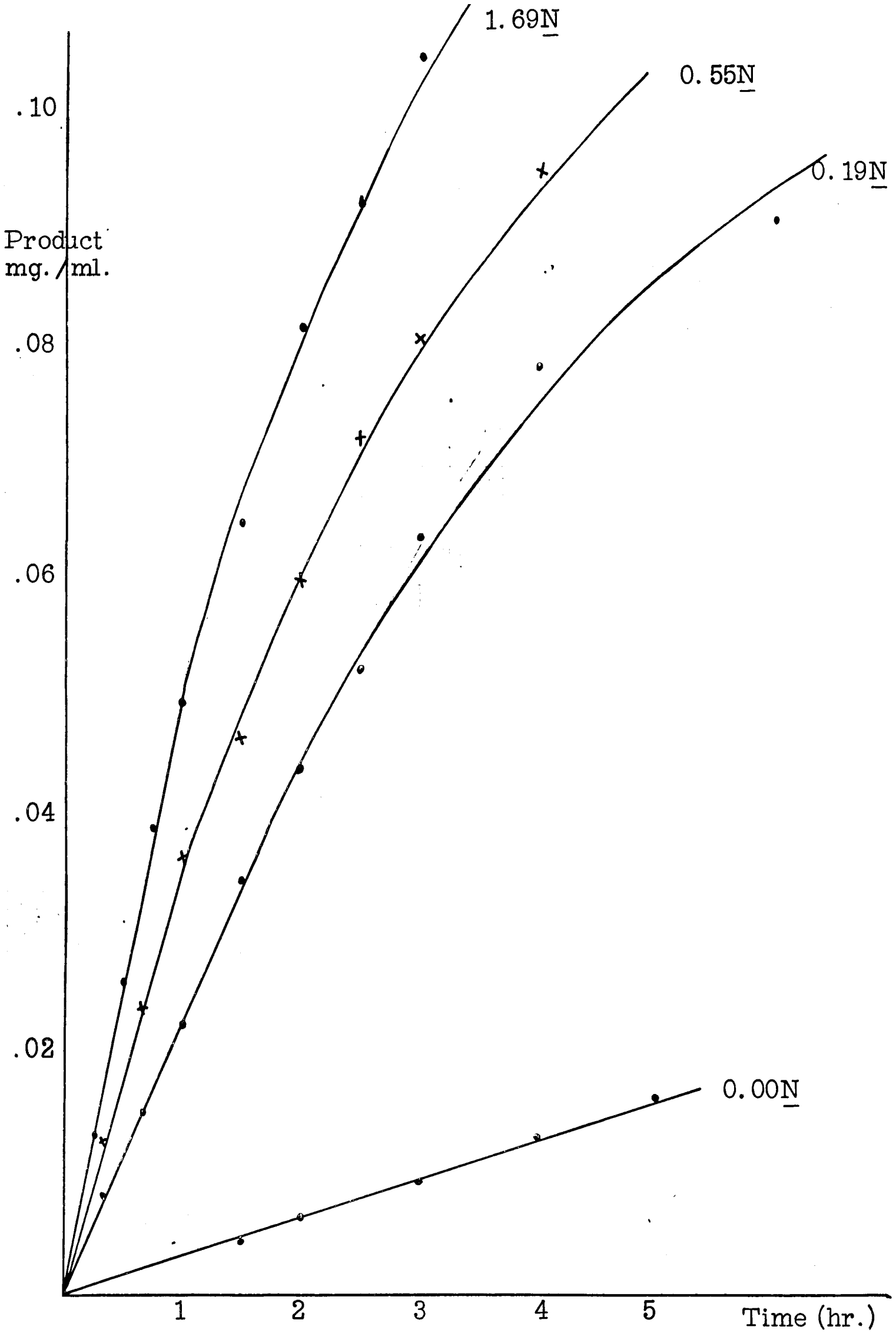



Fig. 4: The Rate of Production of Anisole from Fluorobenzene at various concentrations of Methoxide Ion

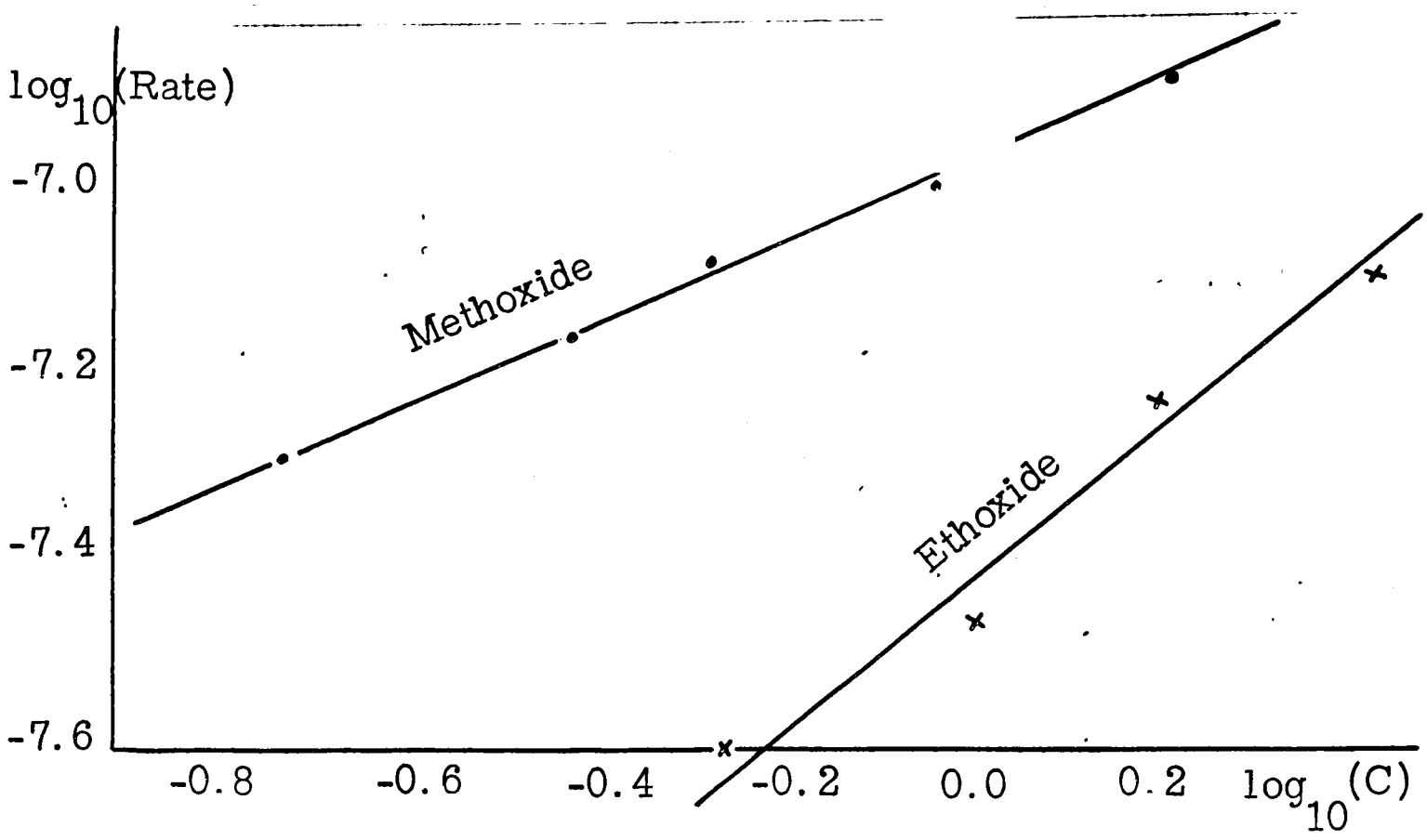



Fig. 5: $\log_{10}$(Rate) vs. $\log_{10}$(Concentration)

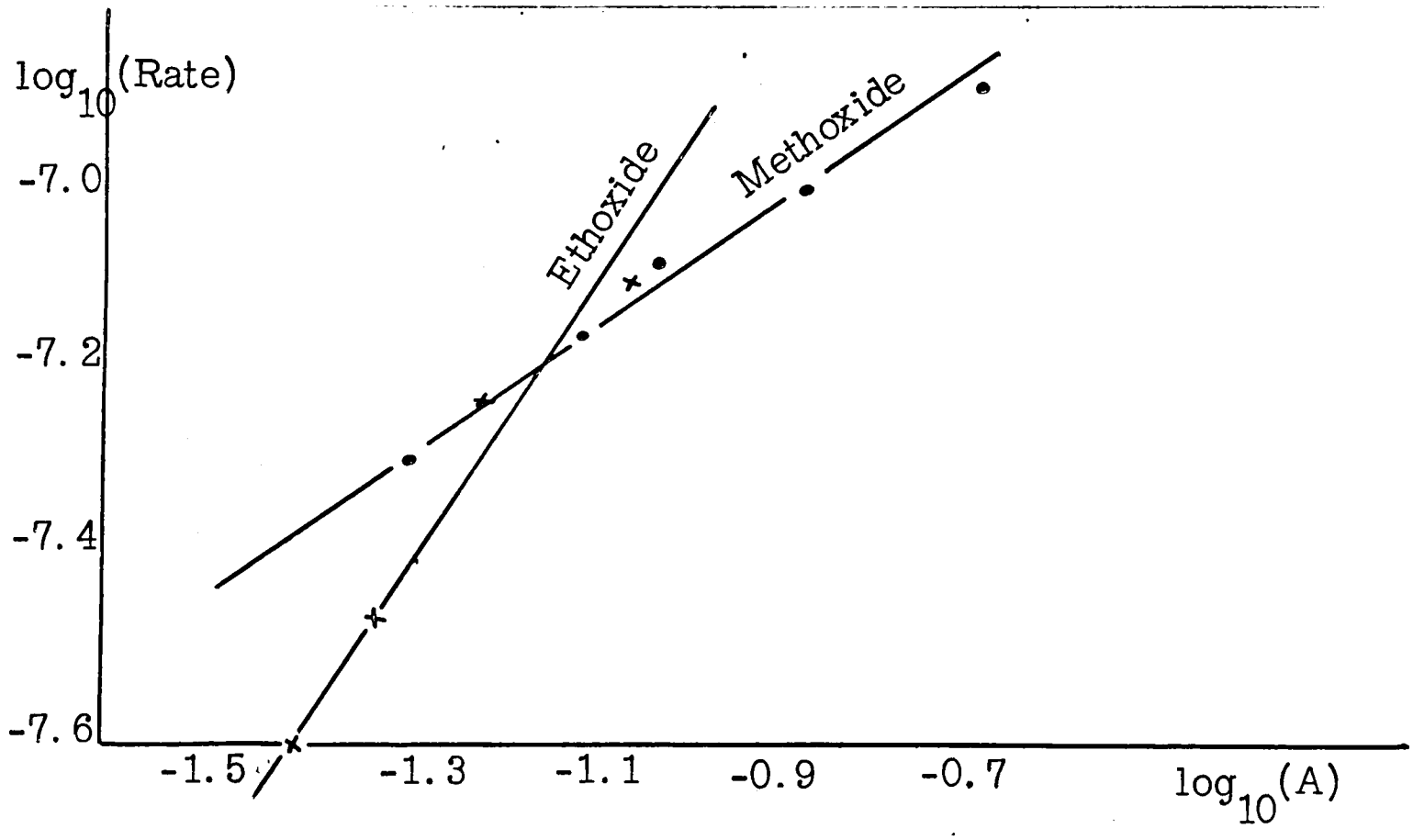



Fig. 6: $\log_{10}$(Rate) vs. $\log_{10}$(Activity)

of a syringe without interrupting the photolysis, and were analysed by g.l.c. The peaks on the g.l.c. traces were measured by cutting them out from the trace and weighing them. Triangulation was also used, but since the results obtained for sample traces varied by less than 2% between the two methods, the less time-consuming procedure was adopted. Because of the unsymmetrical curves obtained (See Fig. 1) the only successful but laborious method of triangulation was to draw several small triangles and measure the areas of these individually. As the method of estimating the product by g.l.c. is inherently somewhat inaccurate, it was felt justified to ignore the variations in lamp output and not to monitor this quantity.

The results of these experiments shewed that the quantity of product formed indeed varied directly with time, at least in the early stages of a run. Later, the rate fell on account of polymer formation on the reactor walls reducing the effective light intensity (See Figs. 2-4).

The slopes of the curves (reaction rates) obtained and the respective nucleophile concentrations were plotted logarithmically against each other (See Appendix 2). The slope of the line obtained should give the order of the reaction with respect to the nucleophile. (It is assumed that the reaction is first order in excited aromatic

component.) The plots for fluorobenzene in both methoxide ion and ethoxide ion had slopes much less than unity, the expected order (See Fig. 5). A corrected plot (Fig. 6) was made using nucleophile activities rather than concentrations, to allow for the strongly ionic solutions used. The relationship used was[92]

$$\log_{10}\gamma_{\pm} = \frac{-A\sqrt{C}}{1+\sqrt{C}} + \frac{C}{10}$$

where 'C' is the concentration of nucleophile and 'A' is a constant

$$\frac{1.83 \times 10^{6}}{(DT)^{3/2}}$$

which was evaluated using T = 300° and D = 25 for ethanol and 33 for methanol.[93] The calculations are reproduced in the Appendix 2. The best fit to the logarithmic plot was found using a computer programme to carry out a least squares analysis.[94]

Even using this correction and after allowing for the small amount of product formed in the alcohol alone, the slope of the graph is still not unity.

The reason seems to be twofold; firstly, it is difficult to calculate activities in non-aqueous solutions as little data is available, and secondly, the solutions are far too concentrated for such calculations to be reliable. In all probability most of the ions are present as ion

pairs and even greater aggregates, so that the addition of a particular quantity of alkoxide ion to a solution adds less than this quantity of free alkoxide ion, and the contribution from the aggregates to the reaction rate is unknown. The difficulty cannot be overcome by using more dilute solutions, for the reaction is so slow and inefficient that the formation of the product would be too small to detect reliably.

Consequently, it must be admitted that the results obtained from this study are less informative than one had hoped. The rate of formation of product indeed increases at greater concentrations of nucleophile, but the order of the reaction cannot be obtained from the available data. That there is less free alkoxide ion present than titration would indicate, suggests that the order may well be unity, but this argument is not conclusive. It is therefore doubly unfortunate that the experiments with amines were so difficult to analyse. Furthermore, there are no reports available concerning the variation of apparent reaction order with nucleophile concentration at such high concentrations (up to 3N).

The results obtained from the kinetic analysis give the order of the photosubstitution reactions, but not their molecularities, because the order is the total of the component orders of the reaction both in free alkoxide ion and in the aggregated species. In Table 3 the

results are summarised; the errors quoted are those obtained from the computed least squares analysis, and are thus the error in the fit of the curve to the points rather than the measuring error. This latter error, the error in estimating the product at any time, is of the order of 14% as calculated in Appendix 2.

Table 3

Order of the photonucleophilic substitution with respect to added nucleophile

| Alkoxide | Order calculated on Molarity | Order calculated on Activity |
|---|---|---|
| Methoxide | 0.42 ± 0.01 | 0.55 ± 0.06 |
| Ethoxide | 0.76 ± 0.02 | 1.30 ± 0.10 |

It was found that the ratio of the reaction rate in 1M alkoxide solution to that in the pure alcohol was, for methoxide 12.6 : 1, and for ethoxide 4.3 : 1.

* * * * *

A brief study of the photonucleophilic substitution in the naphthalene series was now made. The reaction mixtures obtained proved far more intractable than those encountered in the benzene series. This was because unstable compounds were isolated from

the reaction mixtures in a state of greater or lesser purity, but they tended to decompose before satisfactory physical data could be obtained.

The study was limited to the isomeric monofluoro- and monomethoxy-naphthalenes. In connexion with the preparation of the former, it was found that the initial diazotisation to form the fluoroborate salt was very unsatisfactory when a temperature of 0 - 5° was used. The diazonium salt had largely decomposed by the time that all the sodium nitrite solution had been added, and on addition of fluoroboric acid, only a black tar was obtained. It was found that the fluoroborate salt could be isolated in good yield, when the diazotisation was carried out at a lower temperature. The amine hydrochloride was cooled to about -40°, when it became a thick paste, and a strong aqueous solution of sodium nitrite cooled to -5° was added in one portion, with swirling of the flask. Diazotisation occurred rapidly and completely, and the fluoroboric acid solution was added at once, again with swirling and in one portion. This technique was subsequently used for all other diazotisations, and was found to be rapid and effective.

The intractability of the reaction mixtures in this series was particularly noted in the case of 1-naphthyl methyl ether. In

irradiation in piperidine gave, after separation into basic and non-basic material, 1-naphthol from the non-basic fraction. However, the basic fraction on chromatography yielded 1-naphthyl methyl ether, suggesting an unstable addition compound which decomposes in contact with silica gel. This was confirmed by the isolation of two very unstable compounds, which were not identical, but which both contained on i-r and n. m. r. evidence hydroxyl and piperidyl residues. Complete structures could not be assigned to them. Repetition of the irradiation in diethylamine solution was no more successful. Attempts to trap these intermediates by bromination or hydrogenation of the reaction mixtures also failed. Under various conditions, using severally shorter irradiation times, deoxygenated solutions and aqueous diethylamine as solvent, only 1-naphthyl methyl ether was obtained, once more from the basic material.

The mixtures obtained on irradiation of 2-naphthyl methyl ether were again intractable under most conditions. However, when a deoxygenated solution in aqueous diethylamine was irradiated, there was isolated the substituted product, N, N-diethyl-2-naphthylamine, whose structure was deduced from the n. m. r. spectrum, and which had physical data identical to those

of an authentic sample prepared by the action of ethyl iodide upon 2-naphthylamine. Once again, the existence of an unstable addition compound was inferred, for some 2-naphthyl methyl ether was retrieved from the basic material.

The irradiation of more concentrated solutions of 2-naphthyl methyl ether allowed the isolation of a very insoluble crystalline solid. This had properties similar to those reported by Hammond for the dimer [95] of 2-naphthyl methyl ether.

In the case of the fluoronaphthalenes by contrast, substitution proceeded smoothly and the yields, 6 to 9%, were comparable with those observed in the benzene series. The neutral material, however, did not contain significant quantities of the starting material according to t.l.c. analysis, but rather was a mixture of several components.

For 1-fluoronaphthalene there was one major component. Distillation of the non-basic material gave a mixture which was shewn by g.l.c. to contain 1-fluoronaphthalene and one other compound. Distillation, chromatography, heat, and exposure to air caused 1-fluoronaphthalene to be produced to a greater or lesser extent. In view of the reports of the recently discovered valence tautomers of benzene, attempts were made to isolate the compound in a pure state to discover whether it might be a naphthalene analogue.

The substance was isolated in a reasonably pure state by preparative t.l.c. separation of the crude reaction mixture. Decomposition was slight when the operation was carried out rapidly and with minimum exposure to the air. In order to free the product from silica, extraction in a Soxhlet extractor was not possible, for thermal decomposition set in. The silica was therefore shaken several times with cold ether, filtered, and the solvent removed below 20°. T.l.c. indicated that the sample was pure. The mass spectrum, with a molecular ion at $m^+/e$ 146, confirmed that the compound was an isomer of 1-fluoronaphthalene, and the fragmentation pattern was different. Likewise, a different U.V. absorption was observed.

I-r spectrometry indicated an ortho disubstituted benzene, the typical naphthyl bands at 795, 765, and 710 cm.$^{-1}$ being replaced by absorptions at 770 and 700 cm.$^{-1}$ The n.m.r. spectrum was complicated by decomposition to 1-fluoronaphthalene; this was shewn by t.l.c. of the recovered sample. The spectrum was very simple; apart from aromatic protons, the only other resonances, singlets, were observed at $\tau$4.15 and $\tau$6.65, the ratios being 4.5 : 1 : 2. Since the molecular formula is $C_{10}H_7F$, the correct ratio should be 4 : 1 : 2, decomposition accounting for the discrepancy.

The "Dewar" naphthalene structures (xxiv) and (xxv) may be

ruled out as the vinyl hydrogen atoms should not occur as singlets. A "prismane" structure in the naphthalene series is not possible as the tetravalency of carbon would be violated. An alternative structure is the benzobenzvalene structure (xxvi), 2-fluoro-3,4-benz-tricyclo-(3,1,0,$0^{2,6}$)-hex-3-ene. Since the hydrogen atoms in the tricyclohexene ring are orthogonal, they do not split each other; two are equivalent. Thus this structure may fit the n.m.r. data.

Benzvalene (viii) has recently been isolated and its n.m.r. spectrum observed.[50] The olefinic protons at C(3) and C(4) occur at $\tau$4.05; the protons at C(1) and C(6) at $\tau$6.47, and C(2) and C(5) at $\tau$8.47. The former two bands are triplets, the latter is a quintuplet. Irradiation at 8.47 causes collapse of the 4.05 and 6.47 resonances to singlets. Thus the protons at C(2) and C(5) couple with both other types of proton. However, the small coupling constants (all less than 2 c/s) indicate that perhaps in the present case that the splitting of the bands may not have been resolved, for the singlets are rather broad. The downfield shift of the resonances may be due to the effect of the fluorine atom and to the fact that C(1) and C(6) lie, not in the plane of the benzene ring, but above and below it. The relative stability of the proposed benzbenzvalene is consistent with the slow reversion observed for benzvalene to benzene.

What is remarkable about this structure is the stability of the compound to nucleophilic solvents. The substance is formed in diethylamine, is stable to methanol, and is only slowly destroyed by 2N aqueous hydrochloric acid. By contrast, benzvalene is rapidly converted by acidified methanol to methoxybicyclohexenes. Perhaps the basic character of diethylamine explains its stability in this solvent.

Attempts to produce the benzbenzvalene in other solvents were unsuccessful. Only starting material was recovered from irradiations of 1-fluoronaphthalene in ether, isopropanol, or acetonitrile.

In the case of 2-fluoronaphthalene, unstable compounds were observed, and again one substance was predominant on t.l.c. However, even using the isolation procedure adopted for the corresponding 1-naphthyl system, extensive decomposition to 2-fluoronaphthalene had occurred before physical measurements on the product could be made and it is not possible to assign a structure to this compound.

# CHAPTER III

## Photonucleophilic Substitution in Disubstituted Benzenes

The first reports of photonucleophilic substitution in disubstituted benzenes concerned the photochemically assisted solvolyses of m- and p-nitrophenylphosphonates.[96] It was found that the meta isomer was photochemically more reactive and studies with $O^{18}$ shewed that at least part of the reaction proceeded by fission of the substituent from the ring[97] (C-O rather than O-P), (xxvii - xxviii). Extension of the reaction to m-nitroanisole gave substitution of the methoxyl by hydroxide ion to yield m-nitrophenol[98] as the product. Subsequently, other workers found that the methoxyl group was displaced also by cyanide ion.

Kinetic studies, and $O^{18}$ labelling indicated that the reaction with m-nitroanisole was a bimolecular process involving the excited aromatic molecule and the nucleophile, and probably proceeded through the sigma complex (xxix), followed by elimination of methoxide ion.[99] Gold and Rochester[100] have demonstrated the presence of such sigma complexes on irradiation of more highly substituted benzenes with nucleophilic reagents.

Extension of the work to cover p-nitroanisole[101] shewed that hydroxide ion once again caused replacement of the methoxyl group to

yield p-nitrophenol. (The reaction was slower than that of m-nitroanisole, and this was confirmed by the reaction of 3,4-dimethoxynitrobenzene (xxxi),[102] which underwent hydroxyl attack exclusively at the 3-position.) A byproduct of the reaction, 4-methoxyl-2-nitrophenol (xxxii), was explained as having arisen by nitrosation of initially formed p-methoxyphenol (xxxiii) and subsequent aerial oxidation.[103] This seems a little unlikely both because nitrosation does not usually occur in 0.1N alkali, and also because no p-methoxyphenol was detected in the reaction mixture.

Contrasting results were obtained by other workers.[104] p-Nitroanisole was found to give both p-nitrophenol and p-methoxyphenol in the ratio 18:82. The reaction of cyanide ion with p-nitroanisole afforded 2-cyano-4-nitroanisole (xxxiv), and this was explained as arising by way of the intermediate (xxxv).

It would seem that the intermediate (xxxv) does not lose hydride ion very easily for in addition to (xxxiv), the byproduct (xxvi), a substituted azoxybenzene is obtained, probably by disproportionation of (xxxv). In the presence of air or oxygen (xxxv) is oxidised up to (xxxiv) and the formation of the byproduct (xxxvi) is suppressed.

More conflicting evidence was found in the studies using amines as nucleophiles. Havinga and his coworkers found that aqueous methyl-

amine was capable of replacing the methoxyl group of m-nitroanisole to give N-methyl-m-nitroaniline (xxxvii).[97] A similar reaction was observed with p-nitroanisole,[103] although, unlike the situation with hydroxide ion as nucleophile, the rate of substitution was greater for the p- isomer. Once again, illumination with methylamine of 3, 4-dimethoxynitrobenzene (xxxi) demonstrated the point,[102] for the ratio of m- : p-substitution was 1:8.

However, studies by Letsinger and his coworkers again gave a different view. Using pyridines as their amine nucleophiles, they found that both for p-nitrophenyl phosphonate and p-nitroanisole,[104] substitution at the nitro-substituted carbon atom was preferred. No substitution at the alternative position took place.

A similar study by Johnson and Rees[105] who irradiated 4-nitropyridine-N-oxide (xxxviii), which is iso-electronic with p-nitroanisole, with piperidine also led to replacement of the nitro group.

Unlike m-nitroanisole, m-nitrobromobenzene was found to be photochemically inactive to hydroxide ion.[106] By contrast, bromide ion was expelled from 3-bromopyridine in good yield, although 3-methoxypyridine was unreactive. On the other hand, the action of hydroxide ion on 3-bromo-4-methoxy-nitrobenzene (xxxix), led to the formation of 3-hydroxy-4-methoxynitrobenzene (xl),[107] as well as

some 3-bromo-4-hydroxynitrobenzene (xli). Aqueous methylamine as expected led exclusively to the production of 2-bromo-4-nitro-N-methylaniline (xlii).

The present author's interest in disubstituted benzenes arose as an extension of the work described in the previous chapter. Clearly, these apparently conflicting reports of the photochemical substitutions of the compounds described must depend upon electronic factors in the excited state. The approach of Zimmermann to explain the greater activity towards nucleophilic solvolysis of the acetoxy group of m-methoxybenzyl acetate (xliii), compared with the p-isomer, [69] uses a zero-order H.M.O. calculation. This shews that an incipient benzyl cation is stabilized more when a meta methoxy group is present than when the group is absent or para. A similar rationalization in terms of charge density distribution was used in the preceding chapter to explain the reactivity of excited anisole towards nucleophilic reagents.

It therefore seemed appropriate to calculate the excited state charge densities for a variety of disubstituted benzenes, divided into three classes, viz.:

(i) Two electron donating groups,
(ii) Two electron withdrawing groups,
(iii) One donating and one withdrawing group.

Experimentally it is important, if substituent effects are to be studied, that only one group be photolabile. From the information gained in the monosubstituted benzene series it was decided to prepare disubstituted benzenes in which one group was photoreactive, and the other photostable in the presence of nucleophilic reagents.

Thus for p-fluoroaniline, for example, the fluorine may be replaced but the amino group is stable. The only possible substitution product, e.g. with hydroxide ion, would be p-hydroxyaniline.

Suitable photostable electron donating groups are hydroxyl, amino, and dialkylamino: withdrawing groups are nitrile and carboxylate anion. Of these, hydroxyl must be excluded because the excited states of phenols are strong acids, [108] and the production of a negatively charged phenolate anion would repel a nucleophilic reagent. This argument does not apply with such force to the use of the carboxylate anion as a substituent, as the charge cannot in this case be delocalized into the ring.

The results of the calculations are presented in Appendix 1. It was suggested that photo-nucleophilic substitution in the monosubstituted benzene series occurred when a partial positive charge developed on the carbon atom to which the substituent was attached, in the excited $(\pi,\pi^*)$ state of the substrate. These conditions are fulfilled for all isomers in classes (i) and (iii) but for none of the isomers in class (ii).

Experiments were carried out using the following series of compounds:

| | | |
|---|---|---|
| (a) | the anisidines | - class (i) |
| (b) | the fluoroanilines | - class (i) |
| (c) | the nitrobenzonitriles | - class (ii) |
| (d) | the nitrobenzoates | - class (ii) |
| (e) | the fluorobenzonitriles | - class (iii) |
| (f) | the methoxybenzonitriles | - class (iii) |

Although a large number of irradiations was carried out, using a wide variety of experimental conditions, in no case did substitution occur to an extent sufficient to allow any product to be isolated. The reasons for the lack of photochemical activity of these compounds are unknown.

It was therefore not possible to test the predictions of simple H.M.O. theory concerning the relative ease of photochemical substitution of disubstituted benzenes, or to formulate substitution rules.

However, it is of interest that the calculations confirm the results of other workers in the nitroanisole series. p-Nitroanisole is predicted by calculation to undergo photo-nucleophilic substitution of both the methoxyl and the nitro group, for at the carbon attached to each group a partial positive charge develops in the excited state. For m-nitroanisole, by the same criterion, only the methoxyl group would be expected to be photolabile.

# CHAPTER IV

## The Photochemical Reduction of Nitrocompounds

### Introduction

Although in the early days of organic photochemistry around the turn of the century there were several reported observations of the photochemistry of nitrocompounds, in particular of aromatic nitrocompounds and their photo-induced rearrangement reactions, interest in this field has only recently revived. However, a large number of papers has lately appeared on this subject and on related systems containing linked nitrogen and oxygen atoms.

It was early demonstrated that on ultraviolet irradiation nitrogen dioxide fissions into nitric oxide and an oxygen atom.[109] In aliphatic nitrocompounds, by contrast, ultraviolet light causes rupture of the C-N bond; for example, nitromethane gives initially nitrogen dioxide and a methyl radical. Then nitrogen dioxide recombines with the methyl radical to form the isomeric alkyl nitrite.[110] Alkyl nitrites are themselves subject to photolysis and may split up into an alkoxy radical and nitric oxide. The "Barton" reaction applies this phenomenon to the introduction of functionality into the angular methyl positions of the steroid series[111] (xliv, xlv). Simple alkyl nitrites also undergo this kind of photolysis, the alkoxy radical

attacking the solvent:

$$RONO \longrightarrow RO^{\cdot} + NO \xrightarrow{R'H} R.OH + R'.NO$$

Unsaturated aliphatic nitrocompounds may react similarly; for example, irradiation of 1-phenyl-2-nitroprop-1-ene (xlvi) yields 1-phenylpropan-1, 2-dione-1-oxime (xlvii).[112]

The nitrocompound to nitrite ester rearrangement has also been suggested as the pathway involved in the photochemical transformations of certain aromatic nitrocompounds. The rearrangement is favoured by the presence of ortho methyl groups or peri hydrogen atoms near the nitrogroup,[113] exemplified by the behaviour of 2, 3-dimethyl-1-nitro-naphthalene and 9-nitroanthracene[113, 114] and suggesting a steric requirement for the nitrogroup. The formation of anthraquinone in the reaction was formerly thought to proceed by way of peroxidation and the intermediate (xlviii).[115] The fact that oxygen is not required to be present has led to the postulation of a nitrite ester rearrangement, the observed products, anthraquinone (xlix) and 10, 10'-bianthronyl (l), being formed from the intermediate anthronyl radical (li). Support for this mechanism comes from the observation that the yield of anthraquinone increases at the expense of bianthronyl when nitric oxide is bubbled through the solution during the irradiation

A similar pathway is suggested for the transformation of sodium

9-anthroate (lii) first to sodium 9-anthranolate (liii), and then in the presence of air to anthraquinone and bianthronyl.[116] A byproduct in the reaction is anthracene, the decarboxylation possibly representing the first stage in the analogue of the nitrocompound to nitrite ester rearrangement. It has also been suggested that in the latter reaction the nitrogen dioxide may never become free but that there may be an oxazirane intermediate (liv), or in the case of sodium anthroate (lv).

A similar mechanism may be invoked to account for the transformation of nitrobenzene in benzene solution to a mixture of nitrosobenzene and p-nitrophenol.[117] Some support for this mechanism is to be found in the interpretation of Shelegova,[118] that the continuum observed in the gas-phase electronic spectrum of nitrobenzene represents fission of the C-N bond to give nitrogen dioxide and a phenyl radical. On the other hand the observed products could also arise by an initial rupture of the N-O bond, giving nitrosobenzene and an oxygen atom, which inserts into another molecule of nitrobenzene. This mechanism is easier to reconcile with the observation that irradiation of nitrobenzene in the presence of aniline[117] gives nitrosobenzene and p-aminophenol.[119] This supports the hypothesis of Kögel that the continuum in the ultraviolet spectrum of o-nitrobenzaldehyde in the gas-phase is caused by fission of the N-O bond.

The failure to observe nitrogen dioxide in the irradiation of nitrobenzene vapour (when the products were nitrosobenzene and p-nitrophenol)[120] has led Hastings and Metsen to the conclusion that free nitrogen dioxide is not produced. This would indicate, therefore, either the oxaziranе or oxygen atoms as the possible intermediates.

Most photoreactions of nitrocompounds in the absence of other reagents tend to be rather slow and consequently, when suitable substances are present the above mentioned reactions are not normally observed. For example, in the presence of olefins, β-nitrostyrene (lvi) undergoes not a nitrite ester rearrangement, but gives a cycloaddition product (lvii)[114] in a manner reminiscent of the photoreactions of unsaturated carbonyl compounds.[121]

With aromatic nitrocompounds, however, addition to the nitrogroup is thought to be the primary process,[122] followed by breakdown of the intermediate (lviii) to give acetanilide and the heterocyclic compound (lix). An intramolecular example of this reaction is the transformation of the p-chlorophenylanil of 2-nitro-2'-formylbiphenyl (lx), which yields phenanthridone (lxi) and p-chloronitrosobenzene.[123]

Nitrobenzene also adds photochemically to diphenyl acetylene, but here the reaction takes a different course, diphenylketene (lxii) being suggested as an intermediate.[124]

$$PhNO_2 + Ph.C:C.Ph \xrightarrow{h\nu} PhNO + Ph_2C:C:O \xrightarrow{ROH} Ph_2CH.CO_2R$$

(lxii)

The rearrangement reactions of ortho substituted nitrobenzenes have been known for over sixty years. The transformation of o-nitrobenzaldehyde to o-nitrosobenzoic acid was the first such to be studied [125] and it was observed [126] that the rearrangement requires a benzylic hydrogen atom to be situated ortho to a nitrogroup (lxiii). A recent development has been an attempt to utilize this transformation as the basis for a photosensitive protecting group. [127]

The mechanism of the oxygen-transfer rearrangement has been the subject of considerable discussion. The view that the reaction involves the intermediacy of free atomic oxygen (as in the interpretation of the electronic spectrum of o-nitrobenzaldehyde [119]) has been refuted [120] on the grounds that free oxygen should be capable of detection and that m- and p-nitrobenzaldehyde should also react, neither of which is the case. Furthermore, the rearrangement of o-nitrobenzaldehyde takes place at wavelengths corresponding to energy less than sufficient to rupture the N-O bond. The reaction is therefore presumed to be concerted, and this view is consistent with the observation [121] that o-nitrotoluene rearranges to o-nitrosobenzyl alcohol by way of the singlet, rather than the triplet excited state.

Photochromism[20, 130] is the production, on irradiation, of a coloured species which reverts to the starting material, when the source of irradiation is extinguished. It is observed in certain nitro-compounds, the first such example recorded being in crystalline 2-(2', 4'-dinitrobenzyl)-pyridine[131] (lxiv), and has since been observed in solution. It was originally thought that the photochromic intermediate was a form (lxv) in which the pyridine nitrogen atom had accepted a proton from the benzyl group. In view of the fact that 4-(2', 4'-dinitrobenzyl)-pyridine (lxvi) gives rise to a photochromic intermediate which decays to the starting material in a process of first order kinetics, the intermediate cannot be (lxvii), for an intra-molecular hydrogen transfer is not possible and second order kinetics for such a process should be observed. Accordingly the aci-nitro form (lxviii) has been proposed[132] as the photochromic state.

This concept is supported by the fact that the pyridyl ring is not an essential requirement for photochromic activity, the necessary conditions being that there should be a nitrogroup ortho to a benzylic hydrogen atom.[133-135] Another electron-withdrawing group para to the benzyl position favours photochromism, perhaps by rendering the benzyl hydrogen atoms more acidic. For example, the cyano[136] and azoxyphenyl[137] groups may replace the 4'-nitrogroup in structure

(lxiv).

The large negative entropy of activation for the reaction (lxviii - lxiv)[134] indicates that the activated complex must be a very rigid structure, favouring a unimolecular reaction from (lxviii).[139] Morrison has shown that irradiation of o-nitrotoluene in deuterium oxide leads to incorporation of deuterium in the methyl group.

Furthermore, the photochromic intermediate may sometimes be produced chemically; careful neutralization of the anion produced by the action of base on (lxvi) gives a species with an ultraviolet spectrum almost identical with that of the photochromic state, and which decays with the same first order rate constant.[136, 139, 140]

Very recently it has been demonstrated that photochromism is displayed by α-(p-nitrophenyl)-o-toluic acid (lxix). Although the proton is transferred to the carboxylate group ortho to the benzyl group (lxx), it being iso-electronic with a nitro group, the negative charge is delocalised over the p-nitrophenyl group.

Of particular interest is the fact that both the ortho rearrangement (oxygen-transfer) and photochromism have the same structural requirement, viz. a nitrogroup ortho to a benzylic hydrogen atom. Yet, apparently they are unrelated reactions; the oxygen-transfer reaction does not proceed by way of the photochromic intermediate;

indeed, the sole reported reaction of the latter is reversion to the colourless form. No explanation of the relation, if any, between these reactions has yet appeared.

It seems probable, however, that both reactions are concerted and proceed by way of cyclic transition states, probably six membered in each case, especially if the ortho rearrangement involves hydrogen abstraction followed by radical recombination.[141] A recent communication, exceptionally, implies a seven membered transition state; irradiation of N-methyl-2, 6-dinitro-4-(α,α,α-trifluoromethyl)-aniline (lxxi) yields 2-nitro-6-nitroso-4-(α,α,α-trifluoromethyl)-aniline (lxxii), presumably by the loss of formaldehyde from intermediate (lxxiii).[142] Steric crowding around C(1) may be important here, for the analogous reaction of o-nitroanisole is a factor of at least $10^2$ slower.

The substitution reactions of nitro-substituted benzenoid compounds have been investigated recently, but will not be discussed here as an account of them is given in Chapter III.

A few reports of the photochemical reduction of nitro-aromatic compounds have recently been published. In isopropanol, nitrobenzene undergoes reduction to a species having an electronic absorption spectrum similar to that of phenylhydroxylamine;[143] an analogous

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observation has been made for 4-nitropyridine-N-oxide (xxxviii). These communications appeared about the time of the present author's interest in the photochemistry of nitrocompounds. This stemmed from the observation that, during the investigation of the photonucleophilic substitution reactions of monosubstituted benzenes, described in Chapter II, it was found that photolysis of nitrobenzene in diethylamine caused not replacement of the substituent to give N,N-diethylaniline as is commonly observed in these systems, but reduction to aniline. Present in the reaction mixture was a small quantity of 2-hydroxyazobenzene, a known photolysis product of

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azoxybenzene, and this correlates with an earlier report that 1, 3, 5-trinitrobenzene is reduced photochemically by ethanol to 3, 3', 5, 5'-tetranitroazoxybenzene (lxxiii). It seemed appropriate to follow up these observations with a view to determining the scope and the mechanism of the reaction.

## Discussion

A first experiment repeated the irradiation of nitrobenzene in diethylamine, only at a lower concentration of nitrobenzene. The coupled product, 2-hydroxyazobenzene, was not observed. Repetition of the experiment using a Pyrex filter led to almost complete suppression of aniline formation, and moderate yields of azobenzene and 2-hydroxyazobenzene were isolated. Since the wavelength of the exciting radiation caused different products to be formed, other nitrocompounds were irradiated in quartz ($\lambda$>215 m$\mu$) and Pyrex ($\lambda$ > 280 m$\mu$) equipment. The results of the study, given in Table 4, show that the short wavelength light causes predominantly complete reduction to the aniline, whereas using filtered light, the formation of bimolecular species as major products is induced.

Other nitrocompounds, bearing a range of substituents, were irradiated in Pyrex equipment, to determine whether reduction is a phenomenon general to aromatic nitrocompounds. That this is the case is shown by reference to Table 5, where it is seen that, although the product distribution varies considerably, all the nitrocompounds so far studied undergo reduction. The differences in product distribution seem to depend upon the substituents in a way that is not immediately apparent, and in some cases no coupled products are

Table 4

The Wavelength Dependence of the Products of the Photoreduction of Nitrocompounds in Diethylamine

| Substrate | Concentration g. per 100 ml. | Time[a] hr. | ArNH$_2$ % | ArN:NAr % | ArN:N(O)Ar % | 2-Hydroxy-azocompound % |
|---|---|---|---|---|---|---|
| Nitrobenzene[b, d] | 0.50 | 5 | 37 | - | - | - |
| Nitrobenzene[b, d] | 5.0 | 19 | 40 | - | - | 4 |
| Nitrobenzene[c, d, f] | 0.50 | 5 | 6 | 20 | - | 31 |
| m-Nitroanisole[b, d] | 0.50 | 6 | 31 | - | - | -[g] |
| m-Nitroanisole[c, d] | 0.60 | 9 | 11 | 24 | - | 36[g] |
| p-Nitroanisole[b, d] | 0.60 | 6 | 40 | 9 | - | - |
| p-Nitroanisole[b, e] | 0.60 | 6 | 41 | 7 | - | - |
| p-Nitroanisole[c, d] | 0.60 | 6 | - | 72 | - | - |
| p-Nitroanisole[c, e] | 0.60 | 6 | - | 27 | 4[illegible] | - |

Notes:
(a) Conversion 100% except where stated,
(b) Wavelength $\lambda > 215$ mμ,
(c) Wavelength $\lambda > 290$ mμ,
(d) Not deoxygenated,
(e) Deoxygenated prior to irradiation: oxygen bubbled through solution after irradiation,
(f) Conversion 76%,
(g) Total of two isomers.

Table 5

The Products of U. V. Irradiation [a] of some Substituted Nitrobenzenes

| Substrate | Solvent | $ArNH_2$ % | ArN:NAr % | ArN:N(O)Ar. % | 2-Hydroxy-azocompound % |
|---|---|---|---|---|---|
| Nitrobenzene | Ether | 44 | - | - | - |
| Nitrobenzene | Diethylamine | 6 | 20 | - | 31 |
| p-Nitroanisole[c] | Ether | 30 | - | 12 | - |
| p-Nitroanisole[c] | Diethylamine | - | 72 | - | - |
| p-Nitroanisole[c] | Diethylamine | - | 27 | 4[illegible] | -[b] |
| m-Nitrobenzonitrile | Diethylamine | 26 | 19 | 35 | 11[b] |
| m-Nitroanisole | Diethylamine | 11 | 24 | -[b] | 36[b] |
| p-Nitrobiphenyl | Diethylamine | 1 | 1.2 | 67 | - |
| o-Nitrotoluene | Triethylamine | 32 | 2.5 | 5 | 10 |
| 2, 6-Dimethylnitrobenzene | Triethylamine | 43 | - | - | -[d] |
| o-Nitrobenzyl alcohol | Ether | - | - | - | - |
| o-Nitroaniline | Triethylamine | 22 | - | - | - |
| 1-Nitronaphthalene | Diethylamine | 23 | 1.2 | - | 7 |

For irradiation conditions see experimental section

Notes:
(a) Using Pyrex filter,
(b) Total of isomers,
(c) Deoxygenated,
(d) Sole product 2, 2'-azobenzoic acid (3[illegible]%).

formed even using filtered light. Some of these systems are discussed further below.

The next series of experiments concerned the variation of the photoreduction products with the solvent used for the experiment. All these irradiations involved nitrobenzene and were carried out in Pyrex equipment. The results are tabulated in Table 6, from an examination of which the following features emerge: firstly, efficient reduction requires a solvent bearing readily abstractable hydrogen atoms: neither tert.-butanol nor light petroleum led to more than traces of identifiable products; secondly, significant amounts of bimolecular coupled products are encountered only when a basic solvent is used. In particular, whereas in isopropanol only aniline is formed, a mixture of isopropanol and aqueous ammonia gives rise to azobenzene and 2-hydroxyazobenzene in addition to aniline. However, no reduction products could be isolated from an irradiation of nitrobenzene in aqueous ammonia alone.

The importance of the requirement for base to be present for the production of the coupled products was demonstrated in experiments using ether as solvent. When the ether had been dried over sodium, some coupled products were formed, presumably because sodium reacts with the small quantity of ethanol present in the ether to give

Table 6

Solvent Dependence of the Products of the Photoreduction of Nitrobenzene with light $\lambda > 290$ mμ

| Solvent | Time (hr.) | Conversion % | Aniline % | Azobenzene % | 2-Hydroxyazobenzene % |
|---|---|---|---|---|---|
| Petroleum | 5 | 26 | 4 | 2 | 2 |
| Toluene | 5 | 64 | 1 | - | - |
| Ether[a] | 5 | 74 | 45 | 2 | 1 |
| Ether | 5 | 72 | 44 | - | - |
| Isopropanol | 5 | 86 | 13 | - | - |
| Isopropanol | 3 | 60 | 19 | - | - |
| t-Butanol | 5 | 39 | - | - | - |
| 50% Toluene/t-Butanol | 5 | 25 | - | - | - |
| Diethylamine | 5 | 76 | 6 | 20 | 31 |
| Triethylamine | 5 | 97 | 14 | 12 | 5 |
| 33% Aqueous Diethylamine | 2 | 84 | 5 | 8 | 17 |
| 67% Aqueous Diethylamine | 2 | 94 | 21 | 1 | 2 |
| 50% Aqueous Isopropanol | 3 | 53 | 40 | - | - |
| 50% Ammonia/Isopropanol[b] | 2 | 59 | 16 | 4 | 7 |
| Ammonia[b,c] | 5 | 31 | - | - | - |

Notes:
(a) Dried over sodium,
(b) Ammonia: d = 0.88,
(c) Quantity of nitrobenzene = 0.15 g.; all other irradiations used 0.50 g.

sodium ethoxide, which catalyses the condensation. In undried or distilled ether, no coupled products were formed.

Regarding the mechanism of the photoreduction, it is possible that some of the coupled products could be intermediates in the production of aniline. Accordingly some of them were irradiated individually with the results shewn in Table 7. The azocompounds indeed gave aniline but both the rate of conversion and the yield of aniline were insufficient for the major pathway to aniline to be by way of the azocompound.

The photoreduction of azocompounds, first observed by [146] Blaisdell, who isolated anilines and hydrazocompounds, has been investigated by Pitts and his coworkers.[147] In the presence of cumene, the e.s.r. spectrum of the radical (lxxiv) formed by addition of a cumyl ($C_6H_5CMe_2$) radical to the N:N bond of azobenzene was observed; the final product was 1, 2-diphenyl-1-(1'-methyl-1'-phenyl)-ethyl-hydrazine (lxxv). Clearly then, the first stage of the photoreduction of azocompounds is hydrogen abstraction by the azo group; in this case from cumene to give a cumyl radical, which may add to another molecule of azobenzene.

A difficulty in interpretation concerns the formation of the azocompound in such high yields. Irradiation of the azoxycompound (except in the case of 4, 4'-azoxyanisole) leads to only traces of the

Table 7

U. V. Irradiation of some Reduction Products of Nitrobenzene in Diethylamine

| Substrate | Concentration g. per 100 ml. | Time hr. | Conversion % | Products | Yield % |
|---|---|---|---|---|---|
| Azobenzene | 5.0 | 24[a] | 36 | Aniline | 10 |
| p-Azoanisole | 0.25 | 3[a] | 42 | p-Anisidine | 6 |
| Azoxybenzene | 0.10 | ½[b] | 64 | Azobenzene | 1 |
| | | | | 2-Hydroxyazobenzene | 61 |
| p-Azoxyanisole | 0.13 | 2½[b] | 22 | p-Azoanisole | 94 |
| p-Azoxyanisole | 0.10 | 2½[a] | 64 | p-Anisidine | 4 |
| | | | | p-Azoanisole | 30 |

Notes: (a) Irradiated with light $\lambda > 215$ mμ,
(b) Irradiated with light $\lambda > 290$ mμ,

Yields are percentages based upon reactant consumed.
Solutions are not deoxygenated; volume of solution = 100 ml.

azocompound (See Chapter V). Either the azocompound must arise by means of a different coupling reaction:

( e.g. $ArNH_2 + ArNO \longrightarrow Ar.N:N.Ar$ )

or it is formed by the sensitized photoreduction of azoxybenzene, as suggested elsewhere.[143] This latter explanation seems more probable (See Chapter V).

The azoxycompounds gave as major products the corresponding 2-hydroxyazocompounds and thus these too cannot be important intermediates in the production of aniline. Exceptionally, 4, 4'-azoxyanisole in diethylamine gave, not 2-hydroxy-4, 4'-azoanisole, but was reduced to 4, 4'-azoanisole rather slowly, but in good yield.

It seems likely that the course of the photoreduction of nitrocompounds must involve an intermediate having the following properties:

(1) In the presence of base and oxygen it gives rise to the azoxycompound whence other coupled products may be derived.

(2) In the absence of base it is converted photochemically into the aniline. When unfiltered light is used, this reaction becomes faster so that it competes successfully with the rate of the coupling reaction even in basic solution.

These requirements suggest that the phenylhydroxylamine may be the postulated intermediate. In the presence of air some

nitrosocompound will be produced and this will couple, in basic solution, with more of the phenylhydroxylamine to give the azoxy-compound. If this is the case, then the photochemical reduction of nitrobenzene will be analogous to the thermal reduction where, in acid solution, the reaction proceeds down to aniline, whereas in basic solution the coupled products, azoxy-, azo-, or hydrazobenzene, are formed.

In order to determine whether an organic base is sufficiently strong to catalyse the condensation to the coupled products, phenyl-hydroxylamine was oxygenated for ½ hr. in solution in diethylamine; azoxybenzene (94%) was isolated from the reaction mixture. The condensation also occurs in the absence of base; oxygenation of an isopropanol solution of phenylhydroxylamine likewise gave a good yield of azoxybenzene.

Once azoxybenzene is present in the photolysis mixture, another photochemical act gives rise to 2-hydroxyazobenzene.

That phenylhydroxylamine is a possible intermediate in the production of aniline was confirmed by an irradiation of phenyl-hydroxylamine in the non-basic solvent, ether. The yield of aniline was 42%. A possible explanation of the variation in the yield of aniline from nitrobenzene according to the wavelength of the exciting

radiations is that the phenylhydroxylamine, $\lambda$max. 27 m$\mu$ absorbs very little of the light when the Pyrex glass filter is used. When a base is present, coupling is favoured, but in its absence a slow conversion to aniline occurs. When unfiltered light is used, the greater light absorption by the phenylhydroxylamine allows the reduction to aniline to compete successfully with coupling even in basic solution. This is confirmed by the results in Table 4, where it is seen that using unfiltered light, aniline is the major product of irradiation of nitrobenzene in diethylamine. Reduction of the concentration of nitrobenzene tenfold in this reaction leads to suppression of the formation of the byproduct, 2-hydroxynitrobenzene. This is considered to be a filter effect; the lower concentration of nitrobenzene allows relatively more light to be absorbed by the intermediates, so that photoreduction is preferred to coupling.

An alternative hypothesis is that the coupled products might arise by transformations of the nitrosocompound, rather than of the phenylhydroxylamine. It has been shown[149] that in the presence of benzylamine, nitrosobenzene reacts thermally to give azoxybenzene. In the presence of piperidine it was found that an exothermic reaction occurred, the products being nitrobenzene (6%) and azoxybenzene (5%), as well as a number of unidentified byproducts, all in low

yield. Thus in basic solution it is not impossible that the nitroso-compound might provide the route to the coupled products.

By contrast, it seems unlikely that nitrosobenzene is an important intermediate in the production of aniline in non-basic media. Although irradiation of nitrobenzene in ether using a Pyrex filter gives aniline and no azoxybenzene, a similar irradiation of nitrosobenzene gives azoxybenzene (2%) but no aniline. A mixture of about ten compounds, all in very low yield, was found instead in the basic material. Although these were not isolated, it is probable that they were the mixture of diphenylamines observed by other workers.[150] Diphenylamines probably arise from nitrosobenzene photochemically by the reduction of diphenylnitroxide, $(C_6H_5)_2NO$, which has been observed by e. s. r. when solutions of nitrosobenzene are photolysed.[151, 152]

The possibility that nitrosobenzene, once formed, reacts rapidly by absorption of light in the visible region through its long wavelength absorption band, was eliminated by an irradiation of nitrosobenzene in ether using a 100 watt tungsten lamp as the light source. The reaction was extremely slow, and once again no aniline was formed. The products were those obtained in the corresponding ultraviolet irradiation, mainly azoxybenzene, (45%).

There exists also the possibility that nitrosobenzene never attains a detectable concentration in the solution. This might be because sensitization by nitrobenzene causes it to be rapidly converted to other products. Accordingly, low ($10^{-4}$ M) concentrations of nitrosobenzene were irradiated in ethereal solution, but both t.l.c. and g.l.c. analysis failed to detect aniline. Indeed, undeoxygenated solutions were photo-oxidized to nitrobenzene. Little success was achieved using benzene as a sensitizer; the only product of nitrosobenzene (apart from nitrobenzene) observed was azoxybenzene. It may be that in the solution of nitrosobenzene, the dimeric form is preferentially removed to give either azoxybenzene or diphenyl nitroxide, and that the reduction of nitrosobenzene monomer is never observed. This postulate seems unlikely, as in a solution of $10^{-4}$ M there must be a fair proportion of monomer.

The possibility that the nitrosocompound is destroyed by photo-sensitization by the nitrocompound was further excluded by an irradiation in ether of o-nitrobenzyl alcohol. This compound is known to undergo an oxygen transfer reaction to o-nitrosobenzaldehyde. However, no aromatic amine at all was recovered from the reaction mixture; the sole product isolated was the further trans-

formation product of the nitrosocompound, 2, 2'-azobenzoic acid.[153]

Thus, it is clear that in the photoreduction of nitrobenzene, at least in non-basic media, nitrosobenzene if it is present in the reaction mixture is removed neither by direct nor by photosensitized photochemical steps.[154] One possibility remains: Metcalf, by electrochemical reduction of nitrobenzene, has obtained the nitrobenzene radical anion, which is found to be a strong reducing agent. The radical anion is at the same oxidation level as the species $C_6H_5\dot{N}O_2H$, which is believed to be the first intermediate in the photochemical reduction (See below). This radical will abstract a hydrogen atom, giving $C_6H_5N(OH)_2$, the hydrated form of nitrosobenzene. If nitrosobenzene is now reduced by more of the radical $C_6H_5\dot{N}O_2H$ (or its corresponding anion in basic solution) then reduction will occur rather than the photochemical transformation to azoxybenzene. It is in this manner that nitrosobenzene may act as an intermediate in the formation of aniline.

In order to test this hypothesis a solution of nitrosobenzene was dropped slowly into an ethereal solution of nitrobenzene undergoing photolysis. If nitrosobenzene is an intermediate then only aniline should be produced; if it is not, then azoxybenzene should be isolated as in the normal photolysis of nitrosobenzene. The result of

the experiment was that a trace of azoxybenzene, too little to isolate, was formed. The actual quantity was estimated by U. V. and was only 25% of that expected by photolysis of nitrosobenzene alone.

It is concluded that nitrosobenzene may well be an intermediate in the photoreduction of nitrobenzene in both basic and non-basic media. The small quantity of azoxybenzene, produced in the above experiment, must be produced because the nitrobenzene radical was not produced fast enough to reduce all the nitrosobenzene added in any one drop of solution.

The steady-state concentration of nitrosobenzene in the photolysing solution must therefore be very small. However, a very small concentration of nitrosocompound will be sufficient for the base-catalysed condensation with the phenylhydroxylamine to proceed, for Russell and Geels [155] have demonstrated that this is a very rapid process.

An important mechanistic problem is involved in connexion with the nature of the primary process occurring after photochemical excitation. Three such processes must be considered:

(1) Hydrogen abstraction from the solvent by the excited state of the nitrocompound;

(2) Electron transfer from the solvent to the nitrocompound followed by proton exchange;

(3) Oxygen transfer from the nitrocompound to the solvent.

The results in Table 6 (with the possible exception of the data relating to toluene as a solvent) shew that efficient photochemical reduction only occurs when the solvent bears abstractable hydrogen atoms. This, of course, is what would be predicted on the basis of process (1). Toluene, although it has an abstractable hydrogen atom in the benzyl position, does not cause reduction of nitrobenzene. Triplet quenching cannot be the cause, for toluene has $E_T$ = 83 kcal. [156], whereas for nitrobenzene $E_T$ is 60 kcal. The explanation is probably connected with the difficulties that other workers have experienced in abstracting a hydrogen atom from toluene compared with, for example, benzyl alcohol [157].

Electron transfer from the solvent, process (2) cannot be simultaneous with excitation of the nitrocompound since no new (charge-transfer) bands are observed in the U. V. spectra of nitrocompounds in solvents in which the photoreduction proceeds readily. The alternative would be for the electron to be transferred from the solvent to the excited state of the nitrocompound after excitation had occurred. It could be argued that the formation of the nitrobenzene radical anion, on irradiation of nitrobenzene, supports this view. This is not necessarily so, for the radical

anion could equally well be formed by hydrogen atom transfer from the solvent (process (1) ) followed by proton loss from the resulting acid (cf. aci-nitrocompounds):-

$$C_6H_5NO_2^* \xrightarrow{RH} C_6H_5\dot{N}O_2H \rightleftharpoons C_6H_5NO^-_2 + H^+$$

(lxxvi)

Against the view that the photoreduction of nitrocompounds proceeds by way of electron transfer:

(a) It would be expected that the photoreduction of nitrocompounds would proceed readily in aqueous solutions of donor inorganic ions. However, photolyses of nitrobenzene in the presence of iodide ion and of ferrous ion did not lead to reduction; the nitrobenzene was recovered unchanged;

(b) The crucial step in the electron transfer process is as follows:-

$$C_6H_5NO_2^* + RH \longrightarrow C_6H_5NO_2^{\cdot-} + RH^{\cdot+}$$

It would appear that the energetics of this process are unsatisfactory.

Consider the case when the solvent is an aliphatic amine; the following energy terms must be taken into account:

(i) Transfer of an electron from the amine to infinity, producing the species $RH^+$. This requires the expenditure of about 240 kcal./mole.[153] (ionisation potential).

(ii) Transfer of the electron from infinity to the nitrobenzene. In the ground state this liberates 12 kcal./mole. (electron affinity). In the excited state, however, the added electron is to be accommodated in a bonding, rather than in an antibonding orbital. Since the excitation energy of nitrobenzene

is 60 kcal./mole. an approximate value of 72 kcal./mole. for the electron affinity of the excited state is obtained. [158]

(iii) Solvation of the ions produced will stabilize the electron transfer process. Unfortunately, rather little work has been done on solvation energies of ions in non-aqueous solvents, but we may be sure that the stabilization obtained is less than in water. The absolute thermodynamic free energies of hydration of large ions such as iodide ion are of the order of 60 kcal./mole.; therefore we may set an upper limit of 120 kcal./mole. for the solvation energy of the ions produced. To this value must be added a correction for the extra stabilization imparted by the fact that the ions are present as an ion pair, rather than at infinite distance from each other. A calculation, which is reproduced in Appendix 3, shews that the energy required to separate two point charges from an equilibrium distance of 1.5 A to infinity in a medium of dielectric constant 15 is 15 kcal./mole. Thus the total solvation energy of the ions can be no greater than 135 kcal./mole.

The energy required for process (2) is thus seen to be:

240 - 135 - 72 = 37 kcal./mole.

Since the values for the solvation energy of the ions are almost certainly unrealistically high, it seems that we may exclude process (2) on energetic grounds as being the photoreduction mechanism.

The argument in favour of process (3) is that the gas-phase electronic spectrum of o-nitrobenzaldehyde shews a continuum at approximately 290 mμ, and this has been interpreted in terms of N-O bond fission to give atomic oxygen. [119] A similar rationalization has been used to explain the formation of phenols from nitrobenzene on irradiation in benzene, although a more recent interpretation of this

observation favours rearrangement of the nitrocompound to a nitrite, followed by loss of nitric oxide (See Introduction to this Chapter).

It has recently been suggested that oxygen "insertion" reactions are not true insertions at all, but rather that they proceed by way of hydrogen abstraction, followed by radical recombination within the solvent cage.[141] If this is the case, it is clear that the necessity for the solvent to bear abstractable hydrogen atoms will be as important for process (3) as for process (1).

Related to the present discussion are the well known intramolecular oxygen transfer reactions in o-nitrotoluene derivatives. However, these appear to involve the singlet excited state of the nitrocompound,[120] whereas the photochemical reduction proceeds by way of the triplet state (See below).

In order to determine whether or not the oxygen transfer and reduction photoreactions are related, a photolysis of o-nitrotoluene in triethylamine was carried out. If the two reactions are related, then the products of the photoreduction should bear hydroxylated side chains, for it would be expected that an intramolecular oxygen transfer mechanism would be preferred to its intermolecular equivalent. From Table 5 it can be seen that neither for o-nitrotoluene nor for 2, 6-dimethylnitrobenzene could any products having hydroxylated

side chains be isolated; the methyl group was always found to be unchanged. Indeed, in the case of 2, 6-dimethylnitrobenzene, the sole product isolated was 2, 6-dimethylaniline, even when a Pyrex filter was used; presumably steric interactions by the two methyl groups inhibit the coupling reaction by analogy with the difficulty experienced in effecting the condensation between 2, 6-dimethylnitrosobenzene and 2, 6-dimethylphenylhydroxylamine.[160] The result is of interest by contrast with that obtained in the 4-nitropyridine-N-oxide system; although 4-nitropyridine-N-oxide undergoes reduction in alcoholic solution,[144] 3, 5-dimethyl-4-nitropyridine-N-oxide suffers a nitro-compound to nitrite ester rearrangement to give 3, 5-dimethyl-4-hydroxypyridine-N-oxide.[161] No explanation of this phenomenon has appeared to date.

Two further points argue against the oxygen transfer mechanism:

(i) Brown and Williams[162] have observed the e. s. r. spectrum of $C_6H_5NO_2H$ on photolysis of nitrobenzene in tetrahydrofuran, whereas oxygen transfer would bypass this species.

(ii) Oxygen transfer would lead directly to the nitroso-compound. It was suggested above that the removal of this intermediate requires $C_6H_5NO_2H$ for reduction. Moreover, in the only case studied known to proceed by oxygen transfer (o-nitrobenzyl alcohol) the usual reduction products are not obtained (See Table 5).

Thus the balance of the evidence strongly favours the step of hydrogen abstraction to give (lxxvi) immediately following excitation.

The next question is the fate of the intermediate (lxxvi). Once again hydrogen abstraction and oxygen transfer must be considered.

Hydrogen abstraction leads to $C_6H_5N(OH)_2$. This intermediate is iso-electronic with the hydrate of an aldehyde, and may likewise be expected to lose water to give nitrosobenzene. The methods by which nitrosobenzene may be removed from the solution are described above.

An oxygen transfer process :

(i.e. $C_6H_5\dot{N}O_2H + RH \longrightarrow C_6H_5\dot{N}OH + ROH$)

may however be a possible alternative. The product of this step, $C_6H_5\dot{N}OH$, may yield the coupled products by base-catalysed dehydration of its dimer,[155] or may abstract a hydrogen atom to give phenylhydroxylamine, and thence aniline.

In solution in ether, an oxygen "insertion" process on a molecule of the solvent would yield the species 1-ethoxyethanol (lxxvii). Since this is the ethanol adduct of acetaldehyde it will be in equilibrium with acetaldehyde.

However, it is known that 1-ethoxyethyl radicals (lxxviii), which would be produced by a hydrogen abstraction from ether are capable of reacting to give both ethylene and ethanol, and to give

157
acetaldehyde and an ethyl radical. Thus a certain amount of acetaldehyde will be produced even in a hydrogen abstraction reaction. The quantity of acetaldehyde produced by hydrogen abstraction processes (which we have already demonstrated to be responsible for at least one step in the reaction) was estimated by a control photochemical reduction of benzophenone in ether, a reaction known to
163
proceed by such a mechanism. The quantity of acetaldehyde produced in the reaction was estimated by formation of the 2, 4-dinitrophenylhydrazone and was compared with the quantity formed in an irradiation of nitrobenzene. In both cases distilled ether was used and rigorous deoxygenation was carried out to ensure that acetaldehyde would not be formed by peroxidation of the solvent. Before illumination the solution was shewn to be free of acetaldehyde. The comparison was made on the assumption that the photoreduction of nitrobenzene employed no more than one act of oxygen transfer, and it was shewn (See Appendix 4) that the quantity of acetaldehyde produced was in accord with that expected from a hydrogen abstraction mechanism. However, since not all the nitrobenzene is reduced to aniline, but some is converted to polymer, this result must be treated with reserve. The question could be resolved conclusively by the use of nitrobenzene $-O^{18}$ to determine whether or not the labelled oxygen is incorporated into the acetaldehyde.

On the balance of the evidence the probable mechanism for the photoreduction of nitrobenzene is given in Scheme 2.

So far no mention has been made of the nature of the excited state responsible for the photoreduction of the nitrocompound. It is now necessary to discuss whether it is a singlet or a triplet state, and whether it is $n,\pi^*$ or $\pi,\pi^*$, or charge-transfer in origin.

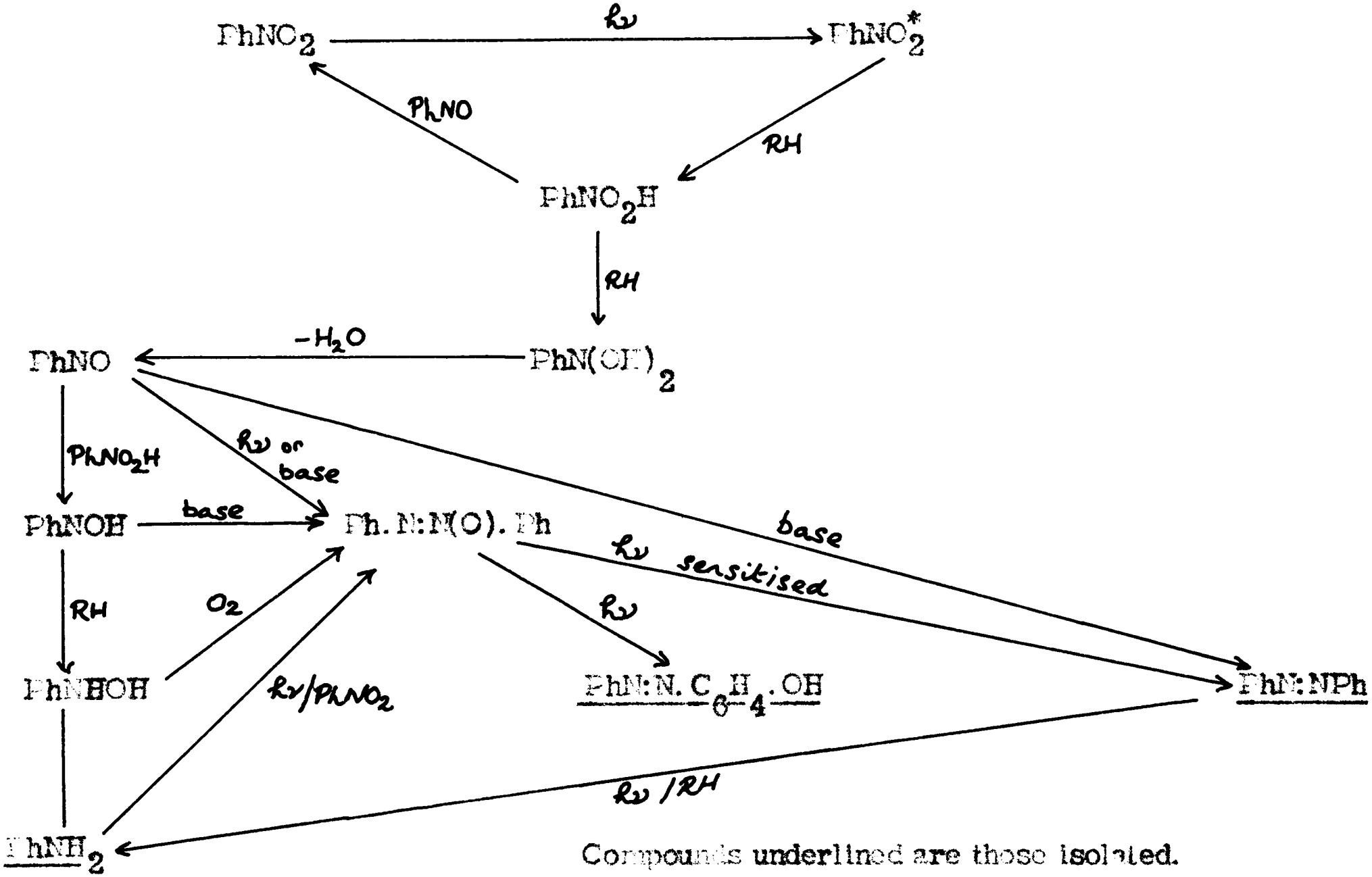
With regard to the multiplicity of the excited state, sensitization and quenching experiments have established that a triplet state is involved. The requirements for energy transfer between molecules have been discussed elsewhere.[1-3] Sensitization occurs if the molecule absorbing the light passes over to its triplet state and having done so, passes its energy on to another molecule which has a lower triplet energy.

$$\text{i.e. } X(\text{triplet}) + Y(\text{ground state}) \longrightarrow X(\text{g. s.}) + Y(t)$$

$$\text{where } E_T(X) > E_T(Y)$$

'X' may be said to sensitize 'Y', or conversely 'Y' may be said to quench excited 'X'. It follows for a meaningful energy transfer experiment that only the species with the higher triplet energy ('X') shall absorb the light initially. If 'Y' also absorbs, the triplet state of 'Y' could be formed by intersystem crossing from the corresponding singlet state rather than by energy transfer from 'X'.

Scheme 2




Compounds underlined are those isolated.

In the presence of benzophenone ($E_T$ = 72 kcal.)[156] the rate of formation of aniline from nitrobenzene was increased sixfold compared with a direct illumination of nitrobenzene. Since the sensitizer absorbed more than 95% of the output of the lamp in the wavelength region relevant to the experiment (for calculations, See Appendix 5), the quantity of aniline formed by direct photolysis of nitrobenzene should have been reduced to 5% of its former value. The increase in rate indicates a triplet state.

Confirmation comes from quenching experiments; the presence of biacetyl ($E_T$ = 52 kcal.)[156] led to complete suppression of the pro - duction of aniline, although nitrobenzene absorbed 95% of the light. However, since biacetyl has a low-lying singlet level ( $\lambda$ max. = 420 mμ, $\epsilon$ = 15) the possibility of singlet quenching (transfer of energy from nitrobenzene singlet level to the singlet level of biacetyl) cannot be excluded,[164, 165] for examples of this phenomenon have recently been observed. Accordingly a second quenching agent, octafluoronaphthalene ($E_T$ = 56 kcal.) was used. In this case the possibility of singlet quench- ing is remote, for nitrobenzene absorbs in the U. V. at much longer wavelengths than octafluoronaphthalene. Once again, although 94% of the light was absorbed by nitrobenzene, the formation of aniline was completely suppressed.[162] Brown and Williams have quenched the

formation of $C_6H_5\dot{N}O_2H$ from nitrobenzene using this same reagent.

That it is the triplet state of nitrobenzene that is being quenched, rather than the triplet state of one of the intermediates, is shewn by the fact that the nitrobenzene could be recovered unchanged after photolysis in the quenching experiments.

In this context the observation of Plant [12] that the oxygen transfer reaction of o-nitrotoluene proceeds via the singlet state prompted the thought that perhaps photochromism is a triplet reaction. This would accord with the conception of photochromism as a hydrogen abstraction reaction (lxxlx - lxxx). Accordingly, Morrison and Migdaloff's [138] irradiation of o-nitrotoluene with deuterium oxide was repeated. A duplicate experiment was carried out using octafluoronaphthalene ($E_T$ = 56 kcal.) [162] to quench any o-nitrotoluene triplets ($E_T$ = 60 kcal.). [156] Octafluoronaphthalene absorbed only 4% (Appendix 5) of the light. It was found that although the uptake of deuterium in each case was very small, its extent was almost the same, implying that photochromism is not a triplet reaction. Thus, a preliminary study would indicate that the difference between photochromism and oxygen transfer is not to be found in the multiplicity of the reaction.

The next question to be considered is the nature ($n,\pi^*,\pi,\pi^*$, or charge-transfer) of the triplet state involved in the photoreduction of

nitrobenzene. It has been suggested[143] that the photoreduction of nitrobenzene in isopropanol proceeds via hydrogen abstraction by the triplet $n,\pi^*$ state of nitrobenzene. However, in view of the considerable discussion about the nature of the long wavelength absorption bands of nitrobenzene, a closer examination of the question is required, and the spectroscopic evidence must be considered.

The U.V. absorption spectra of some nitrocompounds are presented in Table [166]. Because of its low extinction coefficient, Platt ascribes the 330 $m\mu$ band of nitrobenzene to an $n,\pi^*$ transition. However, an important factor in assigning these bands is that they are more intense in o-nitrotoluene and 2,3-dimethylnitrobenzene. These observations are in accord with the interpretation given by Murrell [6, 167] who assigns the 330 $m\mu$ band to a charge-transfer transition, the molecule being polarised $Ph^+ - NO_2^-$ in the excited state. If the nitro group be twisted away from the plane of the ring to avoid steric interactions with the substituents at the ortho positions, this transition can also be considered as one from the highest filled m.o. of the benzene ring to a vacant $\pi^*$ orbital centred on the nitro group. Consequently the characteristics both of a charge-transfer band (greater extinction coefficient in a polar solvent) and those of a $\pi,\pi^*$ band (red shifted in a polar solvent, transition polarised along the symmetry axis of the molecule [167]) will be observed. The extinction coefficient is small

Table 8

| Nitrocompound | In Cyclohexane λmax. mμ | ε | In Ethanol λ max. mμ | ε |
|---|---|---|---|---|
| Nitrobenzene | 252 | 8, 100 | 257 | 8, 200 |
| | 320 (sh.) | 110 | 335 | 130 |
| o-Nitrotoluene | 250 | 4, 900 | 256 | 5, 900 |
| | 325 (sh.) | 330 | 335 (sh.) | 420 |
| 2, 6-Dimethylnitro-benzene | 242 (sh.) | 1, 760 | 250 | 1, 460 |
| | 329 | 260 | 232 | 290 |
| 2, 4-Dinitrotoluene | 235 | 21, 000 | 240 | 17, 000 |
| | 330 (sh.) | 380 | 325 (sh.) | 430 |
| o-Nitroanisole | 250 | 3, 100 | 257 | 3, 100 |
| | 307 | 2, 200 | 318 | 2, 300 |
| m-Nitroanisole | 261 | 5, 900 | 267 | 5, 400 |
| | 315 | 2, 200 | 325 | 2, 000 |
| p-Nitroanisole | 220 | 8, 600 | 227 | 7, 600 |
| | 295 | 11, 000 | 304 | 11, 000 |
| o-Nitroaniline | 270 | 4, 500 | 277 | 5, 300 |
| | 377 | 4, 600 | 404 | 5, 800 |

Notes

(sh.) signifies a shoulder, not a true maximum.

The U. V. Absorption Spectra of some Aromatic Nitrocompounds

because of the small overlap integral between the $\pi$-orbitals of the ring and the (non-coplanar) $\pi^*$ orbitals of the nitro group; it is greater in the case of the o-methylated nitrobenzene because, with the greater steric interaction, the nitro group spends more time in the non-planar conformation, thus favouring the charge-transfer band.

In the case of 2, 4-dinitrotoluene, insertion of another electron-withdrawing nitro group makes the n, $\pi^*$ band now the lowest in energy, and in this case, a blue shift is observed; the assignment is analogous to that given by McConnell [168] for sym. trinitrobenzene.

Insertion of donor substituents frequently leads to a blue shift of n, $\pi^*$ bands and a red shift of $\pi$, $\pi^*$ bands. [88] This seems to be the situation in the nitroanisoles, where the long wavelength shoulders are now absent and a $\pi$, $\pi^*$ band at $\sim$300 m$\mu$ is observed.

However, it would seem that, for both the methylated nitrobenzenes, and the nitroanisoles, the lowest triplet state is not charge-transfer, but $\pi$, $\pi^*$, and it is from this state that the photoreduction takes place. Charge-transfer transitions tend to experience rather small singlet-triplet splittings; for example, Michler's ketone (lxxxi) has $\lambda$ max. = 364 m$\mu$ (77 kcal.) in ethanol and $E_T$ = 65 kcal. in a polar glass, [156] at 77° K. Since in the nitrobenzene charge-transfer band at 330 m$\mu$ the nitro group and the ring are non-coplanar, the

singlet-triplet splitting would be expected to be very small, because the splitting depends upon the overlap integral between the orbitals involved in the transition. Some idea of the effect of this factor can be gained from a consideration of the extinction coefficients, which for a symmetry-allowed transition also depend on the overlap integral; Michler's ketone $\epsilon$ = 27000; nitrobenzene, $\epsilon$ = 13[illegible]. Since the energy of the charge-transfer state of nitrobenzene is [illegible]6 kcal. (330 m$\mu$), the energy of the charge-transfer triplet must be much higher than the 156
60 kcal. observed by Lewis and Kasha as the energy of the lowest triplet state. Equally, since n,$\pi$* singlet-triplet splittings are also small ( approx. 3000 cm.$^{-1}$), the bottom triplet of nitrobenzene cannot be n,$\pi$* in character, and by elimination it is presumably a $\pi$,$\pi$* state. In accord with this interpretation the lifetime of the 156
state has been given as 0.1 to 1 second, a value typical of a $\pi$,$\pi$* 10
state, a measurement in these laboratories gives a value of 0.2 second for this same quantity in an EPA glass at 77° K.* Therefore, it is concluded that the reduction occurs by way of the $\pi$,$\pi$* triplet excited state of the nitrocompound.

As a measure of confirmation of this postulate, o-nitroaniline,

* I should like to thank Mr. H. E. Browning for his help in carrying out this measurement.

which has a very long wavelength charge-transfer band (Table ?) and which therefore probably has a bottom triplet of the charge-transfer type, is very slow to react photochemically under conditions which photoreduce nitrobenzene rapidly (Table 5).

The concept that reduction of nitrobenzene proceeds by way of a $\pi,\pi^*$ state raises a further problem for it has been widely assumed that hydrogen abstraction is a property of $n,\pi^*$ states. This appears to be an over-simplification based on the behaviour of carbonyl compounds. The crucial point seems to be this, that is a significant electron deficiency appears on an oxygen atom in an excited state (as in the case with carbonyl $n,\pi^*$ states), then this deficiency can be made good by the transfer of a hydrogen atom with its electron and photoreduction will then occur.

Zero-order H. M. O. calculations on nitrobenzene give the results shewn in Table [20]. It seems that for a wide variation of the parameters, an electron deficiency develops on the oxygen atoms of nitrobenzene in the $\pi,\pi^*$ excited state, and although the results of such crude calculations must be treated with caution, they do support the concept that the $\pi,\pi^*$ triplet state of nitrobenzene will dehydrogenate hydrogen-donating solvents.

Table 9

Calculated H.M.O. Formal Positive Charges on the Oxygen Atoms of Nitrobenzene in $\pi\ \pi^*$ Excited State

| h(N-O) | h(N) | Formal Charge |
|---|---|---|
| 0.7 | 1 | +0.14 |
| 0.7 | 2 | +0.16 |
| 0.7 | 3 | +0.15 |
| 1.0 | 1 | +0.19 |
| 1.0 | 2 | +0.22 |
| 1.0 | 3 | +0.25 |

Note h(O) = 1.5

To conclude, the present study on the photoreduction of nitro-compounds establishes the following points:

(i) Reduction is a phenomenon general to aromatic nitrocompounds in solvents bearing abstractable hydrogen atoms

(ii) Coupled products are formed only using basic conditions, and predominate when filtered light is used ( $\lambda > 290$ $\mu$).

(iii) Reduction occurs by way of hydrogen abstraction by a triplet $\pi, \pi^*$ state of the nitrocompound

(iv) Oxygen transfer does not seem to be an important process.

(v) Reduction of the intermediates may be a thermal process involving the radical $C_6H_5NO_2H$ or its anion.

Finally, it is appropriate to draw attention to the different reactions of m- and p-nitroanisole in nucleophilic solvents. In

diethylamine, only reduction occurs, yet it is reported (Chapter III) that in aqueous amines substitution products are obtained.[97, 103] An irradiation of m-nitroanisole in 50% aqueous diethylamine led to substitution and complete suppression of reduction. The polarity of the solvent may be a decisive factor here, perhaps according to its ability to solvate the transition states involved in the two reactions.

## Addendum

The intermediacy of nitrosobenzene in the photoreduction of nitrobenzene has been confirmed. A solution of a mixture of nitrosobenzene and o-nitrotoluene was added in drops to a photolysing solution of o-nitrotoluene in ether. The basic material was analysed by g.l.c., and it was found that, in addition to o-toluidine, some aniline had been produced.

The possibility that photo-sensitisation by the nitrocompound had removed the nitrosobenzene was excluded by an irradiation of nitrosobenzene in the presence of naphthalene. Naphthalene has $E_T$ = 60 kcal., similar to that of o-nitrotoluene[156] (and to that of nitrobenzene). No aniline was found among the products of the irradiation, although azoxybenzene was detected by t.l.c. Thus the process responsible for the disappearance of nitrosobenzene is not photochemical.

Confirmation of the postulate that nitrosobenzene is thermally reduced by $C_6H_5NO_2H$ is provided in a recent publication by Russell and his co-workers[210]. They have found that nitrosobenzene is rapidly reduced by the nitrobenzene radical anion according to the equation

$$C_6H_5NO + C_6H_5NO_2^{\cdot-} \longrightarrow C_6H_5NO^{\cdot-} + C_6H_5NO_2$$

and this observation lends support to the concept of a thermal reduction of nitrosobenzene, which is the key step in the reaction pathway proposed in Scheme 2.

# CHAPTER V

## Some Photochemical Reactions of Azoxycompounds and other systems related to Nitrocompounds

### Introduction

The rearrangement of aromatic azoxycompounds to ortho-hydroxyazocompounds (lxxxii - lxxxiii) was discovered in 1903 by Knipscheer,[165] who exposed to sunlight filter papers impregnated with azoxybenzene. The reaction was studied in solution under a variety of conditions by Cumming and Ferrier,[84] who established that a large number of azoxycompounds rearranges under the influence of light. However, in many cases the yield of product was so small that the products could not be adequately characterised.

A more recent study by Badger and Buttery,[170] who photolysed a variety of non-symmetrical azoxycompounds, revealed that the transfer of the oxygen atoms takes place towards the aromatic ring farther from the nitrogen atom to which it was originally attached. A six membered transition state was proposed to explain this selectivity In this work the characterisation of the products was greatly aided by the use of column chromatography to resolve the photochemical mixtures; earlier workers had had to rely on fractional crystallization.

Interest by the present author in the photochemistry of azoxy-

compounds stemmed not only from their intermediacy in the photoreduction of nitrocompounds, but also because of the close electronic similarity of the azoxy group to the nitro group. Indeed, nitrocompounds, azoxycompounds, nitrones, and carboxylic acid anions are all formally iso-electronic (lxxxiv ; lxxxvii), and the first three of these, having a co-ordinate N-O bond, are also related to N-oxides. Some similarities in the photochemistry of these compounds have already been observed; for example, irradiation of both 9-nitro-anthracene[114] and sodium 9-anthroate[116] gives rise to products derived from the anthromyl radical (li) - (See Chapter IV). This radical is probably formed from the intermediate oxaziran (liv), or for the carboxylate anion (lv). Oxazirans are also produced on photolysis of nitrones,[171, 172] and have been postulated as the intermediates (lxxxviii - xc) in the photochemical transformations of certain N-oxides.[173-175]

Equally, there may be some relationship between the photochemical oxygen transfer reactions of azoxycompounds, and of nitrocompounds to an ortho benzyl group. Both, for example, may be considered as occurring by way of six membered transition states (xci, xcii). However, nitrones, which are very similar to azoxycompounds, have not been observed to undergo any transformation of

this type (e.g. xcili - xciv).

The object of the present work then was not to make a complete survey of the photochemistry of azoxycompounds, but rather to carry out experiments to resolve some points of interest arising out of the work on the the photoreduction of nitrocompounds, and to examine whether these formally similar classes of compound might shew parallels in their photochemistry

## Discussion

In this section the photochemical transformations of a variety of azoxycompounds are described. These were all prepared by standard methods, the first tried of which was the reduction of the nitrocompound by refluxing with methanolic sodium hydroxide solution. This method was not always successful; either a moderate to good yield of product was obtained, or else nothing at all. It was observed in this connexion that where the reaction mixture remained a pale colour after 5 to 10 minutes refluxing a good yield was obtained, but where rapid darkening of the solution occurred, no product could be isolated, whether or not a prolonged refluxing period was employed.

2, 2', 6, 6'-Tetramethylazoxybenzene and 2, 6-dimethylazoxybenzene were prepared by oxidation by peracetic acid of the azocompound. This is a useful method, as the azocompounds are often more readily available. 2, 2', 6, 6'-Tetramethylazobenzene was prepared after several methods had been tried, by the lithium aluminium hydride reduction of the nitrocompound, and this may be a useful general method of synthesis of azoxycompounds.

Oxidation of 2, 6-dimethylazobenzene gave a product which shewed two methyl resonances in the n.m.r. spectrum. This is because oxidation gives both possible isomers (xcv and xcvi); the

larger methyl resonance was assigned to the less hindered isomer (xcv), on the grounds that the resonance occurred with the same chemical shift as for 2,6-dimethylazobenzene. For this isomer the effect of the oxygen atom upon the environment of the methyl groups would be less. The isomer ratio was calculated from the n.m.r. spectrum to be 78 : 22.

A first series of irradiations concerned the solvent dependence of the products of irradiation of azoxybenzene. This was of interest in view of the fact that in the irradiation of p-nitroanisole in diethylamine, no hydroxyazocompound (xcvii) was isolated. The corresponding azoxycompound on irradiation in diethylamine gave no hydroxyazocompound, but was reduced to 4,4'-azoanisole.

An irradiation of azoxybenzene in petrol afforded azobenzene as a minor product, and only traces of this product were found in solvents bearing more or less easily abstractable hydrogen atoms. Table 10 shews the results of this study, and it appears that there is no correlation between availability of abstractable hydrogen atoms and the proportion of reduced product. Increased solvent polarity appears to increase the rate of the oxygen transfer reaction, which perhaps suggests that this is not an abstraction / radical recombination process.

Table 10

The Solvent Dependence of the Irradiation Products of Azoxybenzene

| Solvent | Conversion | Azobenzene | 2-Hydroxy-azobenzene |
|---|---|---|---|
| | % | % | % |
| Benzene | 30 in 1 hr. | - | 26 |
| Petrol | 65 in 5 hr. | 8 | 42 |
| Ether | 1[illegible] in 1 hr. | 3 | 17 |
| Diethylamine | 64 in ¼ hr. | 1 | 61 |
| Isopropanol | 32 in ¼ hr. | - | 77 |

It is perhaps appropriate at this point to mention the great advantage in the present work of using preparative t.l.c. Not only is isolation of the products quicker than by column chromatography, but by the choice of a suitable developing solvent system, the bands can be entirely separated and the problem of mixed fractions is eliminated. Furthermore, the isolation of minor components from a reaction mixture now becomes feasible; for example, the small quantities of azobenzene produced in the present series of experiments could not have been isolated by other means, and this must be the reason that previous workers have failed to observe this product.

Azobenzene has been observed once before as an irradiation

product of azoxybenzene; [149] sensitization by benzophenone in an irradiation in ethanol gave azobenzene as the major product.

Irradiations of azoxybenzene in isopropanol using sensitizers only partly confirmed this previous observation. Azobenzene was formed, when either nitrobenzene or naphthalene (both $E_T \sim 60$ kcal. [156]) was used as a sensitizer, but the azocompound was the minor product. However, triplet transfer from nitrobenzene to azoxybenzene probably explains the formation of the azocompound in the photolyses of nitrocompounds and the wide variations in the hydroxyazo- : azo-compound ratio for various nitrocompound reductions may be explained by the effectiveness of a particular nitrocompound in sensitizing the azoxycompound. Alternatively, the ratio may reflect the ease with which the azoxycompound crosses over into its triplet state.

Thus it seems likely that the photoreduction of azoxycompounds, like the photoreduction of nitrocompounds proceeds via the triplet state. Equally, it is also probable for the azoxycompounds, just as for the nitrocompounds, [129] that oxygen transfer is a singlet state process.

An irradiation of 4, 4'-~~iso~~ azoxyanisole in benzene was now carried out, for in this solvent there is no possibility of reduction occurring as in diethylamine, and 2-hydroxy-4, 4'-azoanisole (xcvii) was

indeed isolated. Characterisation of o-hydroxyazocompounds was found to be a simple matter, for all those encountered to date crystallize as red needles, and have a characteristic n.m.r. spectrum, the hydroxyl proton appearing as a singlet at below $\tau$ 0, usually $\tau$ -2 to -4. The exact position of this signal is rather dependent upon the concentration used; generally a lower concentration favours the signal appearing at lower field. The reason for the unusual position of this resonance is probably hydrogen bonding of the hydrogen atom to the polar azo group (xcviii). This is confirmed by the i-r spectrum, which shews no normal O-H stretching frequency at 3600 or 3400 cm.$^{-1}$, the absorption probably being superimposed on the C-H stretching frequency at 3100 cm.$^{-1}$

The mass spectra of these compounds are also useful in characterisation, for in addition to exhibiting a strong molecular ion, aromatic azocompounds fragment according to the scheme:

$$(Ar.N{:}\ N.Ar')^{+} \longrightarrow ArN_2^{+} + Ar' \longrightarrow Ar^{+} + N_2$$

$$\longrightarrow Ar + {}^{+}N_2Ar' \longrightarrow Ar'^{+} + N_2$$

and the fragments $ArN_2^{+}$, $Ar'N_2^{+}$, $Ar^{+}$, and $Ar'^{+}$ are usually observed as the strongest in the spectrum.

Having found that 4, 4'-azoxyanisole is in fact capable of undergoing an oxygen transfer reaction in benzene, the photolysis

was carried out in acetonitrile, from which abstraction is also not favoured, with the same result. In order to discover whether the reluctance of 4, 4'-azoxyanisole to undergo the oxygen transfer reaction in diethylamine was an isolated case, 2, 2'-azoxyanisole was prepared and was photolysed both in diethylamine and in benzene.

In benzene, the normal oxygen transfer reaction was observed although, exceptionally, it was possible to isolate both geometrical isomers of the product, 6-hydroxy-2, 2'-azoanisole. The reason for obtaining both isomers on irradiation in benzene, as against other solvents, is that benzene is known to photosensitize the cis/trans isomerisation of azocompounds.
176

The less polar material was assigned the trans structure on the following grounds:

(i) It gave a higher m. p. :

(ii) By analogy with cis and trans azobenzenes the trans is the less polar:

(iii) With time the more polar material was shewn by t. l. c. to become a mixture of the two isomers:

(iv) The less polar material was identical with material obtained from an irradiation of 2, 2'-azoxyanisole in diethylamine, where photosensitized isomerisation does not occur.

A third product, a red oil, was isolated from this reaction. The mass spectrum shewed it to be a structural isomer of azoxy-

anisole, but the n. m. r. spectrum indicated that it contained no aromatic C-H bonds, for of the four groups of resonances, three were compatible with a mixture of cis- and trans-hydroxyazoanisole in the ratio of 1:2 cis:trans. With increased time, the proportion of these three taken together grew larger at the expense of the other group of resonances, which were found in the alkyl C-H region. No structure can be assigned to this substance which, according to the evidence of t. l. c., was transformed with time into the isomeric hydroxyazocompounds.

A less complicated situation was encountered in an irradiation in diethylamine, where the products were the trans-hydroxyazo-compound and the azocompound in the ratio 10:3.

It seems probable that this is an example of a difference in ability to assume the triplet state. Azoxybenzene reacts in diethylamine to form the hydroxyazocompound almost exclusively, whereas facile intersystem crossing to the triplet state in 4, 4'-azoxyanisole gives the azocompound as the sole product. 2, 2'-Azoanisole is an intermediate case.

When 2, 2'-azoxytoluene was irradiated in benzene, as in the case of o-nitrotoluene, no oxygen transfer to the methyl group was observed. Thus, for this compound, oxygen transfer to a phenyl

ring is a more rapid process than insertion into a methyl group, for if both proceed by way of six membered transition states, there are thrice as many benzyl as phenyl C-H bonds available. The normal hydroxyazocompound was isolated, but in addition there was obtained a compound, which was rather insoluble in most solvents and which shewed a (presumed) molecular ion at 344 in the mass spectrum. The n. m. r. indicated three methyl resonances, and a hydrogen bonded hydroxyl group. The fragmentation pattern of the mass spectrum together with the n. m. r. and molecular weight (344) indicated three tolyl rings, one of them hydroxyl substituted, joined by two azo linkages. In order to test whether this interpretation of the mass spectrum was correct, one of the possible isomers was prepared by substitution of 6-hydroxy-2, 2'-azotoluene by o-tolyl diazonium chloride. The mass and n. m. r. spectra of the photolysis product were identical to those of the synthesised 3-methyl- 2, 4-bis-(o-tolylazo)- phenol.

A point of interest in the n. m. r. spectrum of this compound is that one would expect two methyl resonances rather than three, for the two substituent tolylazo groups are the same. The reason is probably steric: structure (xcix) is probably the preferred conformation and the methyl groups 'A' and 'B' differ on account of the steric

effect on 'A' of the methyl group or the hydrogen bonded hydroxyl group.

A possible rationalisation of the formation of this product could be that 6-hydroxy-2, 2'-azotoluene splits up on photolysis to give a 2-tolyldiazonium radical, which substitutes another molecule of 6-hydroxy-2, 2'-azotoluene para to the hydroxyl group. This would not seem to be the case, for an irradiation of a concentrated solution of 6-hydroxy-2, 2'-azotoluene gives none of the product. Furthermore, in photolyses of azobenzene in the presence of phenol there was no evidence to suggest that fission of the azobenzene was occurring; neither p-hydroxyazobenzene nor biphenyl was detected among the products and the azobenzene was recovered with little loss.

$$ArN:N.Ar \xrightarrow{h\nu} Ar^{\cdot} + ArN_2^{\cdot}$$

$$ArN_2^{\cdot} + C_6H_5OH \longrightarrow ArN:N.C_6H_4.OH$$

$$Ar^{\cdot} + Ar^{\cdot} \longrightarrow Ar.Ar$$

Thus this product must in some way be formed by interaction of two azoxytoluene molecules, or one azoxytoluene with a hydroxyazotoluene. Its formation is suppressed when azoxytoluene is irradiated in dilute solution, when the products are cis- and trans-6-hydroxy-2, 2'-azotoluene, the cis compound being less polar than

the previously known trans.
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Other workers have irradiated 2, 2'-azoxytoluene in ethanolic solution where, in addition to the hydroxyazocompound, they observed small quantities of products (c and ci), which appear to be derived from the hydroxyazocompound by shifts of methyl and hydroxyl groups. The mechanism of these transformations is unknown.

Irradiation in benzene of 2, 6-dimethylazoxybenzene and 2, 2', 6, 6'-tetramethylazoxybenzene led to little change in either. A small diminution of the quanitity of the minor isomer (xcvi) of 2, 6-dimethylazoxybenzene was noted, but there was insufficient of the transformation product to isolate. A complete lack of reactivity has been observed in 2, 4, 6-trimethylazoxybenzene (cii); here, as in (xcv), the oxygen atom is not favourably situated for transfer to either a methyl group or a phenyl group and the azoxycompound is photochemically inactive.

A preliminary irradiation of 1, 1'-azoxynaphthalene was carried out, because a six membered transition state could lead either to 2-hydroxy-1, 1'-azonaphthalene (ciii), or to the yet unknown 8-hydroxy-1, 1'-azonaphthalene (civ). Of these the former has been identified by comparison with authentic material, 84 and this was one

product of the present study. T.l.c. also permitted the isolation of a very small quantity of a second red substance; the mass spectrum shewed a molecular ion at $m^+/e$ 288, but there was insufficient evidence to differentiate between the structure of (civ) and that of the cis form of (ciii).

In conclusion, although some information has been obtained, much about the photochemistry of azoxycompounds remains unclear. The mechanism of the oxygen transfer reaction is known to involve a six membered transition state, but what is the mechanism of the "insertion", whether it be insertion, abstraction followed by recombination, or substitution, is unknown. More research is needed also into the type of C-H bond into which "insertion" is favoured by the use of, for example, more naphthalene derivatives and compounds bearing side chains other than methyl (e.g. - $CH_2OH$, - CHO); when the side chain is a methyl group, it is clear that rearrangement to the ortho hydroxyazocompound is a very much faster process than rearrangement to the benzyl alcohol.

Unknown too is the question of whether the reduction of azoxycompounds is analogous to that of nitrobenzene, although it seems probable that both proceed via triplet states. In this connexion irradiation of sodium benzoate, another compound iso-electronic

with nitrobenzene, in methanol, gave no reduction and irradiation of sodium o-toluate in water gave no evidence of oxygen transfer. The present position is that it is not known whether some of these compounds, carboxylates, nitrones, and N-oxides, might under certain conditions undergo reduction or oxygen transfer, and further study is necessary to elucidate these points and the relevant reaction pathways.

# CHAPTER VI

## Experimental

### General Notes

Melting points were determined on a Kofler hot stage apparatus and are uncorrected.

The word "bath" following a listed boiling point indicates bulb-to-bulb distillation.

Infrared spectra (i-r) were recorded on a Unicam SP. 200 instrument; routine ultraviolet spectra (U. V. ) on a Unicam SP. 800 and accurate U. V. spectra on a Cary 14 M.

The mass spectrometer used for the determination of mass spectra was an A. E. I. MS9 double focussing instrument.

Nuclear magnetic resonance spectra were recorded on a Perkin-Elmer R. 10 machine operating at 60 Mc./sec. The spectra will be set out below as follows:

> n. m. r. (solvent): $\tau$ value (number of protons, multiplicity and coupling constant, assignment)

Silica gel used for column chromatography was Whatman "Chromedia" S. G. 31. Alumina used for column chromatography was Spence, Grade H. Columns were made up by introducing the adsorbent as a slurry. The weight of adsorbent and the size of the fractions will be indicated in parenthesis after the name of the

adsorbent. The composition of each fraction was checked by analytical t.l.c.

Gas-liquid chromatography (g.l.c.) was carried out using a Pye Argon Chromatogram incorporating a $\beta$-ray detector. The columns were glass, 4' in length. The stationary phases used were 5% "Hexaplas" polypropylene adipate on "Embacel", (5% ppa), and 20% Carbowax 20M terminated with terephthalic acid on Chromosorb W, (TPA), supplied by Perkin-Elmer Ltd. The conditions used for the run will be given as follows:

(stationary phase, temperature of column, carrier gas pressure).

Quantitative studies were carried out with the aid of a marker, a substance of Rt different from that of the compound to be estimated. A known quantity of marker was introduced into the test solution and the relative peak areas were measured. The marker and compound to be estimated were calibrated against each other using a test solution containing known quantities of each.

Thin layer chromatography (t.l.c.) for analytical purposes employed glass plates 20 cm. x 5 cm. with an adsorbent layer of thickness 0.3 mm. The plates were developed by ascending chromatography in the solvent mixture. The usual adsorbent was silica gel impregnated with fluorescing agents absorbing at 254 and 366 m$\mu$.

The spots were detected by exposing the plate to ultraviolet light. Otherwise silica gel "G" or alumina plates were used, and the spots were detected by exposing the developed plate to iodine vapour. This technique was found to be satisfactory for most aromatic compounds. Conditions for t.l.c. will be given as follows:

(Adsorbent, developing solvent).

Rf values were not standardised and so will not be quoted.

For preparative purposes the adsorbent used was invariably silica gel impregnated with the fluorescing agents. The adsorbent layer was of thickness 1 mm. on glass plates 1 m. in length, and development was again by ascending chromatography. The experimental conditions will be given as above, but will also include the number of developments necessary, e.g. x 4 for four developments. The compound was freed from the adsorbent by scraping off the band and extracting into an organic solvent, usually ether, using a Soxhlet extractor.

Compounds isolated from chromatographic procedures were purified by bulb-to-bulb distillation, if liquid, or recrystallization if solid.

The presence or absence of expected products in a reaction mixture was determined by t.l.c. or g.l.c. Compounds were

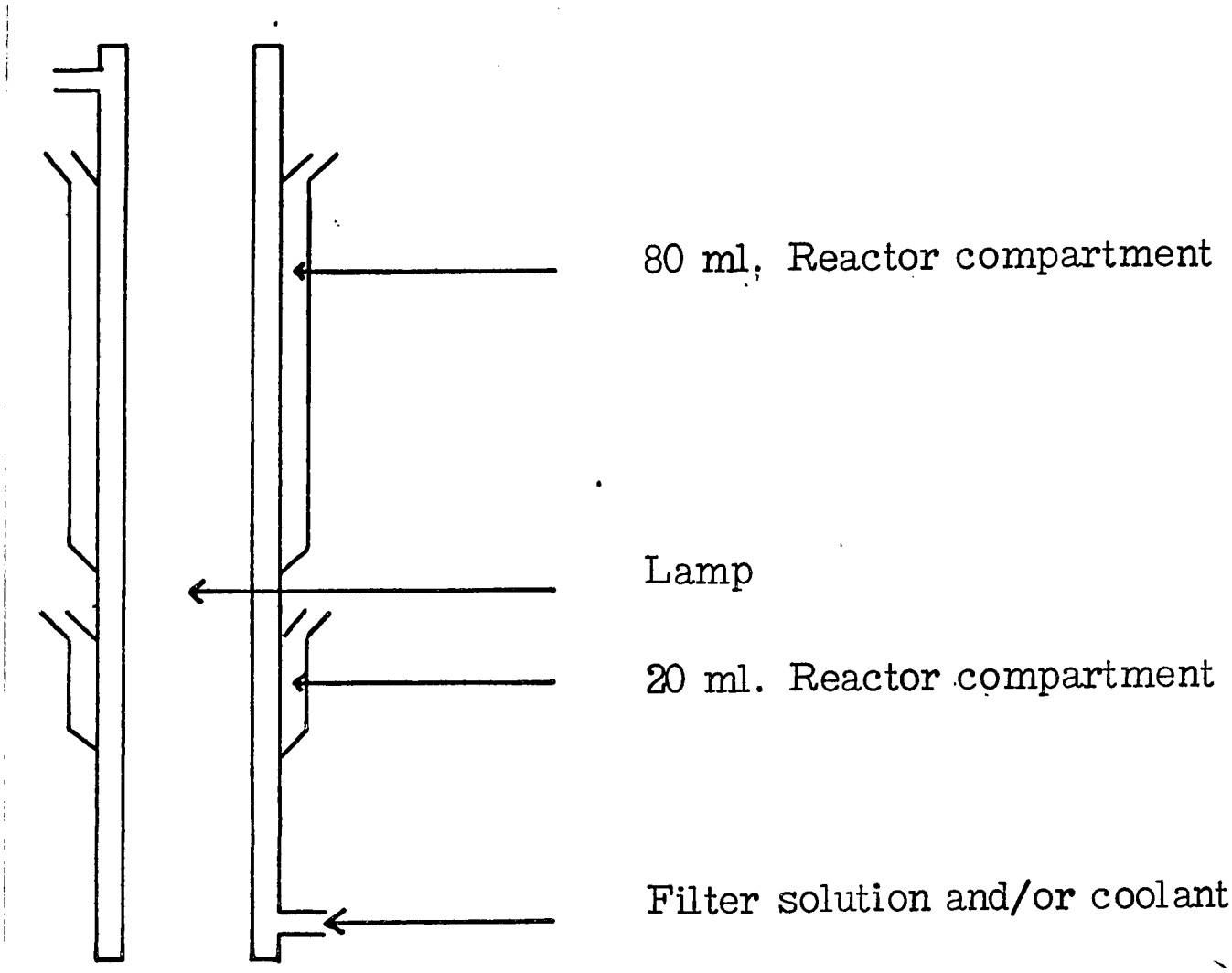



Fig. 7: The all quartz photochemical reactor

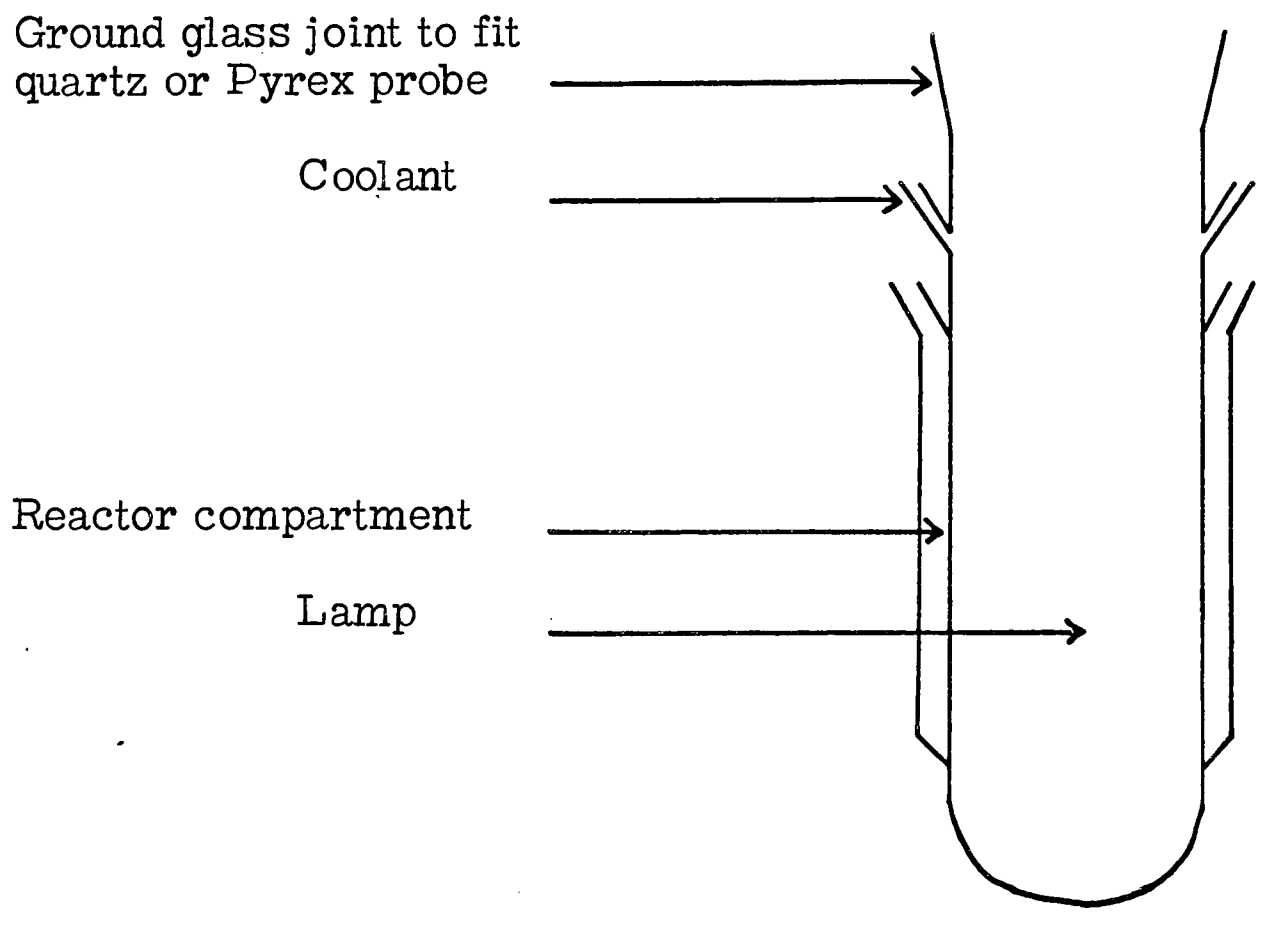



Fig. 8: The 150 ml. photochemical reactor

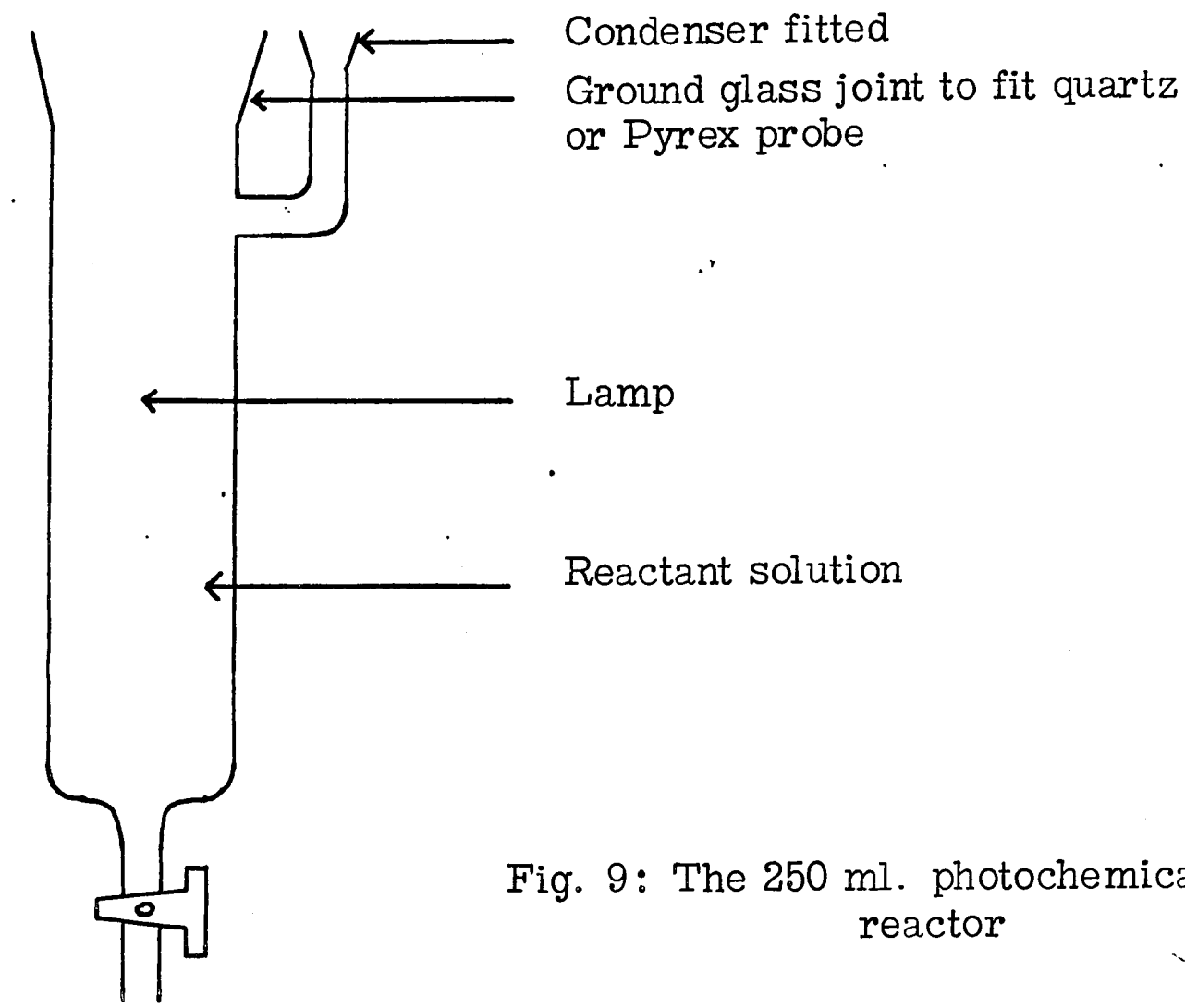



Fig. 9: The 250 ml. photochemical reactor

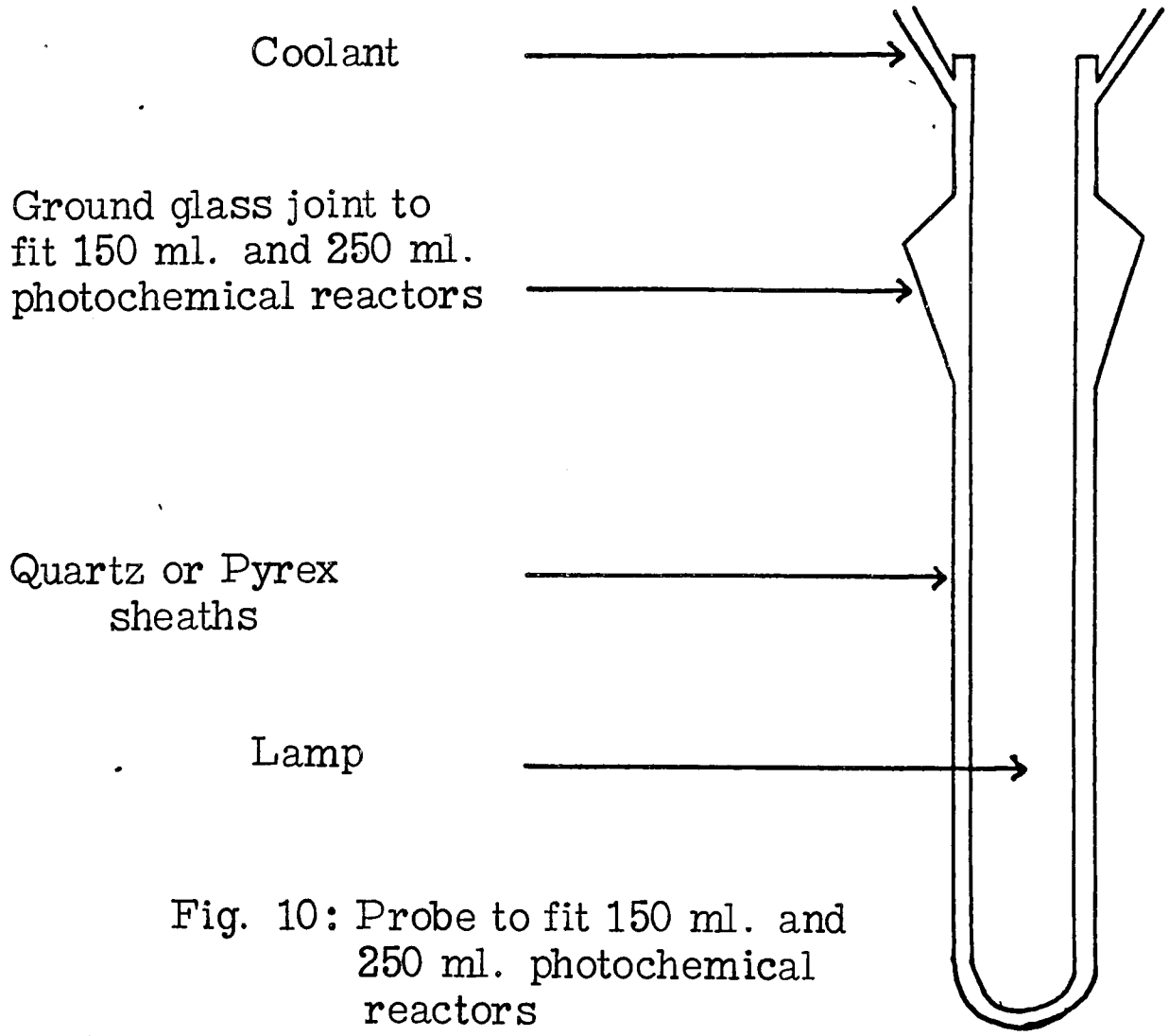



Fig. 10: Probe to fit 150 ml. and 250 ml. photochemical reactors

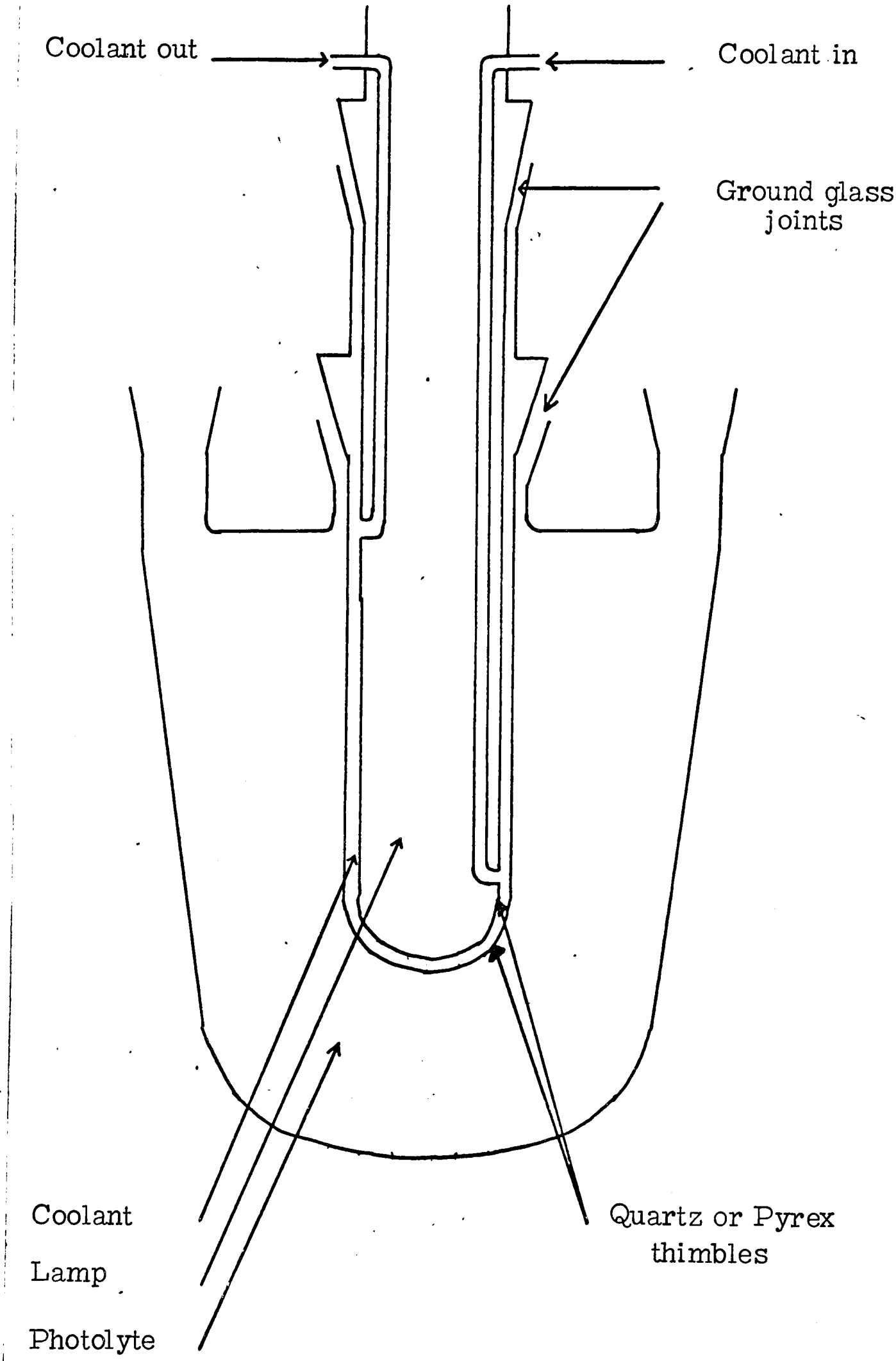



Fig. 11: The 1 litre photochemical reactor

identified by comparison of their i-r spectra and their behaviour on t.l.c. or g.l.c. with those of authentic samples and, where appropriate, by m.p. and mixed m.p.

Organic solutions were dried over magnesium sulphate.

"Petrol" refers to light petroleum, b.p. 40-60°, and was redistilled for use as a recrystallization solvent. However, as a component of a t.l.c. solvent system in conjunction with benzene as the other component, "petrol" refers to the fraction b.p. 60-80°.

The composition of mixed solvents is given in percentages v/v, i.e.'10% benzene in petrol' refers to a mixture containing 10 ml. benzene in 90 ml. petrol.

Irradiations were carried out in solution in the quartz reactor vessels illustrated in Fig. 7 - 11. The all quartz apparatus (Fig. 7) had 80 ml. and 20 ml. compartments. Either cooling water or a filter/cooling solution could be passed through the inner jacket. The 150 ml. (Fig. 8) and 250 ml. (Fig. 9) reactors could be fitted with a quartz or a Pyrex glass probe (Fig. 10). The quartz probe transmitted light of wavelength greater than about 215 mμ; the Pyrex glass probe cut out light of wavelength shorter than 290 mμ. The capacity of the "250 ml." reactor depended upon the size of the probe used, but will still be referred to as the 250 ml. reactor. The

solution in this reactor was stirred by bubbling nitrogen slowly through the solution. With all the above systems the source was a "Hanovia" 500 W. medium pressure mercury arc; the manufacturers' data on the output of the lamp are given in Appendix 6.

A reactor of 1 litre capacity (Fig. 11) was used and could be fitted with quartz or Pyrex thimbles. The source was a "Hanovia" 100 W. medium pressure mercury arc.

Cooling for these reactors was by means of tap water, circulated as illustrated in the Figures. The temperature of the photolyte could be kept below 25°. The water passed through a flowing junction mercury switch, so that any interruption in the flow of coolant would cause the lamp to be switched off.

An alternative method of irradiation employed an external source, a "Hanovia" 125 W. medium pressure "U" shaped mercury arc and a Pyrex flask. Since cooling cannot be incorporated in such a system, these irradiations were perforce carried out under reflux.

Dry oxygen-free nitrogen was obtained by passing commercial "white spot" nitrogen successively through chromous chloride solution and concentrated sulphuric acid, and then over self-indicating silica gel. The chromous chloride solution was

prepared by dissolving mercuric chloride (15 g.) in water (200 ml.) and adding to this solution zinc dust (5 g.) and chromic chloride (5 g.). The solution was carefully protected from the air when not in use.

Deoxygenation of the solutions was effected by passing the nitrogen, as purified above, through the refluxing solution for 30 min. The reactor vessel was then flushed out with nitrogen for 10 min., and the solution transferred to it under nitrogen. In the case of the 150 ml. reactor (Fig. 8), nitrogen was passed very slowly over the surface of the solution during photolysis; evaporation of the solvent was reduced by bubbling the nitrogen through a sample of the same solvent before it entered the reactor vessel. Otherwise the system was sealed, and the pressure, caused by the temperature rise during photolysis, was released at intervals.

Solutions to be irradiated were not deoxygenated unless otherwise stated.

Note on diazotization

All diazotizations referred to in this thesis were carried out by the addition of a strong aqueous solution of sodium nitrite, cooled to $-5^{\circ}$, to the solution of the amine hydrochloride, cooled in a solid $CO_2$/ methylated spirit bath to about $-40^{\circ}$ until the

hydrochloride precipitated out as a slurry. The solution of the diazonium solution was used at once. By this method, the solution of the diazonium salt could be prepared very rapidly (the addition of the sodium nitrite taking only a few seconds), and in excellent yield.

## EXPERIMENTAL SECTION TO CHAPTER II

### Preparations

Diethylchloramine:- [173] Diethylchloramine was prepared by the interaction of chlorine with diethylamine in sodium bicarbonate solution at 10°. The yellow oil separated and was dried over calcium chloride. The yield was 49%.

p-Toluenesulphonylhydrazide:- [179] p-Toluenesulphonyl chloride (10.5 g.) was added in portions during 10 min. with cooling to hydrazine hydrate (11 ml.) The reaction mixture was heated on the water bath for 15 min., and the white solid was collected, and washed with water. p-Toluenesulphonylhydrazide (6.5 g., 64%), m.p. 109½-110° (lit. [179] 112°) was stored in a desiccator.

1-Naphthyl Methyl Ether:- To a solution of 1-naphthol (50 g.) in sodium hydroxide solution (150 ml. of 10%) was added dimethyl sulphate (45 g.) over 1½ hr. with stirring. The reaction was completed by heating the solution to 100° for ½ hr. After distillation the yield of 1-naphthyl methyl ether was 47 g. (85%).

1-Fluoronaphthalene:- [180] To a cold solution of 1-naphthyl diazonium chloride, prepared from 1-naphthylamine (30 g.) and sodium nitrite (15 g.), was added fluoroboric acid (60 ml. of 40%). The buff precipitate was filtered and washed successively with fluoroboric acid,

water, and ethanol (10 ml. each) and with ether (100 ml.). The product, 1-naphthyl diazonium fluoroborate (42 g.), was dried in a desiccator for 2 days.

In an apparatus set up for distillation the diazonium fluoroborate was cautiously heated to about 80°. A vigorous decomposition occurred. The product was distilled to give 1-fluoronaphthalene (12.[illegible] g., 43%), b.p. 210 - 215°/755 mm. The product shewed a single peak on g.l.c. (5% ppa, 125°, 9 p.s.i.) of Rt = 6.5 min.

2-Fluoronaphthalene:- This compound was prepared from 2-naphthylamine in the manner described above. The yield of the fluoroborate was 51 g. (91%). A portion (23 g.) was decomposed to give 2-fluoronaphthalene (5.8, 42%), m.p. 60 - 61° (lit.[180] 61°). The product shewed a single peak on g.l.c. (5% ppa, 125°, 9½ p.s.i.) of Rt = 7.2 min.

Irradiation of Anisole in Diethylamine

1. A solution of anisole (5.0 g.) in diethylamine (75 ml.) was irradiated in the 80 ml. quartz reactor for 15 hr. After evaporation of the solvent and separation to give neutral and basic material, anisole (1.8 g.) was recovered from the neutral extract. Chromatography on silica (100 g., 50 ml.) of the basic material, and eluting with 2% ether in benzene, afforded N, N-diethylaniline (0.86 g.), b.p. 155 - 170° (bath)/12 mm. (Found: N, 9.6; Calc. for $C_{10}H_{15}N$: N, 9.4%).

2. A solution of anisole (2.0 g.) in diethylamine (100 ml.) was irradiated for 15 hr. in the 150 ml. reactor using unfiltered light. A similar work-up procedure afforded anisole (0.52 g.) and N, N-diethylaniline (0.63 g.).

3. When irradiation (2) was repeated using anisole (1.00 g.) in diethylamine (100 ml.) the products were anisole (0.27 g.) and N, N-diethylaniline (0.30 g.).

Irradiation of Thioanisole in Diethylamine

A solution of thioanisole (5.0 g.) in diethylamine (70 ml.) was irradiated for 5 hr. in the 80 ml. quartz reactor. After distillation of the solvent and extraction, thioanisole (0.8 g.) was recovered from the non-basic material. G.l.c. analysis of the basic extract indicated that

N,N-diethylaniline Rt = 14.8 min. (5% ppa, 100°, 10 p.s.i.) was the major component. Chromatography on silica gel (100 g., 100 ml.) gave a product (0.47 g.) whose i-r spectrum was almost identical with that of diethylaniline, but which smelled of sulphur compounds even after distillation; however, g.l.c. indicated that the purity was > 95%.

Irradiation of Anisole in Methanolic Potassium Cyanide

A solution of anisole (2.0 g.) in saturated methanolic potassium cyanide solution (70 ml.) was irradiated for 15 hr. in the 80 ml. quartz reactor. The methanol was distilled, water was added, and the mixture extracted with ether. Chromatography of the residue of this extract on silica gel (60 g., 50 ml.) gave anisole (0.60 g.) and benzonitrile (0.04 g.), $\nu$ max. 2240 $cm.^{-1}$ (C ⋮ N stretching), g.l.c. retention time identical with authentic material, Rt = 8.8 min. (5% ppa, 125°, 10 p.s.i.).

Irradiation of Anisole in Acetic Acid

1. Anisole (15 g.) was irradiated for 22 hr. in solution in acetic acid (60 ml.) in the 80 ml. quartz reactor. After evaporation of the solvent, neutral and acidic ethereal extracts were made. Neither by t.l.c. (Silica G, benzene) nor g.l.c. (5% ppa, 100°, 8 p.s.i.) was there any indication that either phenylacetate was present in the neutral extract or phenol was present in the acidic extract.

2. To a saturated solution of potassium acetate in acetic acid (60 ml.) was added anisole (15 g.) and the mixture was irradiated for 20 hr. in the 20 ml. reactor. Again, neither phenyl acetate nor phenol could be detected among the products.

3. Dry hydrogen chloride was passed into acetic acid (16 ml.) for 2 hr. Anisole (4 g.) was added and the solution was irradiated for 20 hr. in the 20 ml. quartz reactor vessel. Neither phenyl acetate nor phenol was detected among the products.

Irradiation of Benzonitrile in Diethylamine

A solution of benzonitrile (2.0 g.) in diethylamine (18 ml.) was irradiated for 15 hr. in the 20 ml. quartz reactor vessel. The solvent was distilled and neutral and basic extracts were made. G.l.c. (5% ppa, 100°, 10 p.s.i.) indicated that N, N-diethylaniline was not present in the basic extract. The neutral fraction was evaporated and the benzonitrile was distilled to leave a sticky residue. T.l.c. (Silica G, ether) indicated a small spot of Rf similar to that of benzamide. The i-r spectrum had $\nu$ max. 1660 $cm.^{-1}$ (C = O stretch of amide).

Irradiation of Nitrobenzene in Diethylamine

A solution of nitrobenzene (5.00 g.) in diethylamine (70 ml.) was irradiated for 19 hr. in the 20 ml. quartz reactor. After evap-

oration of the solvent, neutral and basic ethereal extracts were made. The basic fraction was examined by g.l.c. (5% ppa, 110°, 10 p.s.i.) and shewed one major component (Rt 9.8 min.). Chromatography on silica gel (100 g., 50 ml.) gave, on elution with 2% ether in benzene (950 ml.), aniline (1.2 g.), b.p. 160 - 170° (bath)/12 mm.; acetyl derivative m.p. 113 - 114°; benzoyl derivative m.p. 162 - 163°. Neither g.l.c. nor t.l.c. (Silica G, benzene) indicated that N,N-diethylaniline was present.

The neutral material was extracted with warm light petrol and the black tarry residue was discarded. Recrystallization from methanol gave red needles (160 mg.), m.p. 68 - 72°. After several recrystallizations the m.p. was 78 - 80° (lit.[84] 81°). From the physical data the structure was deduced to be that of 2-hydroxyazobenzene. (Found: C, 73.0, 72.6; H, 5.6, 5.2; N, 14.1. Calc. for $C_{12}H_{10}N_2O$: C, 72.7; H, 5.1; N, 14.1%). N.m.r. ($CDCl_3$): τ -2.87 (1 proton, singlet, - O<u>H</u>), τ 1.9 to 3.1 (9 protons, complex multiplet, aromatic C - H). The mass spectrum shewed a molecular ion at $m^+/e$ 198 and strong fragments at $m^+/e$ 121 ($C_6H_5N_2O^+$), 93 ($C_6H_5O^+$), and 77 (base peak: $C_6H_5^+$).

<u>Irradiation of Diethylchloramine with Fluorobenzene</u>

A mixture of diethylchloramine (10.0 g.), fluorobenzene (10.0 g.),

and methanol (55 ml.) was irradiated in the 80 ml. quartz reactor for 2 hr. The reaction mixture was analysed by g.l.c. (5% ppa, 100°, 10 p.s.i.). Three compounds of Rt 7 min., 12 min., and 16 min. were present but there was no peak of Rt 14.8 min. corresponding to diethylaniline.

Irradiation of p-Toluenesulphonylhydrazide and Cyclohexene

A mixture of p-toluenesulphonylhydrazide (3.0 g.), cyclohexene (2.0 g.) and benzene (10 ml.) was irradiated for 24 hr. with a 125 W. external source (Pyrex flask, reflux condenser). G.l.c. analysis (5% ppa, 100°, 10 p.s.i.) indicated that bicyclohexenyl (Rt = 4.5 min.) was present in the reaction mixture.

Irradiation of p-Toluenesulphonylhydrazide and Fluorobenzene

A mixture of p-toluenesulphonylhydrazide (3.0 g.), fluorobenzene (2.0 g.), and benzene (10 ml.) was irradiated with a 125 W. external source (Pyrex flask, reflux condenser) for 24 hr. G.l.c. analysis (5% ppa, 150°, 10 p.s.i.) indicated that biphenyl (Rt = 7.7 min.) was not present in the mixture.

Irradiation of 3, 5-Dimethylanisole

A solution of 3, 5-dimethylanisole (2.00 g.) in diethylamine (100 ml.) was irradiated for 14½ hr. in the 150 ml. reactor using unfiltered light. After the usual separation, the extracts were examined

by g.l.c. (5% ppa, 125°, 9 p.s.i.). The neutral fraction shewed a peak at Rt 3.5 min., corresponding to starting materials, and a very weak peak at Rt 5.0 min. (unknown). Distillation of this fraction gave 2, 5-dimethylanisole (1.0 g.).

The basic fraction shewed a strong peak on g.l.c. at Rt 10.7 min. and a very weak peak at Rt 16.5 min. Chromatography of the residue on silica gel (30 g., 50 ml.) on elution with 1% ether in benzene (600 ml.) gave, as the only isolable product, N, N-diethyl -2, 5-dimethylaniline (450 mg.) as colourless plates from petrol, m.p. 45 - 47°. (Found: C, 80.9; H, 10.4; N, 8.3. $C_{12}H_{19}N$ requires C, 81.3; H, 10.7; N, 7.9%). N.m.r. ($CDCl_3$): τ 3.63 (3 protons, singlet, aromatic C - H), τ 6.65 (4 protons, quartet, J 7 c/s, $-CH_2-$), τ 7.72 (6 protons, singlet, ring methyl C - H), τ 8.84 (6 protons, triplet, J 7 c/s, $-CH_2-CH_3$.) λ max. (EtOH): 304 mμ(ε 2100), 263 mμ(13,000), 212 mμ (21,000); ν max. ($CS_2$): 835, 825 $cm.^{-1}$ (1, 3, 5-trisubstituted benzene).

Irradiation of 2, 6-Dimethylanisole

A solution of 2, 6-dimethylanisole (2.0 g.) in diethylamine (100 ml.) was irradiated for 14 hr. in the 150 ml. reactor using unfiltered light. After the usual separation procedure the extracts were examined by g.l.c. (5% ppa, 125°, 9 p.s.i.). The neutral extract contained only starting material (Rt = 1.7 min.) and this (0.95 g.),

was obtained by distillation of the residue of this extract.

The basic fraction contained neither 3, 5-dimethyl-N, N-diethylaniline (Rt = 10.7 min.) nor anything of comparable Rt. T.l.c. (Silica HF, benzene) indicated that no non-polar material was present and the extract evaporated almost to dryness.

Kinetic Experiments

The reactor vessel used was the system of concentric quartz cylinders shewn in Fig. 7. The lamp was placed at the centre, thus providing constant geometry. Short wavelength light was excluded by the use of 8N aqueous acetic acid as a filter solution; this cuts off sharply at 240 mμ. This filter solution helped to reduce the deposition of polymer on the reactor walls.

In each run a measured quantity of the aromatic compound (fluorobenzene) was irradiated with a measured quantity of the nucleophile. The fluorobenzene was weighed directly, as was the nucleophile when this was an amine. Alkoxide solutions were estimated by titration against standard acid. In order to eliminate possible titration errors caused by the non aqueous medium, the alkoxide solution was diluted with a large excess of water before titration commenced.

Samples were removed from the solution using a syringe without interrupting the photolysis. To the sample (0.9 ml.) was added a solution of the marker (0.1 ml.) and the mixture was analysed by g.l.c. Where an amine was the nucleophile, difficulty in measuring the peaks was encountered because of tailing of the peak due to the amine. This problem was overcome in the alkoxide series by passing hydrogen chloride through the sample before adding the

marker. The nucleophile was destroyed and sodium chloride was precipitated.

Knowing the relative sizes of the peaks on the g.l.c. trace by standard solutions, and knowing the concentration of marker in the sample, the concentration of product in the sample may be deduced from the areas of the peaks on the g.l.c. trace (See Appendix 2).

Irradiation of 1-Naphthyl Methyl Ether

1. A solution of 1-naphthyl methyl ether (16.4 g.) in 60% piperidine in methanol (250 ml.) was irradiated for 16½ hr. in the 250 ml. reactor vessel using unfiltered light. After evaporation of the solvent and separation, 1-naphthyl methyl ether (7.3 g.) was recovered from the non-basic material together with 1-naphthol (0.54 g.),(m.p. 93 - 94°). Chromatography of the basic material on silica gel (100 g., 50 ml.) gave 1-naphthyl methyl ether (1.1 g.) on elution with benzene (300 ml.).

1% Ether in benzene (1000 ml.) eluted an oil (0.10 g.), b.p. 180 - 200° (bath)/2 mm. n.m.r. ($CCl_4$): τ 2.3 - 3.0 (complex multiplet, aromatic C - H), τ 4.3 (broad singlet, phenolic O - H), τ 6.05 (singlet, $-OCH_3$), τ 6.8 (distorted quartet, $N - CH_2 -$), τ 8.5 (complex multiplet, $>CH_2$ groups). Weaker resonances appeared at τ 7.7 and 8.7 but could not be assigned.

2% Ether in benzene (700 ml.) eluted a yellow oil (120 mg.), which darkened rapidly on exposure to the air. Similar features to those observed for the compound above were found in the i-r and n.m.r. spectra.

2. A solution of 1-naphthyl methyl ether (3.0 g.) in diethylamine (70 ml.) was irradiated for 5½ hr. in the 80 ml. quartz reactor. After

evaporation of the solvent and separation, the neutral material yielded 1-naphthyl methyl ether (1.0 g.) and an acidic extract yielded 1-naphthol (0.02 g.), m.p. 90 - 93°. Distillation of the basic material yielded 1-naphthyl methyl ether (0.24 g.).

3. A solution of 1-naphthyl methyl ether (5.0 g.) in diethylamine (70 ml.) was irradiated for 16 hr. in the 80 ml. quartz reactor. After evaporation of the solvent, methanol (100 ml.) was added, and the mixture was hydrogenated using 10% palladium on charcoal (0.25 g.) as a catalyst. No hydrogen was taken up, even after several hours. The solution was filtered, and a 1% solution of bromine in carbon tetrachloride was added to the filtrate. A white precipitate formed, but this rapidly changed to an intractable black tar, soluble in acetone but not in most other solvents. T.l.c. (Silica G, benzene) indicated the presence of more than ten compounds.

4. A deoxygenated solution of 1-naphthyl methyl ether (1.00 g.) in 80% diethylamine in water (200 ml.) was irradiated for 1½ hr. in the 250 ml. reactor, using unfiltered light. Ether (100 ml.) and saturated brine (100 ml.) were added. The organic phase was dried and evaporated. Ether (200 ml.) was added, and the separation and evaporation were repeated.

T.l.c. (Silica HF, benzene) indicated four spots, all very

weak. Preparative t.l.c. (40% benzene in petrol, x 2) gave several bands, but none contained sufficient material to identify.

Irradiation of 2-Naphthyl Methyl Ether

1. A solution of 2-naphthyl methyl ether (7.6 g.) in isopropylamine (250 ml.) was irradiated for 12 hr. in the 250 ml. reactor using unfiltered light. White crystals (0.49 g.) were recovered from the solution. These were insoluble in all common solvents and had m.p. 154 - 155° (decomp.); lit.[95] 155 - 160° (decomp.); dimer of 2-naphthyl methyl ether.

After evaporation of the solvent from the rest of the reaction mixture, and separation, 2-naphthyl methyl ether (0.6 g.), m.p. 71 - 72°, was recovered from the neutral fraction. The basic material shewed seven spots on t.l.c. (Silica G, benzene; and Silica G, ether), but none was present in sufficient quantity to isolate by chromatography on silica gel (100 g., 60 ml.).

2. A deoxygenated solution of 2-naphthyl methyl ether (1.00 g.) in 80% diethylamine in water (200 ml.) was irradiated for 1⅓ hr. in the 250 ml. reactor, using unfiltered light. After several additions of ether followed by evaporation the residue was separated by preparative t.l.c. (40% benzene in petrol, x 2) to give 2-naphthyl methyl ether (0.15 g.) and an oil (0.14 g.), which was a mixture of 2-naphthyl methyl ether (0.04 g.) and N, N-diethyl-2-naphthylamine

(0.10 g.), b.p. 200 - 220° (bath) /0.1 mm. N.m.r. ($CCl_4$): $\tau$ 2.3 - 3.4 (7 protons, complex multiplet, aromatic C - H), $\tau$ 6.60 ( 4 protons, quartet J 7 c/s, -N-$CH_2$-), $\tau$ 8.81 (6 protons, triplet J 7 c/s, -$CH_3$). (Found: C, 84.2; H, 8.3; N, 7.3. $C_{14}H_{17}N$ requires C, 84.4; H, 8.5; N, 7.0%). The i-r spectrum was identical to that of an authentic specimen, prepared by the action of ethyliodide upon 2-naphthylamine.

Irradiation of 1-Fluoronaphthalene

1. A solution of 1-fluoronaphthalene (2.1 g.) in diethylamine (100 ml.) was irradiated for 7 hr. in the 150 ml. reactor, using the quartz probe. After evaporation of the solvent, basic and non-basic ethereal extracts were made.

Chromatography on silica gel (80 g., 50 ml.), eluting with 1% ether in benzene (600 ml.) afforded N, N-diethyl- 1-naphthylamine (0.23 g.), b.p. 200 - 210° (bath) /1mm. which gave one peak Rt = 22.8 min. on g.l.c. (5% ppa, 125°, 10 p.s.i.). (Found: C, 84.4; H, 8.1; N, 7.2. $C_{14}H_{17}N$ requires C, 84.4; H, 8.5; N, 7.0%). N.m.r. ($CCl_4$): $\tau$ 1.6 - 3.0 (7 protons, complex multiplet, aromatic C - H), $\tau$ 6.84 (4 protons, quartet J 7 c/s, N-$CH_2$-), $\tau$ 8.98 (6 protons, triplet J 7 c/s, -$CH_3$). The i-r spectrum was identical to an authentic sample prepared by the action of ethyliodide upon

1-naphthylamine.

The neutral material (1. 0 g.) on evaporation had an i-r spectrum unlike that of 1-fluornaphthalene. Distillation of a portion gave a yellow liquid which was shewn by g. l. c. (5% ppa, 125° 9 p. s. i.) to be a mixture of 1-fluoronaphthalene Rt = 6. 5 min. and one other compound Rt = 7. 2 min. The n. m. r. spectrum shewed resonances at $\tau$ 2.0 - 3. 2, 4. 15, and 6. 65 but other smaller peaks in the spectrum were observed.

2. A solution of 1-fluoronaphthalene (1.0 g.) in diethylamine (200 ml.) was irradiated using unfiltered light for 3½ hr. in the 250 ml. reactor. The solvent was evaporated at room temperature and the residue was separated by preparative t. l. c. (40% benzene in petrol, x 2). The least polar material (0. 13 g.) was shewn by t. l. c. (Silica HF, 20% benzene in petrol) to be a mixture and was separated on a 20 cm. x 20 cm. x 1 mm. layer plate (15% benzene in petrol). The less polar major component, on freeing from silica by Soxhlet extraction had an n. m. r. spectrum similar to that obtained before.

The second component of the first preparative t. l. c. was shewn to be N, N- diethyl-2-naphthylamine (0. 10 g.).

3. A solution of 1-fluoronaphthalene (1.0 g.) in diethylamine (150 ml.) was irradiated for 4 hr. in the 150 ml. reactor using unfiltered light. The solvent was evaporated at room temperature and

the residue was separated by preparative t.l.c. (10% benzene in petrol, x 2). The least polar material was freed from silica by shaking with ether (3 x 50 ml.) and the ether was removed at room temperature to give 2-fluoro-3, 4-benz-tricyclo-(3, 1, 0, $0^{2,6}$)-hex-3-ene (0.12 g.).

$\lambda$ max. ($Et_2O$): 310 m$\mu$ (no fine structure; unlike 1-fluoronaphthalene, several maxima in this region). $\nu$ max. (film): 770, 700 cm.$^{-1}$ (ortho disubstituted benzene), 1240 cm.$^{-1}$ (C - F); n.m.r. ($CCl_4$): $\tau$ 2.1 - 3.4 (4 protons, complex multiplet, aromatic C - H), $\tau$ 4.15 (1 proton, broad singlet, C(5) - H), $\tau$ 6.65 (2 protons, broad singlet, C(1) - H and C(6) - H). The mass spectrum shewed a molecular ion at $m^+/e$ 146, and a strongly produced fragment at $m^+/e$ 91 which was absent from the mass spectrum of 1-fluoronaphthalene.

4. Irradiations of 1-fluoronaphthalene (2.0 g.) in the 150 ml. reactor in 100 ml. each of acetonitrile, ether, and isopropanol led, according to the evidence of t.l.c. (Silica HF, benzene) and g.l.c. (5% ppa, 125°, 9 p.s.i.), only to recovery of the starting material, which was isolated in recoveries of from 70 to 90%.

Irradiation of 2-Fluoronaphthalene

1. A solution of 2-fluoronaphthalene (2.0 g.) in diethylamine (30 ml.) was irradiated using unfiltered light for 6½ hr. in the 150 ml. reactor. After evaporation of the solvent and separation, chromato-

graphy on silica gel (60 g., 50 ml.) of the basic fraction, eluting with 1% ether (300 ml.), gave N, N-diethyl-2-naphthylamine (0.16 g.), identical to an authentic sample.

Distillation of the neutral material gave a mixture which was largely 2-fluoronaphthalene.

2. A solution of 2-fluoronaphthalene (1.0 g.) in diethylamine (200 ml.) was irradiated for 3½ hr. in the 250 ml. reactor using unfiltered light. After evaporation of the solvent, the residue was separated by preparative t.l.c. (40% benzene in petrol, x 2). The least polar material (0.09 g.) did not crystallize, and was shewn by t.l.c. to be a mixture of three compounds.

The more polar material (0.13 g.) was N, N-diethyl-2-naphthylamine.

3. The irradiation was repeated and the solvent was removed at room temperature. The first band from preparative t.l.c. (10% benzene in petrol x 2) was freed from silica with cold ether (3 x 50 ml.) and the ether was evaporated at room temperature to give the product (0.05 g.). The n.m.r. spectrum shewed, together with a large number of small peaks, resonances at $\tau$ 2.97 (broad singlet) and $\tau$ 6.55 (distorted quartet) in the ratio of 5:2. The sample decomposed very rapidly, and when recovered from the n.m.r. tube, shewed several spots on t.l.c.

## EXPERIMENTAL SECTION TO CHAPTER III

### Preparations

The isomeric fluoro- and methoxy-benzonitriles were prepared from the fluoro- and methoxy-anilines with cuprous cyanide by the method of Sandmeyer.[181] They were purified by distillation or recrystallization, and the yields are presented in Table 11. The scale of the preparations was 0.1M.

Table 11

Preparation of substituted benzonitriles

| Substituent | Yield % | m.p. | lit. | Analysis |
|---|---|---|---|---|
| o-$OCH_3$ | 38 | 22 - 23° | 24.5° [a] | 10.8 [b] |
| m-$OCH_3$ | 30 | oil | - | 10.8 [b] |
| p-$OCH_3$ | 40 | 58 - 59° | 60° [c] | 10.6 [b] |
| o-F | 21 | oil | - | 15.8 [d] |
| m-F | 23 | oil | - | 15.6 [d] |
| p-F | 52 | 33½ - 34½° | 34.6° [e] | 15.7 [d] |

Notes: (a) Ref. 182,
(b) Analysed for N: calculated value 10.5%,
(c) Ref. 183,
(d) Analysed for F: calculated value 15.7%,
(e) Ref. 184

Irradiations

Since no products were isolated from the irradiations, the conditions only will be given; these are found below in Table 12. All irradiations used unfiltered light.

Table 12

Irradiation Conditions for Disubstituted Benzenes

| Substrate | Quantity (g) | Solvent | Quantity (ml.) | Reactor (ml.) | Time (hr.) | Note |
|---|---|---|---|---|---|---|
| o-Fluoroaniline | 0.06 | Diethylamine | 100 | 150 | 6 | c |
| m-Fluoroaniline | 0.10 | Diethylamine | 100 | 150 | 3 | c |
| m-Fluoroaniline | 0.60 | Diethylamine | 100 | 150 | 6 | c |
| m-Fluoroaniline | 1.00 | Diethylamine | 100 | 150 | 14 | c |
| m-Fluoroaniline | 2.00 | Diethylamine | 100 | 150 | 6 | c |
| p-Fluoroaniline | 0.60 | Diethylamine | 100 | 150 | 7 | c |
| p-Fluoroaniline | 2.00 | Diethylamine | 100 | 150 | 6 | c |
| p-Fluoroaniline | 1.00 | 50% Aqueous Diethylamine | 100 | 150 | 14 | c |
| p-Anisidine | 2.00 | Diethylamine | 100 | 150 | 8 | e |
| o-Fluorobenzonitrile | 0.43 | Diethylamine | 150 | 150 | 1½ | d |
| m-Fluorobenzonitrile | 0.31 | Diethylamine | 100 | 150 | 1¼ | d |

Continued /

Table 12 (Continued)

| Substrate | Quantity (g) | Solvent | Quantity (ml.) | Reactor (ml.) | Time (hr.) | Note |
|---|---|---|---|---|---|---|
| p-Fluorobenzonitrile | 0.34 | Diethylamine | 100 | 150 | 2 | d |
| o-Methoxybenzonitrile | 0.41 | Diethylamine | 100 | 150 | 4 | d |
| p-Methoxybenzonitrile | 0.52 | (a) | 170 | 250 | 4 | e |
| p-Methoxybenzonitrile | 0.92 | (a) | 150 | 150 | 13½ | e |
| m-Nitrobenzaldehyde | 1.00 | (a) | 150 | 150 | 1[illegible] | e |
| m-Nitrobenzoic acid | 2.00 | (b) | 900 | 1 l. | 4 | f |
| p-Nitrobenzoic acid | 1.00 | (b) | 900 | 1 l. | 5 | f |
| o-Methoxybenzoic acid | 1.12 | (b) | 900 | 1 l. | 7 | f |
| p-Methoxybenzoic acid | 1.00 | (b) | 900 | 1 l. | 6 | f |
| m-Nitrobenzonitrile | 1.00 | (a) | 150 | 150 | 7 | e |
| p-Dimethoxybenzene | 4.00 | Diethylamine | 170 | 250 | 14 | d |

Continued /

Table 12 (Continued)

Notes: (a) ~ 0.1N Sodium hydroxide in aqueous acetonitrile,

(b) ~ 0.1N Aqueous sodium hydroxide,

(c) Worked up by acetylation, followed by acid/base separation; the basic fraction showed a large number of spots in low yield on t.l.c. (Silica G, 10% ether in benzene),

(d) As (c), without prior acetylation,

(e) Examined by g.l.c. (TPA, 175°, 10 p.s.i.); only starting material detected;(f) as (e) after esterification with methanol/sulphuric acid.

## EXPERIMENTAL SECTION TO CHAPTER IV

### Preparations

6-Hydroxy-3, 3'-azoanisole:- A solution of m-anisidine (1.0 g.) in N hydrochloric acid (20 ml.) was cooled to -4°° and diazotised with a solution of sodium nitrite (0.6 g.) in water (10 ml.). The resultant solution was poured into a cooled solution of p-methoxyphenol (1.0 g.) in 5N sodium hydroxide solution (10 ml.). Extraction into ether of the acidified solution and chromatography on silica gel (100 g., 100 ml.) gave, on elution with 4% ether in benzene (600 ml.), 6-hydroxy-3, 3'-dimethoxyazobenzene (1.4 g., 67%) as orange needles from petrol, m.p. 74 - 75° (softened at 67° even after several recrystallizations). (Found: C, 65.1; H, 5.3; N, 10.8. $C_{14}H_{14}N_2O_3$ requires C, 65.2; H, 5.4; N, 10.9%). N.m.r. ($CDCl_3$): $\tau$ -2.35 (1 proton, singlet, -O<u>H</u>), $\tau$ 2.4 to 3.1 (7 protons, complex multiplet, aromatic C - <u>H</u>), $\tau$ 6.15 (6 protons, singlet, 2 x -OC<u>H</u>$_3$). $\lambda$ max. (EtOH): 420 m$\mu$ ($\epsilon$ 7,200), 322 m$\mu$ (16,000), 258 m$\mu$ (9,500). The mass spectrum showed a molecular ion at $m^+/e$ 258.

Phenylhydroxylamine:- Phenylhydroxylamine was prepared by the reduction of nitrobenzene by zinc dust in alkaline solution. The yield of phenylhydroxylamine, m.p. 80 - 81°, was 75%.

Nitrosobenzene:- Nitrosobenzene was prepared by the oxidation

at 0° of phenylhydroxylamine by sodium dichromate solution. After steam-distillation the yield of nitrosobenzene was 53%; recrystallized from methanol, m. p. 66 - 67°.

o-Nitrobenzoyl Chloride:- A mixture of o-nitrobenzoic acid (16.7 g.) and thionyl chloride (30 g.) was refluxed on the water bath for 1½ hr. The excess thionyl chloride was removed by passing nitrogen for 12 hr. through the reaction mixture at 40° and the o-nitrobenzoyl chloride was used undistilled. (An attempt to distil the compound led to an explosion.[185])

o-Nitrobenzyl Alcohol from o-Nitrobenzoyl Chloride:-[186] A mixture of o-nitrobenzoyl chloride (prepared above) and sodium borohydride (7 g.) in dry dioxan (40 ml.) was heated on the water bath for 2 hr. The mixture was cooled to room temperature and water (20 ml.) was added. The mixture was evaporated to dryness and the residue crystallized from hot water to give o-nitrobenzyl alcohol (2.6 g.), m.p. 70 - 71° (lit.[187, 188] 72°, 74°). (Found: C, 54.7; H, 4.7; N, 9.1. Calc. for $C_7H_7NO_3$: C, 54.9; H, 4.6; N, 9.2%).

m-Nitrobenzonitrile:- Benzonitrile (10 g.) was nitrated by the method of Baker, Cooper and Ingold.[189] The reaction mixture was diluted with water (1 l.) and the product (13.3 g.) was filtered and dried over calcium chloride. Crystallization from petrol was unsatisfactory,

20% methanol in petrol afforded pure m-nitrobenzonitrile (3.6 g.), m.p. 116 - 117°, which was pure by g.l.c. (5% ppa, 125°, 10 p.s.i.), Rt = 12 min.

The reaction was repeated, and the reaction mixture was neutralized with sodium carbonate, and extracted into chloroform. The extract was allowed to crystallize, filtered and the process repeated, giving m-nitrobenzonitrile (9.7 g.), m.p. 115 - 117°.

Oxygenation of Phenylhydroxylamine

1. A stream of oxygen was bubbled for 30 min. through a solution of phenylhydroxylamine (160 mg.) in diethylamine (20 ml.). T.l.c. (Silica HF, 40% benzene in petrol) indicated that only one compound was present in the reaction mixture. After evaporation of the solvent, the residue was chromatographed on silica gel (30 g., 250 ml.) when benzene (500 ml.) eluted azoxybenzene (141 mg.), m.p. 34½ - 35°.

2. A solution of phenylhydroxylamine (323 mg.) in isopropanol (30 ml.) was oxygenated for 16 hr. Isolation by the above method afforded azoxybenzene (258 mg.), m.p. 34 - 35°.

Reaction of Nitrosobenzene with Piperidine

A mixture of nitrosobenzene (0.53 g.) and piperidine (0.42 g.) was dissolved in benzene (15 ml.). When the exothermic reaction had subsided, the reaction mixture was refluxed for 30 min. After evaporation of the solvent, t.l.c. (Silica HF, 40% benzene in petrol) indicated two major components while t.l.c. (Silica HF, 30% ether in benzene) indicated a large number of minor components.

The major components were isolated by preparative t.l.c. (40% benzene in petrol, x 2) and were shewn to be azobenzene (18 mg.), m.p. 65 - 67°, and azoxybenzene (245 mg.), m.p. 35 - 36°.

Irradiation of Nitrobenzene in Diethylamine
(See also experimental section to Chapter II)

1. A solution of nitrobenzene (0.50 g.) in diethylamine (100 ml.) was irradiated with unfiltered light in the 150 ml. reactor for 5 hr. The solvent was distilled and the residue was separated into basic and neutral material. Distillation of the basic material afforded aniline (140 mg., b.p. 150 - 160° (bath)/12 mm.); acetyl derivative, m.p. 113 - 114°. No product could be isolated from the neutral fraction.

2. A solution of nitrobenzene (0.50 g.) in diethylamine (100 ml.) was irradiated for 5 hr. in the 150 ml. reactor using the Pyrex probe. After separation as above, distillation of the basic material yielded aniline (17 mg.). The neutral extract was separated by preparative t.l.c. (40% benzene in petrol, x 1) yielding, in increasing order of polarity, azobenzene (56 mg.) m.p. 68 - 69°, (Found: N, 15.0. Calc. for $C_{12}H_{10}N_2$: N, 15.4%); 2-hydroxyazobenzene (92 mg.), m.p. 80 - 82°, (Found: N, 13.9. Calc. for $C_{12}H_{10}N_2O$; N, 14.1%), and nitrobenzene (119 mg.), b.p. (bath) 150 - 170°/1 mm.

Irradiation of m-Nitroanisole in Diethylamine

1. A solution of m-nitroanisole (0.53 g.) in diethylamine (100 ml.) was irradiated for 6 hr. in the 150 ml. reactor using the quartz probe. After separation into neutral and basic fractions, distillation of the latter

afforded m-anisidine (145 mg.), b.p. 130 - 190° (bath)/12 mm.; acetyl derivative, m.p. 75 - 80°. No product was isolated from the non-basic material.

2. A solution of m-nitroanisole (0.60 g.) in diethylamine (100 ml.) was irradiated for 9 hr. in the 150 ml. reactor using the Pyrex probe. After separation as above, distillation of the basic material yielded m-anisidine (55 mg.). Chromatography on silica gel (50 g., 25 ml.) eluting with 10% ether in benzene (100 ml.) eluted an orange solid (145 mg.), m.p. 52 - 60°, (A). A further 25 ml. fraction eluted an orange solid (55 mg.) which was shewn by t.l.c. (Silica G, 30% ether in benzene) to be a mixture of 'A' and the subsequent material, and was rechromatographed (20 g., 20 ml.) to give 25 mg. of each component. The third component (105 mg.) eluted with more 10% ether in benzene (150 ml.), and crystallized from methanol as dark red needles, m.p. 125 - 126°, and was identified as 2-hydroxy-3,3'-azoanisole. (Found: C, 65.4; H, 5.9; N, 10.7; $C_{14}H_{14}N_2O_3$ requires C, 65.2; H, 5.4; N, 10.9%). N.m.r. ($CDCl_3$): $\tau$ -3.20 (1 proton, singlet, -OH). $\tau$ 2.3 - 3.1 (7 protons, complex multiplet, aromatic C - H), $\tau$ 6.05 (3 protons, singlet, $-OCH_3$), $\tau$ 6.11 (3 protons, singlet, $-OCH_3$). $\lambda$ max. (EtOH): 435 mμ (sh.) ($\epsilon$ 2,600), 335 mμ (15,000), 255 mμ (sh.) (3,500). The mass spectrum shewed a molecular ion at $m^+/e$ 258.

The material 'A' was shewn by t.l.c. (Silica HF, 50% benzene in petrol) to be a mixture of two compounds. Preparative t.l.c. on a 20 cm. x 20 cm. plate with a 1 mm. layer of silica (40% benzene in petrol, x 2) gave two bands. The first was extracted to give 3, 3'-dimethoxyazobenzene, m.p. 76½ - 77½°. (Found: N, 11.3. Calc. for $C_{14}H_{14}N_2O_2$; N, 11.5%). The second band was shewn to be identical with a synthesised sample of 6-hydroxy-3, 3'-azoanisole and had m.p. 73 - 74°. (Found: N, 10.5. Calc. for $C_{14}H_{14}N_2O_3$: N, 10.4%). The relative quantities of the two compounds (116 mg. and 54 mg. respectively) were determined from the integration of an n.m.r. ($CDCl_3$) of the crude mixture 'A'.

Irradiation of p-Nitroanisole in Diethylamine

1. A solution of p-nitroanisole (0.60 g.) in diethylamine (100 ml.) was irradiated for 6 hr. in the 150 ml. reactor using unfiltered light. After evaporation of the solvent, the residue was chromatographed on silica gel (50 g., 40 ml.). 2% Ether in benzene (200 ml.) eluted a yellow solid (45 mg.), which was identical with authentic 4, 4'-azoanisole, m.p. 162 - 163°. 10% Ether in benzene (200 ml.) eluted a brown oil (100 mg.) which was distilled to give p-anisidine, b.p. 130 - 140° (bath)/12 mm. and had an acetyl derivative identical with p-methoxyacetanilide, m.p. 128 - 129°.

2. The photolysis was repeated, but the solution was deoxygenated

before irradiation. After a similar isolation procedure the products were 4, 4'-azoanisole (85 mg.), m.p. 160 - 162° and p-anisidine (195 mg.), acetyl derivative, m.p. 128 - 129°.

3. A solution of p-nitroanisole (0.60 g.) in diethylamine (100 ml.) was irradiated for 6 hr. in the 150 ml. reactor using a Pyrex filter. After evaporation of the solvent, t.l.c. (Silica HF, 10% ether in petrol) indicated only one spot. Chromatography on silica gel (50 g., 100 ml.), eluting with benzene (200 ml.) gave 4, 4'-azoanisole (340 mg.), m.p. 158 - 161°, after recrystallization from petrol, m.p. 162 - 163°.

4. Photolysis (3) was repeated with prior deoxygenation of the reactants. After oxygen had been bubbled through the solution for ½ hr., t.l.c. (Silica HF, 40% benzene in petrol) indicated that two compounds were present in the reaction mixture. Chromatography on silica gel (50 g., 100 ml.) gave a yellow solid (570 mg.) on elution with 2% ether in benzene (400 ml.). This was separated by preparative t.l.c. (40% benzene in petrol, x 5) to give 4, 4'-azoanisole (130 mg.), m.p. 162 - 163°, and 4, 4'-azoxyanisole (240 mg.), yellow plates from 1:1, benzene: petrol, m.p. 118½ - 119°. (Found: C, 64.8; H, 5.6; N, 10.3. Calc. for $C_{14}H_{14}N_2O_3$: C, 65.2; H, 5.4; N, 10.9%.

Irradiation of p-Nitroanisole in Ether

A deoxygenated solution of p-nitroanisole (1.03 g.) in ether (120 ml.)

was irradiated for 2½ hr. in the 150 ml. reactor using the Pyrex filter. The reaction mixture was split into two equal portions.

The first portion was immediately extracted with 2N hydrochloric acid. From the aqueous extract was isolated p-anisidine (44 mg.) by distillation. The neutral material was separated by preparative t.l.c. (40% benzene in petrol, x 5) to give p-nitroanisole (350 mg.), m.p. 52 - 53°, and 4,4'-azoxyanisole (17 mg.), m.p. 116 - 118°.

To the second portion was added triethylamine (10 ml.) and the reaction mixture was oxygenated for ½ hr. After a similar isolation procedure, the products were p-anisidine (38 mg.), p-nitroanisole (35[illegible] mg.), and 4,4'-azoxyanisole (16 mg.).

Irradiation of Nitrobenzene in Solvents other than Diethylamine

Nitrobenzene (0.5[illegible] g.) was dissolved in the appropriate solvent (100 ml.) and irradiated in the 150 ml. reactor using the Pyrex filter. After evaporation of the solvent, the residue was extracted to give basic and non-basic ethereal solutions.

The basic fraction was dried and evaporated, and the residue examined by t.l.c. (Silica G, 10% ether in benzene) to determine whether aniline was present. When this was the case the residue was distilled to give aniline, identified by i-r spectrometry and by preparation of the acetyl derivative.

The non-basic material was separated by preparative t.l.c. (20% benzene in petrol, x 1 or x 2). The bands were extracted to give, in increasing order of polarity, azobenzene, 2-hydroxyazobenzene, and nitrobenzene. The former two compounds were identified by their m.p. and i-r spectra; nitrobenzene i-r alone; $\nu$ max. 675, 690, 700, 740, 855, 1350, 1525 cm.$^{-1}$ (all strong absorptions).

The results of these experiments are summarised in Table 13.

Irradiation of 4-Nitrobiphenyl

A solution of p-nitrobiphenyl (1.00 g.) in diethylamine (150 ml.) was irradiated for 3 hr. in the 150 ml. reactor, using the Pyrex filter. The solvent was evaporated and neutral and basic extracts in chloroform were made. The basic material (15 mg.) was intractable. The neutral extract was separated by preparative t.l.c. (20% benzene in petrol, x 12) to give 4, 4'-azobiphenyl (2 mg.), m.p. 254 - 255° (lit.[190] 249°), molecular ion $m^+/e$ 334; 4-nitrobiphenyl (10 mg.), m.p. 113 - 114°; 4, 4'-azoxybiphenyl (221 mg.), orange needles from benzene m.p. 212 - 215° (lit.[190] 212°), mixed m.p. 212 - 215°, molecular ion $m^+/e$ 350; and cis-4. 4'-azoxybiphenyl (372 mg.) as minute round plates from benzene, m.p. 218 - 220°, molecular ion $m^+/e$ 350. (Found: N, 8.2; $C_{24}H_{18}N_2O$ requires N, 8.0%).

Table 13

Solvent Dependence of the Products from the Irradiation of Nitrobenzene

| Solvent | Time hr. | Aniline mg. | Acetyl Deriv. m. p. | Azobenzene mg. | Azobenzene m. p. | 2-Hydroxy-azobenzene[a] mg. | 2-Hydroxy-azobenzene[a] m. p. | Nitrobenzene mg. |
|---|---|---|---|---|---|---|---|---|
| Petrol | 5 | 4 | - | - | - | - | - | 270 |
| Toluene | 5 | 3 | - | - | - | - | - | 320 |
| t-Butanol | 5 | - | - | - | - | - | - | 305 |
| 50% t-Butanol/Toluene | 5 | - | - | - | - | - | - | 375 |
| Ether[b] | 5 | 120 | 112-3° | 16 | 67° | 15 | 80° | 130 |
| Ether[c] | 5 | 110 | 113-4° | - | - | - | - | 145 |
| Isopropanol | 5 | 45 | 112-3° | - | - | - | - | 69 |
| Isopropanol | 3 | 43 | 112-4° | - | - | - | - | 200 |
| 50% Aqueous Isopropanol | 4 | 79 | 113-4° | - | - | - | - | 240 |
| Triethylamine | 5 | 52 | 113-4° | 42 | 68° | 20 | 91° | 12 |
| 33% Aqueous Diethylamine | 2 | 14 | 113-4° | 13 | 67° | 29 | 82° | 79 |
| 67% Aqueous Diethylamine | 2 | 74 | 112-4° | 3 | - | 6 | 80° | 29 |
| Aqueous Ammonia[d,e] | 5 | - | - | - | - | - | - | 88 |
| 50% Aqueous Ammonia[d] / Isopropanol | 2 | 35 | - | 9 | 68° | 16 | 80° | 210 |

Notes: (a) lit. 81° (Ref. 84), (b) Dried over sodium, (c) Not dried, (d) d = 0.88 (e) Mass of starting material = 0.15 g.

Irradiation of m-Nitrobenzonitrile

A solution of m-nitrobenzonitrile (0.67 g.) in diethylamine (150 ml.) was irradiated for 3 hr. in the 150 ml. reactor using the Pyrex filter. The basic material consisted of m-aminobenzonitrile (0.11 g.), m.p. 50 - 52°, identical to a sample, m.p. 51 - 53°, prepared by reduction of m-nitrobenzonitrile. The neutral compounds were separated by preparative t.l.c. (benzene, x 3) to give m-nitrobenzonitrile (135 mg.), m.p. 116 - 117°; 3,3'-dicyanoazobenzene (81 mg.), orange needles from methanol, m.p. 167 - 168°. (Found: C, 72.3; H, 3.5; N, 24.2. $C_{14}H_8N_4$ requires C, 72.4; H, 3.5; N, 24.1%). $\lambda$ max. (EtOH): 432 mμ(ε 540), 310 mμ(17,000), 244 mμ(sh.) (14,000). The mass spectrum shewed a molecular ion at $m^+/e$ 232; 3,3'-dicyanoazoxybenzene (15 mg.), as pale orange needles from methanol, m.p. 186 - 187°. (Found: C, 67.3; H, 3.0; N, 22.9. $C_{14}H_8N_4O$ requires C, 67.7; H, 3.2; N, 22.6%). $\lambda$max. (EtOH): 375 mμ(sh.) (ε 4,400), 313 mμ (16,000), 220 mμ(20,000). The mass spectrum shewed a molecular ion at $m^+/e$ 240; and dark red needles (45 mg.), m.p. 240 - 255°, probably a mixture, but which could not be separated.

Irradiation of 1-Nitronaphthalene

A solution of 1-nitronaphthalene (1.25 g.) in diethylamine (150 ml.) was irradiated for 2 hr. in the 150 ml. reactor using a Pyrex filter. The

residue of the reaction mixture was separated by preparative t.l.c. (40% benzene in petrol, x 2) to give 1, 1'-azonaphthalene (8 mg.), m.p. 187 - 190° (lit.[191] 190°); molecular ion $m^+/e$ 282, 1-nitronaphthalene (652 mg.), m.p. 55 - 57°, and 2-hydroxy-1, 1'-azonaphthalene (18 mg.), m.p. 118 - 122° (lit.[84] 125°); molecular ion $m^+/e$ 298. To the residue from the preparative t.l.c. dissolved in ether was added 4N hydrochloric acid (50 ml.), and the solution was continuously extracted. After basification, continuous extraction into ether, and distillation, 1-naphthylamine (115 mg.), m.p. 47 - 49°, molecular ion $m^+/e$ 143, was isolated.

Irradiation of o-Nitroaniline

A solution of o-nitroaniline (0.45 g.) in triethylamine (170 ml.) was irradiated for 8 hr. in the 250 ml. reactor using a Pyrex filter. Chromatography on silica gel (50 g., 50 ml.) gave, on elution with 1% ether in benzene (400 ml.), o-nitroaniline (0.38 g.). Further elution (300 ml.) gave a brown oil, which gave on distillation a solid (20 mg.), m.p. 94 - 96°, having an i-r spectrum almost identical to that of o-phenylene diamine (lit.[192] 102°).

Irradiation of o-Nitrotoluene

1. A solution of o-nitrotoluene (1.00 g.) in triethylamine (100 ml.) was irradiated for 8 hr. in the 150 ml. reactor using the Pyrex filter. The solvent was distilled and neutral and basic extracts were made. The

basic extract was distilled to give a pale yellow liquid (240 mg.) whose i-r spectrum shewed N - H absorptions but not O - H. Benzoylation afforded a product identical with N-benzoyl-o-toluidine, needles from ethanol, m.p. 144 - 145°.

T.l.c. (Silica HF, 50% benzene in petrol) indicated that the neutral material was a mixture. Separation of the mixture was carried out by preparative t.l.c. (40% benzene in petrol, x 3), when there were isolated, in order of increasing polarity, 2-2'-dimethylazobenzene (13 mg.), m.p. 52 - 54° (lit.[193] 55°) as rods from methanol; n.m.r. ($CCl_4$): $\tau$ 2.3 to 3.0 (8 protons, complex multiplet, aromatic C - H), $\tau$ 7.28 (6 protons, singlet, $-CH_3$). There were no resonances below $\tau$ 0; 6-hydroxy-2, 2'-dimethylazobenzene (30 mg.), m.p. 96 - 97° (lit.[177] 97°) as red needles from methanol; n.m.r. ($CDCl_3$): $\tau$ -3.73 (1 proton, singlet, O - H), $\tau$ 2.1 to 3.3 (7 protons, complex multiplet, aromatic C - H), $\tau$ 7.30 (3 protons, singlet, C - $H_3$), $\tau$ 7.42 (3 protons, singlet, C - $H_3$); and 2, 2'-azoxytoluene (44 mg.) as yellow needles from methanol, m.p. 54 - 56°.

2. A solution of o-nitrotoluene (133 mg.) in a 60% solution of deuterium oxide in dry acetonitrile* (5 ml.) was irradiated for 15 hr. in a 10 ml. Pyrex flask using an external source. Acetone (10 ml.) and silica gel

* I should like to thank Mr. I. G. Click for the gift of a sample of dry acetonitrile.

(10 g.) were added, and the residue after evaporation formed the upper part of a chromatographic column (Silica gel, 50 g., 5[illegible] ml.). Benzene (300 ml.) eluted a yellow oil (107 mg.) which was identical (i-r) with the starting material.

3. A mixture of o-nitrotoluene (138 mg.) and octafluoronaphthalene (38 mg.) in 60% deuterium oxide in acetonitrile (5 ml.) was irradiated for 15 hr. under the same conditions as irradiation (2). A similar isolation procedure afforded pure o-nitrotoluene (43 mg.) and mixed fractions containing both starting materials (82 mg.).

Irradiation of 2, 6-Dimethylnitrobenzene

A solution of 2, 6-dimethylnitrobenzene (1.38 g.) in triethylamine (150 ml.) was irradiated for 5 hr. in the 250 ml. reactor using a Pyrex filter. After evaporation of the solvent, neutral and basic extracts were made. The basic material, on distillation, afforded 2, 6-dimethylaniline (456 mg.), identical to an authentic sample; no products were isolated from the neutral extract.

Irradiation of o-Nitrobenzylalcohol

A solution of o-nitrobenzyl alcohol (0.75 g.) in ether (100 ml.) was irradiated for 5 hr. in the 15[illegible] ml. reactor using the Pyrex filter. Neutral and basic extracts were made but no basic material was present. T.l.c. (Silica F[illegible], 20% methanol in chloroform) showed one spot.

Crystallization from chloroform afforded 2, 2'-azobenzoic acid (0.23 g.), m.p. 241 - 243° (lit.[194] 245°).

Irradiation of Azoxybenzene in Diethylamine

A solution of azoxybenzene (160 mg.) in diethylamine (170 ml.) was irradiated for ½ hr. in the 250 ml. reactor using the Pyrex probe. After evaporation of the solvent, the reaction mixture was separated by preparative t.l.c. (20% benzene in petrol, x 3). The least polar material (1 mg.) was identified as azobenzene by its U.V. absorption spectrum. The two major components of the mixture were 2-hydroxyazobenzene (61 mg.), m.p. 79 - 81°, and azoxybenzene (63 mg.), m.p. 35 - 36°.

Irradiation of Azobenzene in Diethylamine

A solution of azobenzene (5.0 g.) in diethylamine (70 ml.) was irradiated for 24 hr. in the 80 ml. quartz reactor. After evaporation of the solvent and separation into neutral and basic fractions, azobenzene (3.2 g.), m.p. 66 - 69°, was recovered from the neutral extract. G.l.c. analysis of the basic material shewed that aniline Rt = 9.8 min. (5% ppn, 100°, 10 p.s.i.) was the major component. This was confirmed by distillation of the residue to give aniline (0.13 g.); acetyl derivative, m.p. 113 - 114°.

Irradiation of 4, 4'-Azoxyanisole in Diethylamine

1. A solution of 4, 4'-azoanisole (180 mg.) in diethylamine (100 ml.) was irradiated for 2¼ hr. in the 150 ml. reactor using the Pyrex filter. The solvent was distilled and the residue was separated by preparative t.l.c. (40% benzene in petrol, x 3) to give 4, 4'-azoanisole (35 mg.), m.p. 162 - 164°. (Found: N, 11.3. Calc. for $C_{14}H_{14}N_2O_2$: N, 11.5%). The more polar material was 4, 4'-azoxyanisole (140 mg.), m.p. 117 - 119°.

2. A solution of 4, 4'-azoxyanisole (104 mg.) in diethylamine (100 ml.) was irradiated for 2½ hr. in the 150 ml. reactor using unfiltered light. After separation into neutral and basic extracts, the basic fraction yielded p-anisidine (7 mg.), while the neutral material afforded, after preparative t.l.c. (40% benzene in petrol, x 3), 4, 4'-azoanisole (28 mg.), m.p. 162 - 163°, and 4, 4'-azoxyanisole (42 mg.), m.p. 116 - 118°.

Irradiation of 4, 4'-Azoanisole in Diethylamine

A solution of 4, 4'-azoanisole (250 mg.) in diethylamine (100 ml.) was irradiated for 3 hr. in the 150 ml. reactor using the quartz probe. Evaporation and separation in the usual way gave, from the basic fraction, p-anisidine (6 mg.) and, from the neutral material, after preparative t.l.c. (40% benzene in petrol, x 1) 4, 4'-azoanisole (144 mg.),

m.p. 162 - 164°.

Irradiation of 3, 3'-Azoxyanisole in Diethylamine

A dilute solution of 3, 3'-azoxyanisole in diethylamine was irradiated for 2 hr. in a 25 ml. Pyrex flask using the 125 W. external source. T.l.c. analysis (Silica HF, 40% benzene in petrol) indicated that compounds of Rf similar to those of 3, 3'-azoanisole, 2-hydroxy-3, 3'-azoanisole, 6-hydroxy-3, 3'-azoanisole, and 3, 3'-azoxyanisole were present. Isolation of the products was not attempted.

Irradiation of Benzophenone in Ether

A deoxygenated solution of benzophenone (2.25 g.) in dry, distilled, acetaldehyde-free[195] ether (150 ml.) was irradiated for 3½ hr. in the 15 ml. reactor with a slow stream of ether-saturated nitrogen passing over the surface of the photolyte. The effluent gases were trapped at -78°. A bath of water at 50° was placed around the reactor and part of the ether (30 ml.) was distilled and condensed in the cold trap. The ethereal solution obtained was shaken with a solution of 2, 4-dinitrophenylhydrazine in 5N aqueous sulphuric acid, and benzene (50 ml.) was added. The organic phase was washed successively with the 2, 4-dinitrophenylhydrazine reagent solution, 5N sulphuric acid, and water, and then dried. Evaporation yielded acetaldehyde-2, 4-dinitrophenylhydrazone (203 mg.), orange needles from ethanol, m.p. 145 - 146° (lit.[196] 146°).

Evaporation of the photolyte gave a colourless residue (2.2 g.). Crystallization from acetone afforded benzpinacol, m.p. 195 - 197° (lit.[197] 196°).

Irradiation of Nitrobenzene in Ether

1. A solution of nitrobenzene (0.50 g.) in distilled, dry, acetaldehyde-free[195] ether (150 ml.) was irradiated using the above conditions for 9 hr. Treatment of the solution in the cold trap with 2, 4-dinitrophenylhydrazine reagent, as above, afforded acetaldehyde-2, 4-dinitrophenylhydrazone (396 mg.) as orange needles from ethanol, m.p. 145 - 146° (lit.[196] 146°).

The photolyte was worked up by the usual acid/base extraction procedure, to give nitrobenzene (25 mg.), and aniline (155 mg.); acetyl derivative, m.p. 113 - 114°.

2. A solution of nitrobenzene (5[illegible]4 mg.) in dry ether (100 ml.) was irradiated for 45 min. in the 150 ml. reactor using the Pyrex filter. After separation to give basic and neutral extracts, aniline (16 mg.) was isolated from the basic fraction, and nitrobenzene (450 mg.) was recovered from the non-basic material.

3. In the presence of benzophenone:- A mixture of nitrobenzene (0.50 g.) and benzophenone (20.0 g.) in dry ether (100 ml.) was irradiated for 45 min. in the 150 ml. reactor using the Pyrex filter.

From the basic material was isolated aniline (30 mg.) but the residual nitrobenzene in the neutral fraction could not satisfactorily be separated from benzophenone.

4. In the presence of biacetyl:- A mixture of nitrobenzene (499 mg.) and biacetyl (643 mg.) in dry ether (100 ml.) was irradiated for 45 min. in the 150 ml. reactor using the Pyrex filter. The usual work-up yielded nitrobenzene (452 mg.) from the neutral fraction and an involatile tar (22 mg.) from the basic material.

5. In the presence of octafluoronaphthalene:- A mixture of nitrobenzene (504 mg.) and octafluoronaphthalene (84 mg.) in dry ether (100 ml.) was irradiated for 45 min. in the 150 ml. reactor using the Pyrex filter. No material was isolated from a basic extract. The dried neutral material was separated by preparative t.l.c. (30% benzene in petrol, x 1) to give octafluoronaphthalene (23 mg.), m.p. 81 - 83° (pure compound, m.p. 83 - 84°) and nitrobenzene (491 mg.).

Irradiation of Nitrobenzene with Aniline

A mixture of nitrobenzene (2.0 g.), aniline (1.5 g.), sodium hydroxide (1.0 g.), water (15 ml.), and acetonitrile (5 ml.) was irradiated with an external source in a 100 ml. Pyrex flask for 12 hr. Preparative t.l.c. (10% benzene in petrol, x 2) on the neutral material afforded azobenzene (3 mg.) and 2-hydroxyazobenzene (5 mg.).

Irradiation of Phenylhydroxylamine

A deoxygenated solution of phenylhydroxylamine (0.20 g.) in ether (200 ml.) was irradiated for 2 hr. in the 250 ml. reactor using the Pyrex filter, with a stream of nitrogen passing through.

A basic extract was evaporated and distilled to give aniline (72 mg.) which on acetylation afforded acetanilide, m.p. 113 - 113½°.

The neutral material shewed three spots on t.l.c. (Silica HF, 40% benzene in petrol) and no more polar material (Silica HF, 50% ether in petrol). Separation by preparative t.l.c. on a 20 cm. x 20 cm. plate with the adsorbent layer of thickness 1 mm. (20% benzene in petrol, x 3) gave azobenzene (3 mg.), m.p. 60 - 65°, and azoxybenzene (27 mg.), as yellow rods from methanol, m.p. 34 - 36°. There was insufficient of the third compound to isolate.

Irradiation of Nitrosobenzene

(a) With ultraviolet light:- A solution of nitrosobenzene (0.20 g.) in ether (200 ml.) was irradiated for 1½ hr. in the 250 ml. reactor, using the Pyrex filter. The reaction mixture was extracted to give basic and neutral fractions.

T.l.c. (Silica HF, 40% benzene in petrol) on the neutral material indicated that one compound was present. This was isolated by chromatography on silica gel (25 g., 100 ml.) when benzene (200 ml.) eluted

azoxybenzene (53 mg.) which crystallized from methanol as yellow rods, m.p. 35 - 36°.

The basic material was evaporated to give a brown gum (13 mg.). T.l.c. (50% ether in petrol) on this residue indicated that at least nine components were present, and the mixture was discarded.

(b) With visible light:- A solution of nitrosobenzene (338 mg.) in ether (100 ml.), in a Pyrex, 100 ml., round-bottomed flask fitted with a reflux condenser, was illuminated for 90 hr. with an external, 100 W., tungsten lamp. The reaction mixture was extracted to give neutral and basic material.

T.l.c. (Silica HF, 10% ether in petrol) on the basic material indicated that several compounds were present, so the residue (16 mg.) was discarded.

The neutral fraction was steam distilled until no more green material distilled over. Extraction of this into ether and evaporation afforded nitrosobenzene (107 mg.), m.p. 64 - 66°. The residue from the steam-distillation shewed one spot on t.l.c. (Silica HF, benzene). Chromatography on silica gel (12 g., 20 ml.), on elution with benzene (80 ml.), gave azoxybenzene (63 mg.), which crystallized as yellow rods from methanol, m.p. 34 - 35°.

(c) In dilute solution:- A solution of nitrosobenzene (5 to 8 mg.) in

ether (1 l.) was irradiated in the 1 l. reactor, using the Pyrex filter. Deoxygenation, when required, was effected in situ under reflux. The reaction mixture was concentrated to ca. 1 ml. and analysed by g.l.c. (5% ppa, 100°, 10 p.s.i.) for nitrosobenzene, Rt = 1.2 min., nitrobenzene, Rt = 6.0 min., and aniline Rt = 5.5 min. (the latter two were shewn to separate in test mixtures); and by t.l.c. (Silica HF, 20% benzene in petrol, and benzene). The results of the study are shewn in Table 14.

Table 14

Irradiation Products of Nitrosobenzene in Dilute Ethereal Solution

| Time (min.) | Nitrosobenzene [c, d] | Nitrobenzene [c, d] | Azoxybenzene [d] | Aniline [c, d] |
|---|---|---|---|---|
| 75 | - | + | - | - |
| 15 | + | + | - | - |
| 5 [a] | + | + | - | - |
| 15 [b] | + | - | - | - |
| 15 [a, b] | + | - | + | - |

Notes: '+' and '-' indicate the presence or absence of the product;

(a) Sensitized by the addition of benzene (10 ml.) to the reaction mixture;

(b) Deoxygenated;

(c) By g.l.c.

(d) By t.l.c.

(d) In the presence of Nitrobenzene:- To a solution of nitrobenzene (525 mg.) in ether (50 ml.) undergoing photolysis in a 100 ml. Pyrex flask was added in drops over 2 hr. 20 min. a solution of nitrosobenzene (101 mg.) in ether (30 ml.). The irradiation was continued 10 min. more. After evaporation of the photolyte, t.l.c. (Silica HF, 15% benzene in petrol; benzene) indicated the presence of nitrobenzene, a trace of azoxybenzene, and aniline, but no nitrosobenzene. After preparative t.l.c. (10% benzene in petrol, x 2), U.V. analysis estimated the azoxybenzene at 6 mg.

(e) In the presence of o-Nitrotoluene:- A portion (20 ml.) of a solution of o-nitrotoluene (2.01 g.) in ether (130 ml.) was mixed with a solution of nitrosobenzene (47 mg.) in ether (20 ml.). The mixture was added dropwise, over 1½ hr., to the remainder of the o-nitrotoluene solution, undergoing photolysis in the 150 ml. reactor, using filtered light. The irradiation then continued ½ hr. more.

The reaction mixture was extracted with dilute hydrochloric acid, and the mixture of bases was extracted into ether, and examined by g.l.c. (5% ppa, 100°, 10 p.s.i.). Aniline (Rt = 5.6 min.) and o-toluidine (Rt = 8.1 min.) were found.

(f) In the presence of Naphthalene:- A solution of nitrosobenzene (95 mg.) and naphthalene (212 mg.) in ether (150 ml.) was

irradiated for ½ hr. in the 150 ml. reactor, using filtered light. The reaction mixture was evaporated to ca. 1 ml. Analysis by g.l.c. (5% ppa, 100°, 10 p.s.i.) indicated that aniline was not among the products, while t.l.c. (Silica HF, 10% benzene in petrol) shewed the presence of azoxybenzene.

Irradiation of Nitrobenzene in Aqueous Solution

1. A mixture of nitrobenzene (0.20 g.), hydrated ferrous sulphate (2.52 g.), and water (170 ml.) was irradiated for 1½ hr. in the 250 ml. reactor, using filtered light. Extraction with ether and evaporation afforded only nitrobenzene (0.17 g.).

2. A mixture of nitrobenzene (164 mg.), sodium iodide (1.03 g.), and water (160 ml.) was irradiated for 1½ hr. in the 150 ml. reactor, using a Pyrex filter. Extraction into ether of the colourless solution and evaporation gave nitrobenzene (151 mg.).

## EXPERIMENTAL SECTION TO CHAPTER V

### Preparations

3, 3'-Azoanisole and 3, 3'-Azoxyanisole:- A well stirred mixture of m-nitroanisole (3.0 g.), m-anisidine (2.6 g.), finely ground potassium hydroxide (7 g.), and paraffin oil (60 ml.) was heated to 175° for 3 hr. The cooled reaction mixture was dissolved in benzene (100 ml.), filtered and chromatographed on silica gel (150 g., 100 ml.) to remove the paraffin oil. 2% Ether in benzene (500 ml.) eluted the product mixture, which was separated by preparative t.l.c. (40% benzene in petrol, x 4) to give 3, 3'-azoanisole (1.20 g. = 27%), m.p. 77 - 78° (lit.[198] 73 - 74°), and 3, 3'-azoxyanisole (0.65 g. = 12%), m.p. 51 - 52° (lit.[198] 51°).

4, 4'-Azoanisole:- The above method was employed using p-nitroanisole and p-anisidine. Chromatography on silica gel (150 g., 100 ml.), eluting with 2% ether in benzene (600 ml.), gave 4, 4'-azoanisole (1.6 g. = 32%), m.p. 162 - 164° (lit.[199] 160 - 162°), but 4, 4'-azoxyanisole was not present in the reaction mixture.

Reduction of Nitrocompounds with Methanolic Sodium Hydroxide:

This method was applied to the preparation of several azoxycompounds. The nitrocompound (0.05 M) was refluxed in a mixture of

sodium hydroxide (10 g.) and methanol (50 ml.) for 1½ hr. The cooled reaction mixture was poured into excess ice cold water, and the product filtered and crystallized from 1:1 benzene:petrol. Table 15 gives the results of these preparations.

1,1'-Azoxynaphthalene:- [204] To a mixture of 1-nitronaphthalene (8.5 g.), ammonium chloride (20 g.), and sodium hydroxide (12 g.) was added zinc (15 g.) in portions over ½ hr. while the mixture was heated to 70°. The mixture was maintained at this temperature for a further 2 hr., cooled and filtered. The solid obtained was refluxed with benzene (2 x 50 ml.) and the benzene solution obtained was chromatographed on silica gel (100 g., 250 ml.), when benzene (150 ml.) eluted a sticky red solid. The mixture was resolved by preparative t.l.c. (40% benzene in petrol, x 2) to give 1,1'-azonaphthalene (0.15 g. = 2%), m.p. 190 - 192° (lit. [191] 190°), recovered 1-nitronaphthalene (0.40 g.), m.p. 57 - 58°, and 1,1'-azoxynaphthalene (1.28 g. = 19%), as small yellow plates from ethanol, m.p. 129 - 129½° (lit. [204] 127°). (Found: N, 9.2; Calc. for $C_{20}H_{14}N_2O$: N, 9.4%).

2,6-Dimethylazoxybenzene:- To a solution of nitrosobenzene (1.6 g.) in ethanol (15 ml.) was added a solution of 2,6-dimethylaniline (3 ml.) in acetic acid (5 ml.). The mixture was heated to 70° for 15 min., cooled, neutralised with sodium carbonate, extracted, acidified, and

Table 15

**The Preparation of Azoxycompounds by Reduction of the Nitrocompound with Methanolic Sodium Hydroxide**

| Azoxycompound | Yield % | m.p. | lit. m.p. | Reference |
|---|---|---|---|---|
| 4, 4'-Azoxyanisole | 79 | 117 - 118° | 118° | 200 |
| 2, 2'-Azoxytoluene | 27 | 58 - 59° | 60° | 201 |
| 2, 2'-Azoxyanisole | 64 | 79½ - 80° | 81° | 202 |
| 4, 4'-Azoxybiphenyl | 47 | 213 - 214° | 212° | 190 |
| 3, 3'-Dichloro-2, 2'-azoxytoluene | - | - | - | - |
| 2, 2'-Azoxybenzyl alcohol | - | - | 123° | 198 |
| 1, 1'-Azoxynaphthalene | - | - | 127° | 84 |
| 2, 2', 6, 6'-Tetramethylazoxybenzene | - | - | 91° | 203 |
| 3, 3'-Dicyanoazoxybenzene | - | - | 187° | - |

re-extracted. The residue of the organic phase was chromatographed on silica gel (60 g., 100 ml.) when 30% benzene in petrol (300 ml.) eluted 2, 6-dimethylazobenzene as a red oil [205] (1.07 g. = 34%) pure by t.l.c. (Silica G, 40% benzene in petrol) (Found: N, 13.5. Calc. for $C_{14}H_{14}N_2O$: N, 13.3%).

2, 6-Dimethylazobenzene (1.03 g.) was oxidised in a mixture of 30% aqueous hydrogen peroxide (2 ml.) and acetic acid (15 ml.), and heated to 60° for 6 hr., when the solution had become pale yellow. [206] After neutralization and extraction, the organic phase shewed a single spot on t.l.c. (Silica HF, 10% benzene in petrol; benzene), and was evaporated to give 2, 6-dimethylazoxybenzene (1.00 g. = 89%) as a pale yellow oil. (Found: N, 12.5. $C_{14}H_{14}N_2O$ requires N, 12.6%). N.m.r. ($CCl_4$): $\tau$ 1.5 - 3.2 (8 protons, complex multiplet, aromatic C - H), $\tau$ 7.73, 7.93 (6 protons, 2 singlets, ratio 22: 78: $-CH_3$).

2, 2', 6, 6'-Tetramethylazoxybenzene:- To a solution of lithium aluminium hydride (5.0 g.) in dry ether (500 ml.) was added in small portions a solution of 2, 6-dimethylnitrobenzene (20 g.) in ether (30 ml.). The mixture was refluxed for 17 hr. after the completion of the addition.

Ethyl acetate (40 ml.) was added and the ethereal solution was extracted with 3N sulphuric acid. The residue of the organic phase was chromatographed on silica gel (120 g., 100 ml.), when 5% benzene

in petrol (700 ml.) eluted 2, 2', 6, 6'-tetramethylazobenzene (2.0 g. = 30%), m.p. 46 - 47° (lit.[207] 47°); 10% benzene in petrol eluted 2, 6-dimethylnitrobenzene (3.1 g.).

The azocompound (1.65 g.) was oxidised with a mixture of 30% hydrogen peroxide (10 ml.) and acetic acid (100 ml.) to give 2, 2', 6, 6'-tetramethylazoxybenzene in quantitative yield.[206] The product crystallized from methanol as yellow rods, m.p. 89½ - 90° (lit.[203] 91°). (Found: C, 75.8; H, 6.8; N, 11.2. Calc. for $C_{16}H_{18}N_2O$: C, 75.5; H, 7.1; N, 11.0%).

3-Methyl-2, 4-bis-(o-tolylazo)-phenol:- To a solution of 6-hydroxy-2, 2'-azotoluene (0.04 g.) in a mixture of sodium hydroxide (1.0 g.) and methanol (5 ml.) was added excess 2-methylphenyl diazonium chloride. Filtration and crystallization from methanol of the solid gave 3-methyl-2, 4-bis-(o-tolylazo) -phenol (0.03 g. = 4%), m.p. 168 - 171°, brown needles from methanol. (Found: N, 16.7. $C_{21}H_{20}N_4O$ requires N, 16.3%). N.m.r. ($CDCl_3$): $\tau$ -4.65 (1 proton, singlet, -OH), $\tau$ 2.0; 3.4 (10 protons, complex multiplet, aromatic C - H), $\tau$ 6.38, 7.30, 7.39 (9 protons, three singlets, $-CH_3$). The mass spectrum shewed a molecular ion at $m^+/e$ 344. $\lambda$ max. (EtOH): 420 mμ(sh.) (ε 5,900), 350 mμ(32,000), 235 mμ(11,000).

Irradiation of azoxybenzene

1. A solution of azoxybenzene, in the appropriate solvent, was irradiated in the 150 ml. reactor, using the Pyrex filter. After evaporation of the solvent, the residue was separated by preparative t.l.c. (20% benzene in petrol, x 2). The products developed in the order azobenzene, 2-hydroxyazobenzene, azoxybenzene, and were identified by their m.p., and i-r spectrum. The results of the study are summarised in Table 16.

2. In the presence of naphthalene:- A solution of azoxybenzene (105 mg.) and naphthalene (520 mg.) in isopropanol (100 ml.) was irradiated for 1 hr. in a 100 ml. Pyrex flask, using an external source. After evaporation of the solvent, preparative t.l.c. (25% benzene in petrol, x 2) afforded azobenzene (10 mg.), m.p. 66 - 67°, 2-hydroxyazobenzene (36 mg.), m.p. 81 - 82°, and azoxybenzene (44 mg.), m.p. 34 - 35°.

3. In the presence of nitrobenzene:- A solution of azoxybenzene (122 mg.) and nitrobenzene (460 mg.) in isopropanol (100 ml.) was irradiated under the above conditions for 1 hr. A similar isolation procedure afforded azobenzene ( mg.), 2-hydroxyazobenzene (34 mg.), and azoxybenzene (56 mg.).

Table 16

The Solvent Dependence of the Irradiation Products of Azoxybenzene

| Solvent | Concentration mg./ml. | Time hr. | Azobenzene mg. | 2-Hydroxyazobenzene mg. | Azoxybenzene mg. |
|---|---|---|---|---|---|
| Benzene | 159/150 | 1 | - | 17 | 127 |
| Petrol | 153/160 | 5 | 7 | 42 | 53 |
| Ether | 149/150 | 1 | < 1 | 5 | 120 |
| Diethylamine | 160/170 | ½ | < 1 | 61 | 63 |
| Isopropanol | 152/150 | ½ | - | 33 | 103 |

Irradiation of 4, 4'-Azoxyanisole (See also Chapter IV)

1. A solution of 4, 4'-azoxyanisole (146 mg.) in benzene (150 ml.) was irradiated for 2 hr. in the 150 ml. reactor using a Pyrex filter. After evaporation of the solvent the residue was resolved by preparative t.l.c. (40% benzene in petrol, x 4) to give 2-hydroxy-4, 4'-azoanisole (21 mg.), m.p. 136 - 137°. (Found: N, 11.1. $C_{14}H_{14}N_2O_3$ requires N, 10.9%). N.m.r. ($CCl_4$): $\tau$ -3.13 (1 proton, singlet, -OH), $\tau$ 2.2 - 3.3 (7 protons, complex multiplet, aromatic C - H), $\tau$ 6.17 (6 protons, singlet, 2 x $-OCH_3$). $\lambda$ max. (EtOH): 415 m$\mu$ (sh.) ($\epsilon$ 24,000), 385 m$\mu$(33,000), 256 m$\mu$(16,000). The mass spectrum showed a molecular ion at $m^+/e$ 258.

The more polar material isolated from the t.l.c. was 4, 4'-azoxyanisole (91 mg.), m.p. 118 - 119°.

2. A solution of 4, 4'-azoxyanisole (20 mg.) in acetonitrile (50 ml.) was irradiated in a Pyrex flask with external illumination. T.l.c. (Silica HF, 40% benzene in petrol) indicated the presence of the same two compounds as isolated above.

Irradiation of 2, 2'-Azoxyanisole

1. A solution of 2, 2'-azoxyanisole (0.25 g.) in benzene (190 ml.) was irradiated for $\frac{1}{2}$ hr. in the 250 ml. reactor, using the Pyrex filter. After evaporation of the solvent, the mixture was separated by

preparative t. l. c. (40% benzene in petrol, x 5; then benzene x5) to give trans-6-hydroxy-2, 2'-azoanisole (24 mg.) as deep orange needles from methanol, m. p. 172 - 173°. (Found: C, 65.0; H, 5.5; N, 11.3. $C_{14}H_{14}N_2O_3$ requires C, 65.2; H, 5.4; N, 10.9%). N.m.r. ($CDCl_3$): $\tau$-4.67 (1 proton, singlet, -OH), $\tau$2.0 - 3.7 (7 protons, complex multiplet, aromatic C - H), $\tau$6.03 (6 protons, singlet, 2x $-OCH_3$). $\lambda$max. (EtOH): 425 mμ(sh) (ε4,700), 390 mμ (11,000), 250 mμ(sh.) (3,300), 240mμ(3,800). The mass spectrum shewed a molecular ion at $m^+/e$ 258.

A second band was isolated and identified as cis-6-hydroxy-2, 2'-azoanisole (54 mg.), red needles from methanol, m. p. 131 - 132°. (Found: N, 10.5%). N. m. r. ($CDCl_3$): $\tau$-4.90 (1 proton, singlet, -OH), $\tau$2.0 - 3.6 (7 protons, complex multiplet, aromatic C - H), $\tau$6.05, 6.18 (6 protons, two singlets $-OCH_3$). $\lambda$max. (EtOH): 505mμ(sh.) (ε4,300), 395 mμ(21,000), 340 mμ(sh.) (9,400), 254 mμ(8,400). The mass spectrum shewed a molecular ion at $m^+/e$ 258.

Further development of the t. l. c. plate (20% ethyl acetate in ether, x 1) gave a bright red oil (31 mg.). N. m. r. ($CCl_4$): $\tau$2.0 - 3.7 (complex multiplet), $\tau$6.10, 6.23 (2 singlets), $\tau$7.5 - 9.2 (complex multiplet). The respective intensities were 15 : 8 : 3: 102. An attempt at purification by preparative t.l.c. on a 20 cm. x 20 cm. x 1 mm.

plate (ether, x 1) gave a red oil (21 mg.) having the same resonances in the n.m.r., but with the ratio of the intensities changed to 36 : 20 : 7 : 13. The mass spectrum shewed no peaks at $m^+/e > 253$.

2. A solution of 2, 2'-azoxyanisole (183 mg.) in diethylamine (100 ml.) was irradiated for 12 hr. in a 100 ml. Pyrex flask using an external source.

After evaporation of the solvent, preparative t.l.c. afforded trans-6-hydroxy-2, 2'-azoanisole (96 mg.), m.p. 175 - 176°, with spectral properties identical to those described above, and 2, 2'-azoanisole (27 mg.), m.p. 145 - 147°, (lit. [123, 203] 141, 153°).

Irradiation of 2, 2'-Azoxytoluene

1. A solution of 2, 2'-azoxytoluene (0.20 g.) in benzene (180 ml.) was irradiated for ½ hr. in the 250 ml. reactor using the Pyrex filter. The solvent was evaporated and the residue resolved by preparative t.l.c. (40% benzene in petrol, x 3) to give 6-hydroxy-2, 2'-azoxytoluene (97 mg.), red needles from methanol, m.p. 95 - 96°, identical to the compound described on p. (Found: N, 12.4. Calc. for $C_{14}H_{14}N_2O$: N, 12.4%) and 3-methyl-2, 4-bis-(o-tolylazo)-phenol (12 mg.), m.p. 167 - 169°, which had n.m.r., i-r, and mass spectra identical to those of the authentic material.

2. A solution of 2, 2'-azoxytoluene (130 mg.) in benzene (250 ml.)

was irradiated for 3 hr. in the 1 l. reactor vessel using the Pyrex filter. After evaporation of the solvent, the mixture was separated as above. Two compounds were obtained. The first, red needles, (30 mg.), m.p. 74 - 77° was assigned the structure of cis-6-hydroxy-2, 2'-azotoluene on the grounds that after refluxing in methanol for some hours, the normal, trans, compound was recovered.

The second component of the mixture was trans-6-hydroxy-2, 2'-azotoluene (36 mg.), m.p. 95 - 97°.

Irradiation of 6-Hydroxy-2, 2'-azotoluene

A solution of 6-hydroxy-2, 2'-azotoluene (26 mg.) in benzene (2.0 ml.) was irradiated for 6 hr. in a 5 ml. Pyrex flask, using an external source. T.l.c. (Silica HF, 20% benzene in petrol) indicated only one spot, and chromatography on silica gel (2 g., 100 ml.) eluting with benzene, allowed isolation of the starting material (22 mg.), m.p. 94 - 96°.

Irradiation of Azobenzene (See also Chapter IV)

1. A solution of azobenzene (0.75 g.) in benzene (200 ml.) was irradiated for 13 hr. in the 250 ml. reactor using the Pyrex filter. The residue after evaporation of the solvent was chromatographed on alumina (60 g., 100 ml.) to give azobenzene (0.53 g.), m.p. 67 - 68°,

on elution with 20% benzene in petrol (400 ml.). Benzene (400 ml.) eluted cis-azobenzene (0.14 g.), which reverted to the trans form when refluxed in benzene.

2. A mixture of azobenzene (0.1 g.), phenol (2.0 g.), and benzene (180 ml.) was irradiated for 3 hr. in the 250 ml. reactor, using a Pyrex filter. After evaporation of the solvent, acid and neutral extracts were made. The neutral extract yielded (t.l.c. analysis (alumina, 30% benzene in petrol) ) mixed cis- and trans-azobenzene (0.09 g.). The acidic material gave phenol (1.95 g.).

3. A mixture of azobenzene (0.50 g.), phenol (0.25 g.), and benzene (190 ml.) was irradiated for 2 hr. under the above conditions. An acid extract yielded phenol (0.1[illegible] g.). The neutral material was reduced with tin in hydrochloric acid until the colour was discharged. Evaporation of a neutral ethereal extract of this reaction mixture yielded no product.

Irradiation of 2, 6-Dimethylazoxybenzene

A solution of 2, 6-dimethylazoxybenzene (107 mg.) in benzene (75 ml.) was irradiated for 1 hr. in the 150 ml. reactor using a Pyrex filter. Chromatography of the residue, after evaporation of the solvent, on alumina (50 g., 100 ml.) gave the starting material (98 mg.), on elution with benzene (500 ml.). N.m.r. ($CCl_4$): $\tau$ 1.6 - 3.1 (8

protons, complex multiplet, aromatic C - H), $\tau$ 6.10, 6.31 (6 protons, 2 singlets, ratio 1:10, $-CH_3$).

Irradiation of 2, 2', 6, 6'-Tetramethylazoxybenzene

A solution of tetramethylazoxybenzene (495 mg.) in benzene (950 ml.) was irradiated for 5 hr. in the 1 l. reactor, using a Pyrex filter. The solvent was evaporated, and the residue separated by preparative t.l.c. (20% benzene in petrol, x 3). The only compound present in isolable quantity was the starting material (386 mg.), m.p. 90 - 91°.

Irradiation of 1, 1'-Azoxynaphthalene

A solution of 1, 1'-azoxynaphthalene (276 mg.) in benzene (900 ml.) was irradiated for 1 hr. in the 1 l. reactor using the Pyrex filter. Evaporation of the solvent, followed by preparative t.l.c. (40% benzene in petrol, x 2) gave three bands: the first, dark red crystals (4 mg.), m.p. 102 - 105°, shewed a molecular ion in the mass spectrum at $m^+/e$ 298; the second, yellow plates (139 mg.), m.p. 126 - 127°, was starting material; and the third, dark red crystals (12 mg.), m.p. 122 - 124° was 2-hydroxy-1, 1'-azonaphthalene.

Irradiation of Sodium Benzoate in Methanol

A solution of sodium benzoate (0.62 g.) in methanol (240 ml.) was irradiated for 4 hr. in the 250 ml. reactor, using unfiltered light.

After evaporation of the solvent, dilute caustic soda solution was added and the solution extracted with ether. Evaporation of the extract gave a residue (0.04 g.), which shewed several small spots and one large spot on t.l.c. (Silica HF, 50% ether in petrol). The aqueous solution was acidified and extracted to give benzoic acid (0.36 g.), m.p. 121 - 122°.

Irradiation of Sodium o- Toluate in Water

A solution of o-toluic acid (2.00 g.), in water (240 ml.) was basified with sodium hydroxide and irradiated for 14½ hr. in the 250 ml. reactor using unfiltered light. After evaporation of the solvent, neutral and acidic extracts were made. The acidic fraction was o-toluic acid (1.82 g.), m.p. 105½ - 106°. The neutral material (0.01 g.) was shown by t.l.c. (50% ether in petrol) to be a mixture of several compounds.

# APPENDIX 1

## H. M. O Calculations[80, 202] of the Formal Charges in the Ground and Excited States of some Aromatic Molecules

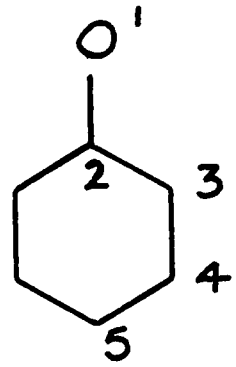
For all heteroatoms: $\alpha_x = \alpha_c + h_x \beta_{(c-c)}$

For all bonds: $\beta_{(x-y)} = k_{(x-y)} \beta_{(c-c)}$

An auxiliary inductive parameter of 0.1 was used as the 'h' value for the carbon atom adjacent to each heteroatom in all the calculations.

(a) Anisole

h (O) = 2, k (C - O) = 1




| Atom | q[a] | n, π* | π, π* |
|---|---|---|---|
| 1 | +0.092 | +1.092 | +0.257 |
| *2[b] | -0.004 | -0.004 | +0.233 |
| 3 | -0.032 | -0.232 | -0.160 |
| 4 | +0.001 | -0.249 | -0.206 |
| 5 | -0.026 | -0.026 | +0.240 |

(a) Columns 2, 3, and 4 refer respectively to the formal charges in the ground state and n, π* and π, π* excited states.

(b)* indicates a position to which a substituent is attached.

h(O) = 1.5, k(C - O) = 1
a

| Atom | q | $n,\pi^*$ | $\pi,\pi^*$ |
|---|---|---|---|
| 1 | +0.126 | +1.126 | +0.301 |
| * 2 | +0.015 | +0.015 | +0.191 |
| 3 | -0.052 | -0.302 | -0.166 |
| 4 | +0.002 | -0.248 | -0.220 |
| 5 | -0.042 | -0.042 | +0.191 |

h(O) = 0.9, k(C - O) = 0.8

| | | | |
|---|---|---|---|
| 1 | +0.132 | +1.132 | +0.610 |
| *2 | +0.011 | +0.011 | +0.103 |
| 3 | -0.052 | -0.302 | -0.182 |
| 4 | +0.002 | -0.247 | -0.123 |
| 5 | -0.044 | -0.044 | +0.122 |

h(O) = 1.5, k(C - O) = 0.8

| | | | |
|---|---|---|---|
| 1 | +0.083 | +1.917 | +0.338 |
| *2 | -0.008 | -0.008 | +0.198 |
| 3 | -0.027 | -0.276 | -0.160 |
| 4 | +0.001 | -0.245 | -0.213 |
| 5 | -0.022 | -0.022 | +0.216 |

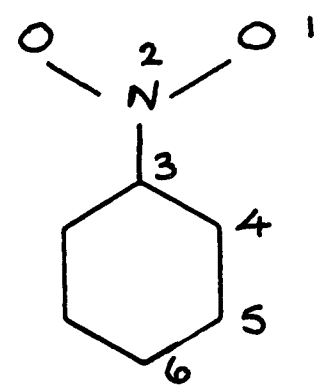
(b) Chlorobenzene

h(Cl) = 2, k(C - Cl) = 0.4

| | | | |
|---|---|---|---|
| 1 | +0.015 | +1.009 | +0.009 |
| *2 | -0.066 | -0.390 | -0.390 |
| 3 | +0.021 | -0.077 | +0.273 |
| 4 | -0.001 | -0.075 | +0.275 |
| 5 | +0.013 | -0.314 | -0.314 |

(c) Nitrobenzene

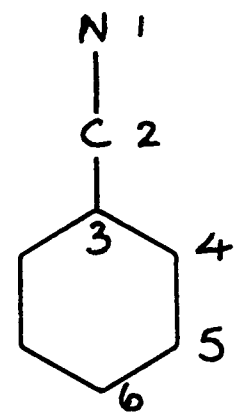
$h(N) = 2$; $h(O) = 1$, $k(N - O) = 0.7$, $k(C - N) = 1$




| Atom | q [a] | $n_2\pi^*$ | $\pi, \pi^*$ |
|---|---|---|---|
| 1 | -0.127 | +0.110 | +0.110 |
| 2 | +0.321 | +0.331 | +0.331 |
| *3 | +0.019 | +0.002 | +0.002 |
| 4 | +0.351 | +0.265 | +0.269 |
| 5 | +0.170 | +0.269 | +0.252 |
| 6 | +0.105 | +0.032 | +0.032 |

(d) Benzonitrile

$h(N) = 0.5$, $k(C - N) = 1.1$, $k(C - C) = 1.2$



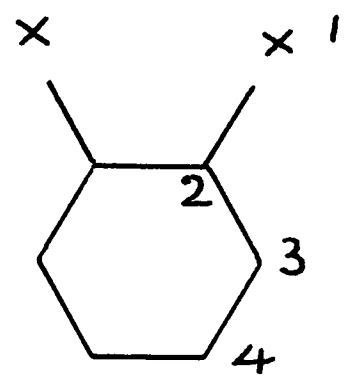

| | | | |
|---|---|---|---|
| 1 | -0.261 | +0.461 | -0.184 |
| 2 | +0.156 | -0.070 | -0.036 |
| *3 | -0.016 | -0.033 | +0.003 |
| 4 | +0.043 | -0.030 | +0.003 |
| 5 | -0.001 | -0.011 | +0.024 |
| 6 | +0.037 | -0.122 | +0.075 |

(e) Disubstituted Compounds

The calculations assumed the presence of a typical electron donating group (X), such as methoxyl with h(X) = 1.5 and k(C - X) = 1, and a typical electron withdrawing group (Y), with h(Y) = 2 and k(C- Y) = 0.5

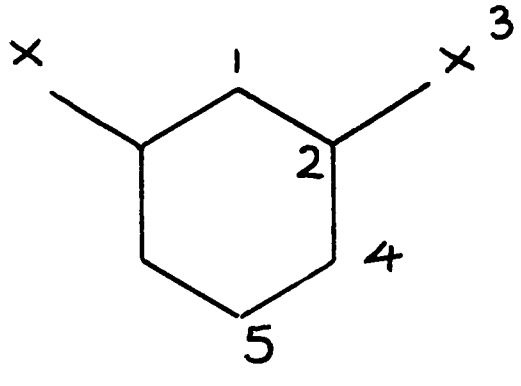
(i) Two electron donating groups:

ortho



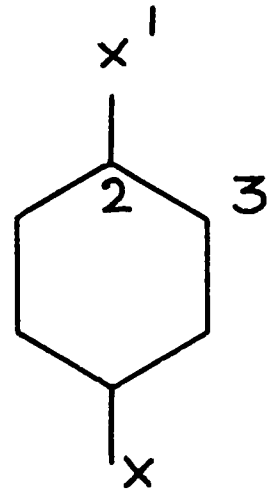

| Atom | $q^a$ | $\pi, \pi^*$ | $\pi, \pi^*$ |
|---|---|---|---|
| 1 | +0.118 | +0.604 | +0.288 |
| *2 | -0.027 | -0.123 | +0.054 |
| 3 | -0.054 | -0.363 | -0.342 |
| 4 | -0.038 | -0.113 | +0.001 |

meta



| Atom | $q^a$ | $n,\pi^*$ | $\pi,\pi^*$ |
|---|---|---|---|
| 1 | -0.107 | -0.386 | -0.386 |
| *2 | +0.017 | -0.056 | +0.040 |
| 3 | +0.126 | +0.614 | +0.347 |
| 4 | -0.091 | -0.157 | +0.077 |
| 5 | +0.005 | -0.351 | -0.351 |

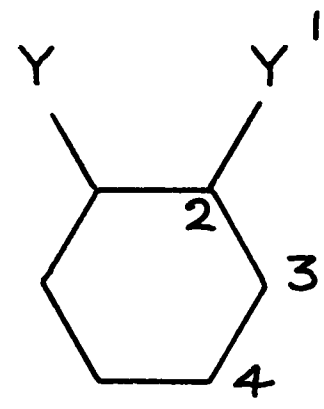
para




| | | | |
|---|---|---|---|
| 1 | +0.118 | +0.618 | +0.290 |
| *2 | -0.020 | -0.020 | +0.143 |
| 3 | -0.049 | -0.209 | -0.221 |

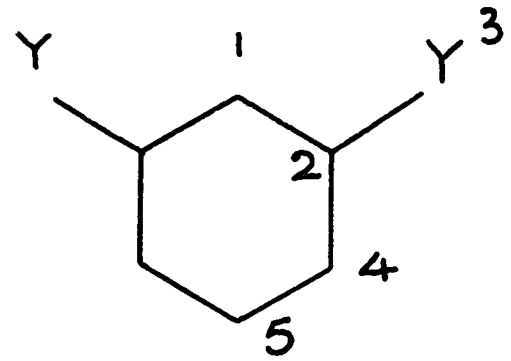
(ii) Two electron withdrawing groups:

ortho



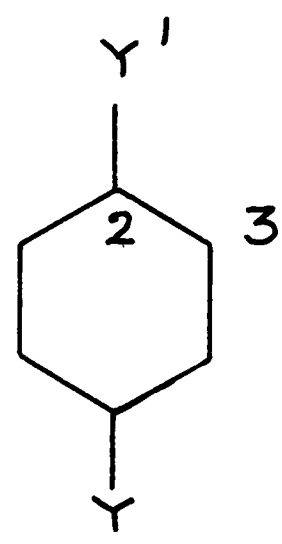

| | | | |
|---|---|---|---|
| 1 | +0.024 | +0.517 | +0.071 |
| *2 | -0.045 | -0.304 | -0.076 |
| 3 | +0.014 | +0.014 | +0.014 |
| 4 | +0.009 | -0.224 | -0.006 |

meta




| Atom | $q^a$ | $n, \pi^*$ | $\pi, \pi^*$ |
|---|---|---|---|
| 1 | +0.02 | +0.02 | +0.02 |
| *2 | -0.060 | -0.203 | -0.074 |
| 3 | +0.023 | +0.517 | +0.069 |
| 4 | +0.02 | -0.237 | -0.008 |
| 5 | -0.002 | -0.002 | -0.002 |

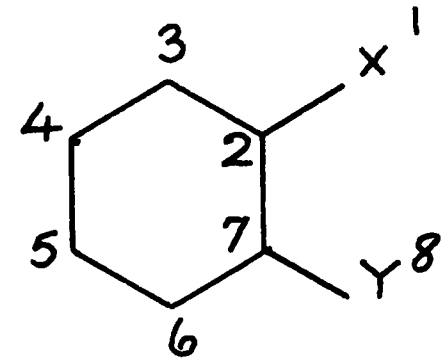
para




| | | | |
|---|---|---|---|
| 1 | +0.024 | +0.515 | +0.08 |
| *2 | -0.051 | -0.368 | -0.083 |
| 3 | +0.014 | -0.072 | +0.001 |

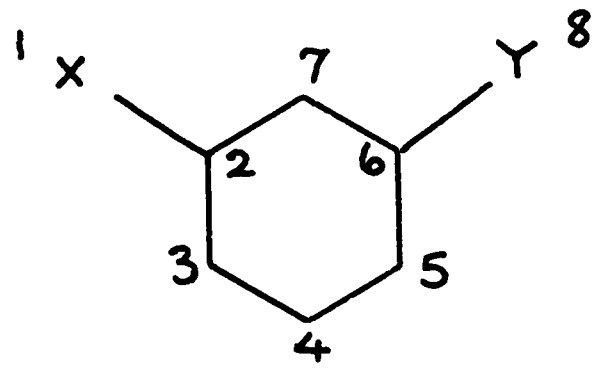
(iii) One donating and one withdrawing group:

ortho



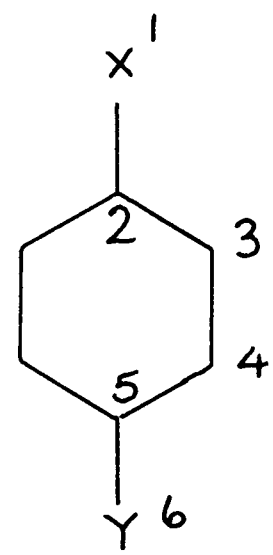

| Atom | $q_r^a$ | $n_2\pi^*$ | $\pi,\pi^*$ |
|---|---|---|---|
| 1 | +0.130 | +0.129 | +0.388 |
| *2 | +0.021 | +0.020 | +0.102 |
| 3 | -0.053 | -0.258 | -0.123 |
| 4 | +0.010 | -0.272 | -0.246 |
| 5 | -0.043 | -0.047 | +0.173 |
| 6 | +0.017 | -0.205 | -0.177 |
| *7 | -0.112 | -0.382 | -0.250 |
| 8 | +0.021 | +1.013 | +0.092 |

meta



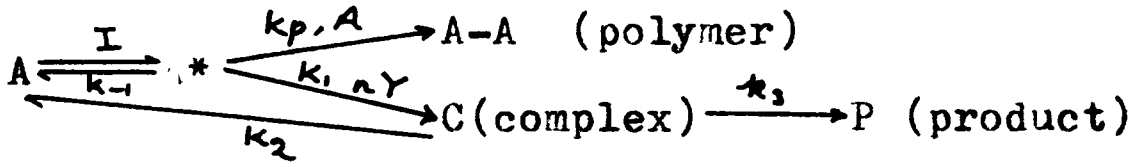

| | | | |
|---|---|---|---|
| 1 | +0.126 | +0.125 | +0.338 |
| *2 | +0.014 | +0.007 | +0.180 |
| 3 | -0.044 | -0.324 | -0.191 |
| 4 | +0.001 | -0.191 | -0.163 |
| 5 | -0.027 | -0.040 | +0.191 |
| *6 | -0.057 | -0.347 | -0.320 |
| 7 | -0.037 | -0.255 | -0.119 |
| 8 | +0.026 | +0.015 | +0.019 |

para




| Atom | $q^a$ | $n,\pi^*$ | $\pi,\pi^*$ |
|---|---|---|---|
| 1 | +0.129 | +0.129 | +0.385 |
| *2 | +0.023 | +0.023 | +0.192 |
| 3 | -0.053 | -0.303 | -0.171 |
| 4 | +0.017 | -0.233 | -0.207 |
| *5 | -0.101 | -0.101 | +0.114 |
| 6 | +0.021 | +1.021 | +0.154 |

From the suggested mechanism:




$$\frac{dP}{dt} = k_3C \quad \ldots\ldots 1$$

Steady state of A*:

$$I = k_{-1}(A^*) + k_1(Y)^n(A^*) + k_p(A^*) \quad \ldots\ldots 2$$

Steady state of C:

$$k_2C + k_3C = k_1(Y)^n(A^*) \quad \ldots\ldots 3$$

Substituting (2) into (3) and putting the result into (1):

$$\frac{dP}{dt} = \text{Rate} = \frac{k_1.k_3.I.(Y)^n}{(k_2+k_3)(k_{-1}+k_p(A)+k_1(Y)^n)} \quad \ldots 4$$

This is of the form:

$$\text{Rate} = \frac{K(Y)^n}{K'+(Y)^n} \quad \text{or} \quad \frac{1}{\text{Rate}} = a + \frac{b}{(Y)^n} \quad \ldots 5$$

From the data on pp.175-176, plotting Y in terms of both concentration and activity, and taking n=1 and n=2, we obtain the curves shewn overleaf. Neither for n=1 nor for n=2 is a linear relationship obtained. It is therefore concluded that the order, n, of the reaction in added nucleophile is non-integral, and this result is consistent with the arguments set out on pp.171-1.

However, if the quantum yield for the formation of the product, , were very small, i.e. $(k_{-1}+k_p) >> k_1$ , then equation (4) would reduce to the form:

$$\frac{dP}{dt} = \frac{k_1k_3I.(Y)^n}{(k_2+k_3)(k_{-1}+k_p(A))} = K.(Y)^n \quad \ldots\ldots 6$$

Thus:

$$\log_{10}(\text{Rate}) = \log_{10}K + n.\log_{10}(Y) \quad \ldots\ldots 7$$

## APPENDIX 2

For the pathway 'A', representing the suggested reaction mechanism:

$$Ar.X \xrightarrow{h\nu} (Ar.X)^* \underset{k_2}{\overset{nY,\ k_1}{\rightleftharpoons}} Ar.XY \xrightarrow{k_3} Ar.Y + X$$

Assuming steady state concentrations of $(Ar.X)^*$ and $Ar.XY$:

$$\frac{d(Ar.XY)}{dt} = 0 = k_1(Ar.X)^*(Y)^n - (k_2 + k_3).(Ar.XY)$$

$$\therefore (Ar.XY) = \frac{k_1(Ar.X)^*(Y)^n}{(k_2 + k_3)}$$

$$\frac{d(Ar.Y)}{dt} = k_3(Ar.XY) = \frac{k_3.k_1.(Ar.X)^*(Y)^n}{(k_2 + k_3)} = K.(Y)^n$$

$$\therefore (Ar.Y) = K(Y)^n.t + \text{Constant}$$

When $t = 0$, $(Ar.Y) = 0$;

$$\therefore \text{Rate of formation of product} = \frac{Ar.Y}{t} = K(Y)^n$$

$$\log_{10}(\text{Rate}) = \log_{10}(K) + n.\log_{10}(Y)$$

The order of the reaction 'n' in added nucleophile is obtained as the slope of the logarithmic plot.

'Y' may be either a concentration, or, more properly, an activity.

METHOXIDE

CONCENTRATION

ACTIVITY

2·0 ×10⁷

1/Rate

1·5 ×10⁷

1·0 ×10⁷

0·5 ×10⁷

0 2 4 6

0 10 20 30

4 8 12 16 • 1/Y

0 100 200 300 × 1/Y²

ETHOXIDE

CONCENTRATION

ACTIVITY

4×10⁷

1/Rate

3×10⁷

2×10⁷

1×10⁷

0 0·5 1·0 1·5

0 1 2 3

10 15 20 25 • 1/Y

100 300 500 700 × 1/Y²

The quantity 'Ar. Y' is measured from the g.l.c. trace by comparison of the area under the trace due to the product with that due to a marker.

If a sample solution gives rise to peaks of area M from m mg./ml. of marker and area P from an unknown x mg./ml. of product then

$$x = \frac{Km.P}{M} = \frac{K'P}{M}$$

where K is a constant obtained from test solutions indicating the relative peak areas due to known concentrations of each component.

The error, dx, in calculating x is dk + dm + dP + dM.

dK was found to be reproducible to within 1.5%. dm, according to data obtained with test solutions varied about $\pm$ 2%.

dP, representing a small product peak was found to be less easy to measure accurately, and a reliability of only $\pm$ 10% can be placed upon it. For the experiments where the nucleophile was an amine the reliability, $\pm$ 70% at times, was so poor that no analysis of the data was made.

dM, from the larger peak due to the marker could be measured to within 2%. Therefore total error dx = 1.5 + 2 + 10 + 2 $\sim$ 16%

Good straight lines were obtained from the early points in the

METHOXIDE CONCENTRATION

ACTIVITY

$2.0 \times 10^7$

$\frac{1}{Rate}$

$1.5 \times 10^7$

$1.0 \times 10^7$

$0.5 \times 10^7$

0 2 4 6
0 10 20 30

4 8 12 16 • 1/Y
0 100 200 300 × 1/Y²

ETHOXIDE CONCENTRATION

ACTIVITY

$4 \times 10^7$

$\frac{1}{Rate}$

$3 \times 10^7$

$2 \times 10^7$

$1 \times 10^7$

0 0.5 1.0 1.5
0 1 2 3

10 15 20 25 • 1/Y
100 300 500 700 × 1/Y²

The quantity 'Ar. Y' is measured from the g.l.c. trace by comparison of the area under the trace due to the product with that due to a marker.

If a sample solution gives rise to peaks of area M from m mg./ml. of marker and area P from an unknown x mg./ml. of product then

$$x = \frac{Km.P}{M} = \frac{K'P}{M}$$

where K is a constant obtained from test solutions indicating the relative peak areas due to known concentrations of each component.

The error, dx, in calculating x is dk + dm + dP + dM.

dK was found to be reproducible to within 1.5%. dm, according to data obtained with test solutions varied about $\pm$ 2%.

dP, representing a small product peak was found to be less easy to measure accurately, and a reliability of only $\pm$ 10% can be placed upon it. For the experiments where the nucleophile was an amine the reliability, $\pm$ 70% at times, was so poor that no analysis of the data was made.

dM, from the larger peak due to the marker could be measured to within 2%. Therefore total error dx = 1.5 + 2 + 10 + 2 $\sim$ 16%

Good straight lines were obtained from the early points in the

The following argument shews that the use of the approximate form, (6), of equation (4), is justified.

Fluorobenzene has $\lambda_{max}$ = 255 mμ, corresponding to an excitation energy of 115 kcal./mole.

From Appendix 6, the output of the lamp in the region where fluorobenzene absorbs, 235 - 275 mμ, is 16.7 w.

Energy absorbed by fluorobenzene = $7.0 \times 10^{-2}$ kcal./sec.

= $6.1 \times 10^{-4}$ einstein/sec.

The rate of the reaction, experimentally determined, (p.175) is of the order $1 \times 10^{-7}$ mole/litre/sec.

= $8 \times 10^{-9}$ mole/80 ml./sec.

Thus, the approximate quantum yield for the formation of product $= \frac{8 \times 10^{-9}}{6.1 \times 10^{-4}} = 1.3 \times 10^{-5}$

i.e. only 1 quantum in 77,000 absorbed by the starting material leads to product.

plot of 'Ar. Y' against time. The errors in these slopes, and in measuring time, and nucleophile concentration are ignored.

Using the above expression to calculate the amount of product present in each sample we gain the results shewn in the following tables.

1. Fluorobenzene/Diethylamine System

Marker: Phenol K = 0.74
Conditions for g.l.c.: 5% ppa, 100°, 10 p.s.i.
N,N-Diethylaniline Rt = 14 min.
Phenol Rt = 24 min.

(a) Fluorobenzene (321 mg.) and diethylamine (461 mg.) in ethanol (80 ml.)

| Time (min.) | Product (mg./ml.) |
|---|---|
| 20 | 0.0161 |
| 40 | 0.0290 |
| 75 | 0.0332 |
| 120 | 0.0513 |
| 180 | 0.0562 |
| 270 | 0.0513 |

(b) Fluorobenzene (320 mg.) and diethylamine (921 mg.) in ethanol (80 ml.)

| Time (min.) | Product (mg./ml.) |
|---|---|
| 15 | 0.0154 |
| 30 | 0.0468 |
| 55 | 0.0811 |
| 85 | 0.0936 |
| 120 | 0.108 |
| 160 | 0.112 |
| 210 | 0.114 |
| 285 | 0.112 |

2. Fluorobenzene/Ethoxide Ion System

Marker: Tetralin K' = 1.09
Conditions for g.l.c.: 5% ppa, 75°, 8 p.s.i.
Phenetole Rt = 8 min.
Tetralin Rt = 15 min.

(a) Fluorobenzene (105 mg.) in ethanol (20 ml.)

| Time (min.) | Product (mg./ml.) |
|---|---|
| 60 | 0.0038 |
| 120 | 0.0082 |
| 180 | 0.0122 |
| 240 | 0.0165 |
| 300 | 0.0197 |

(b) Fluorobenzene (103 mg.) in 0.57N sodium ethoxide (20 ml.)

| Time (min.) | Product (mg./ml.) | Corrected for Solvent |
|---|---|---|
| 30 | 0.0063 | 0.0043 |
| 60 | 0.0150 | 0.0103 |
| 90 | 0.0270 | 0.0209 |
| 120 | 0.0318 | 0.0236 |
| 150 | 0.0382 | 0.0280 |
| 180 | 0.0480 | 0.0357 |
| 240 | 0.0644 | 0.0479 |
| 300 | 0.0737 | 0.0531 |

(c) Fluorobenzene (106 mg.) in 1.06N sodium ethoxide (20 ml.)

| Time (min.) | Product (mg./ml.) | Corrected for Solvent |
|---|---|---|
| 60 | 0.0220 | 0.0179 |
| 90 | 0.0351 | 0.0280 |
| 120 | 0.0472 | 0.0380 |
| 150 | 0.0585 | 0.0483 |
| 180 | 0.0667 | 0.0544 |

(c) (Continued)

| Time (min.) | Product (mg./ml.) | Corrected for Solvent |
|---|---|---|
| 210 | 0.0736 | 0.0642 |
| 270 | 0.0840 | 0.0755 |
| 330 | 0.1021 | 0.0902 |

(d) Fluorobenzene (410 mg.) in 1.66N sodium ethoxide (90 ml.)

| Time (min.) | Product (mg./ml.) | Corrected for Solvent |
|---|---|---|
| 30 | 0.0150 | 0.0130 |
| 60 | 0.0300 | 0.0259 |
| 90 | 0.0444 | 0.0383 |
| 120 | 0.0534 | 0.0452 |
| 150 | 0.0631 | 0.0529 |
| 180 | 0.0770 | 0.0647 |
| 210 | 0.0836 | 0.0692 |
| 240 | 0.0880 | 0.0715 |

(e) Fluorobenzene (399 mg.) in 2.81N sodium ethoxide (90 ml.)

| Time (min.) | Product (mg./ml.) | Corrected for Solvent |
|---|---|---|
| 10 | 0.0067 | 0.0060 |
| 20 | 0.0132 | 0.0119 |
| 30 | 0.0211 | 0.0191 |
| 40 | 0.0267 | 0.0240 |
| 60 | 0.0423 | 0.0381 |
| 80 | 0.0504 | 0.0450 |
| 100 | 0.0713 | 0.0646 |
| 120 | 0.0777 | 0.0695 |
| 150 | 0.0891 | 0.0799 |
| 180 | 0.1057 | 0.0934 |
| 240 | 0.1160 | 0.0995 |
| 300 | 0.1242 | 0.1016 |

3. Fluorobenzene/Methoxide Ion System

Marker: Tetralin K' = 1.10
Conditions for g.l.c.: 5% ppa, 75°, 8 p.s.i.
Anisole Rt = 6min.
Tetralin Rt = 15 min.

(a) Fluorobenzene (106 mg.) in methanol (20 ml.)

| Time (min.) | Product (mg./ml.) |
|---|---|
| 90 | 0.0044 |
| 120 | 0.0063 |
| 180 | 0.0096 |
| 240 | 0.0133 |
| 300 | 0.0164 |

(b) Fluorobenzene (105 mg.) in 0.13N sodium methoxide (20 ml.)

| Time (min.) | Product (mg./ml.) | Corrected for Solvent |
|---|---|---|
| 20 | 0.0079 | 0.0068 |
| 40 | 0.0154 | 0.0132 |
| 60 | 0.0231 | 0.0198 |
| 90 | 0.0350 | 0.0300 |
| 120 | 0.0444 | 0.0377 |
| 150 | 0.0527 | 0.0444 |
| 180 | 0.0638 | 0.0538 |
| 240 | 0.0784 | 0.0671 |
| 360 | 0.0907 | 0.0740 |

(c) Fluorobenzene (407 mg.) in 0.39N sodium methoxide (20 ml.)

| Time (min.) | Product (mg./ml.) | Corrected for Solvent |
|---|---|---|
| 20 | 0.0101 | 0.0090 |
| 40 | 0.0215 | 0.0193 |
| 60 | 0.0291 | 0.0255 |
| 90 | 0.0413 | 0.0363 |

(c) (Continued)

| Time (min.) | Product (mg./ml.) | Corrected for Solvent |
|---|---|---|
| 120 | 0.0526 | 0.0459 |
| 150 | 0.0677 | 0.0593 |
| 180 | 0.0769 | 0.0679 |
| 240 | 0.0852 | 0.0746 |
| 300 | 0.0926 | 0.0819 |

(d) Fluorobenzene (99 mg.) in 0.55N sodium methoxide (20 ml.)

| Time (min.) | Product (mg./ml.) | Corrected for Solvent |
|---|---|---|
| 20 | 0.0123 | 0.0117 |
| 40 | 0.0240 | 0.0218 |
| 60 | 0.0364 | 0.0335 |
| 90 | 0.0464 | 0.0414 |
| 120 | 0.0603 | 0.0536 |
| 150 | 0.0724 | 0.0640 |
| 180 | 0.0809 | 0.0709 |
| 240 | 0.0952 | 0.0819 |
| 300 | 0.0965 | 0.0798 |

(e) Fluorobenzene (399 mg.) in 0.96N sodium methoxide ( 0 ml.)

| Time (min.) | Product (mg./ml.) | Corrected for Solvent |
|---|---|---|
| 20 | 0.0133 | 0.0127 |
| 40 | 0.0200 | 0.0253 |
| 60 | 0.0413 | 0.0380 |
| 80 | 0.0533 | 0.0488 |
| 120 | 0.0700 | 0.0642 |
| 150 | 0.0826 | 0.0742 |
| 180 | 0.0952 | 0.0852 |
| 210 | 0.1036 | 0.0919 |
| 240 | 0.1133 | 0.1000 |
| 300 | 0.1140 | 0.1063 |

(f) Fluorobenzene (407 mg.) in 1.69N sodium methoxide (30 ml.)

| Time (min.) | Product (mg./ml.) | Corrected for Solvent |
|---|---|---|
| 15 | 0.0136 | 0.012[illegible] |
| 30 | 0.0266 | 0.0250 |
| 45 | 0.0393 | 0.0369 |
| 60 | 0.0509 | 0.0476 |
| 90 | 0.0651 | 0.0601 |
| 120 | 0.0817 | 0.0750 |
| 150 | 0.0926 | 0.0842 |
| 180 | 0.1047 | 0.0947 |
| 210 | 0.1100 | 0.0983 |
| 240 | 0.1169 | 0.1035 |
| 300 | 0.1348 | 0.1181 |

* * * * *

These results were plotted in graphical form (Figs. 2 - 4) from which the following rates were obtained.

Fluorobenzene/Ethoxide ion system

| N ($EtO^-$) | Rate (mg./ml./hr.) | Rate (mole./litre/sec.) | $\log_{10}$(Rate) |
|---|---|---|---|
| 0.57 | $1.1 \times 10^{-2}$ | $2.51 \times 10^{-8}$ | -7.600 |
| 1.06 | $1.9 \times 10^{-2}$ | $4.33 \times 10^{-8}$ | -7.463 |
| 1.66 | $2.6 \times 10^{-2}$ | $5.93 \times 10^{-8}$ | -7.227 |
| 2.81 | $3.5 \times 10^{-2}$ | $7.98 \times 10^{-8}$ | -7.098 |

Fluorobenzene/Methoxide ion system

| N ($MeO^-$) | Rate (mg./ml./hr.) | Rate (mole./litre/sec.) | $\log_{10}$(Rate) |
|---|---|---|---|
| 0.19 | $2.3 \times 10^{-2}$ | $5.16 \times 10^{-8}$ | -7.287 |
| 0.38 | $2.7 \times 10^{-2}$ | $6.97 \times 10^{-8}$ | -7.157 |
| 0.55 | $3.25 \times 10^{-2}$ | $8.38 \times 10^{-7}$ | -7.077 |
| 0.96 | $3.9 \times 10^{-2}$ | $1.01 \times 10^{-7}$ | -6.997 |
| 1.67 | $5.0 \times 10^{-2}$ | $1.29 \times 10^{-7}$ | -6.889 |

Plotting the $\log_{10}$ (N) against $\log_{10}$(Rate) are obtained the curves shewn in Fig. 5. An improved result is obtained by using activities rather than concentrations.

The activities were calculated from the activity coefficients using the formula

$$\log_{10} \gamma \pm = \frac{-A\sqrt{N}}{1+\sqrt{N}} + \frac{N}{10}$$

where $A = \frac{1.825 \times 10^6}{(DT)^{3/2}}$

Using T = 300° and a dielectric constant of 25 for ethanol and 33 for methanol:

A (Ethanol) = 2.81
A (Methanol) = 1.86

Fluorobenzene/Ethoxide ion system

| Concentration N | Activity Coefficient | Activity | $\log_{10}$(Activity) |
|---|---|---|---|
| 0.57 | 0.0706 | 0.0403 | -1.395 |
| 1.06 | 0.0468 | 0.0496 | -1.304 |
| 1.66 | 0.0386 | 0.0640 | -1.194 |
| 2.81 | 0.0332 | 0.0939 | -1.027 |

Fluorobenzene/Methoxide ion system

| Concentration N | Activity Coefficient | Activity | $\log_{10}$(Activity) |
|---|---|---|---|
| 0.19 | 0.285 | 0.0542 | -1.266 |
| 0.30 | 0.211 | 0.0623 | -1.205 |
| 0.55 | 0.183 | 0.1007 | -0.997 |
| 0.96 | 0.150 | 0.1440 | -0.842 |
| 1.68 | 0.132 | 0.2230 | -0.652 |

Using the relationship

$$\log_{10}(\text{Rate}) = \log_{10} K + n\log_{10}(A)$$

were obtained the curves shewn in Fig. 6.

## APPENDIX 3

Consider two unit point charges a distance 'r' cm. apart in a medium of dielectric constant D:

Force required to move them a distance dr

$$dE = \frac{1}{D} \times \frac{e_2^2}{r^2} \cdot dr$$

To move them from a distance 'a' apart to infinity

$$\therefore E = \int_a^\infty \frac{1}{D} \cdot \frac{e_2^2}{r^2} \cdot dr$$

$$= \left[\frac{e^2}{Dr}\right]_\infty^a = \frac{e^2}{Da.}$$

Charge on an electron = $4.803 \times 10^{-10}$ e. s. u.

$$\therefore E = \frac{2.31 \times 10^{-19}}{Da} \text{ dyne - cm.}$$

$$= \frac{2.31 \times 10^{-26}}{Da} \text{ joules} = \frac{5.53 \times 10^{-30}}{Da} \text{ kcal.}$$

On a molar scale:

$$E = \frac{3.34 \times 10^{-6}}{Da} \text{ kcal./mole.}$$

In a medium of dielectric constant 15:

$$E = \frac{2.22 \times 10^{-7}}{a} \text{ kcal./mole.}$$

Putting 'a' in Angstroms rather than cm.:

$$E = \frac{22.2}{a} \text{ kcal./mole.}$$

Therefore, for various interionic distances:

| Ionic Distance a, Å | Energy of separation E, kcal./mole. |
|---|---|
| 1.0 | 22.2 |
| 1.5 | 14.8 |
| 2.0 | 11.1 |
| 2.5 | 8.9 |
| 3.0 | 7.4 |

## APPENDIX 4

### Formation of Acetaldehyde in the Photolyses of Nitrobenzene and Benzophenone in Ethereal Solution

For the process:

$$R^{\cdot} + C_2H_5.O.C_2H_5 \longrightarrow RH + C_2H_5.O.\dot{C}H.CH_3$$
(i)

$$(i) \longrightarrow C_2H_5^{\cdot} + CH_3.CHO$$

the radical (i) may, among other reactions, give acetaldehyde. The calculation assumes that the same proportion of radicals (i) always splits up in this fashion.

In the benzophenone irradiation, one molecule of benzophenone gives rise to one radical (i)

$$2Ph_2CO + 2H^{\cdot} \longrightarrow Ph_2C(OH).C(OH).Ph_2$$

and, experimentally, 2.25 g. benzophenone affords 203 mg. acetaldehyde-2,4-dinitrophenylhydrazone (ii)

$$\text{or } \frac{2.25}{182} \text{ moles. (i)} \longrightarrow \frac{0.203}{224} \text{ moles. (ii)}$$

Therefore 1 molecule of (ii) is produced on average by 13.65 acts of hydrogen abstraction.

In the nitrobenzene irradiation, if only one possible act of oxygen

transfer is admitted then acetaldehyde is produced either by six acts of hydrogen abstraction (Process A), or by four acts of hydrogen abstraction and one of oxygen transfer (Process B). This latter process yields one molecule of acetaldehyde for each act of oxygen transfer:

$$RO + C_2H_5.O.C_2H_5 \longrightarrow R + CH_3.CH(OH).OC_2H_5 \quad \text{(iii)}$$

$$\text{(iii)} \longrightarrow CH_3.CHO + C_2H_5OH$$

over all: $PhNO_2 + 4H^{\cdot} \longrightarrow PhNH_2 + H_2O + (O)$

Process B:

The ~~six~~ four acts of hydrogen abstraction will produce $\frac{4 \times 1}{13.65}$ molecules of acetaldehyde.

Therefore 475 mg. nitrobenzene will produce

$$\frac{4}{13.65} \times \frac{475}{123} \times 224 \text{ mg. (ii)} = 254 \text{ mg.}$$

Therefore only 142 mg. remain for oxygen transfer, whereas this would require $\frac{475}{123} \times 224 = 364$ mg.

For Process A:

$$PhNO_2 + 6H \longrightarrow \frac{0.336}{224} \text{ moles. (ii)}$$

Therefore 1 molecule of (ii) is produced on average by 13.20 acts of hydrogen abstraction.

It is concluded that hydrogen abstraction is the process actually occurring.

# APPENDIX 5

## Sensitization and Quenching Experiments

Accurate U. V. spectra of the compounds concerned were used to calculate extinction coefficients at the various wavelengths corresponding to the lines in the mercury spectrum. The lines which must be considered are those in the region 290 - 400 mμ. Below 290 mμ the Pyrex filter excludes the light; above 400 mμ nitrobenzene does not absorb. The quantity 'D' in the Tables below is the optical density per mg./ml. for a cell of path length 5 mm. The quantity 'Q' is the power of the lamp, taken from the manufacturers' data and corrected for the differences in the energy of the quanta at different wavelengths and, at 300 and 313 mμ, for incomplete transmission through the filter. At 300 mμ the transmission is 50%; at 313 mμ 80%.

The two lines at 297 and 302 mμ were considered as a composite line at 300 mμ.

(a) Sensitization with Benzophenone

Having obtained the optical densities D in terms of the absorbance of 1 mg./ml. the light absorbed by each component will depend upon the relative optical densities and the weight of each component in solution. Thus the corrected output Q will be divided between the

Table 18

The U. V. Absorption of Some Compounds at Various Wavelengths

| Wavelength mμ | $PhNO_2$ | | $CH_3.CO.CO.CH_3$ | | $C_{10}F_8$ | | $Ph_2CO$ | | $C_7H_7NO_2$ | |
|---|---|---|---|---|---|---|---|---|---|---|
| | ε | D | ε | D | ε | D | ε | D | ε | D |
| 300 | 600 | 2.44 | 16 | 0.[illegible]3 | 1[illegible]50 | 2.4[illegible] | 550 | 1.51 | 1510 | 5.[illegible]5 |
| 313 | 25[illegible] | 1.[illegible]1 | 10 | 0.[illegible]5 | 1[illegible]50 | 2.48 | 153 | 0.42 | [illegible]06 | [illegible].57 |
| 336 | 11[illegible] | 0.4[illegible] | - | - | 50 | 0.0[illegible] | 190 | 0.53 | [illegible]3 | 1.51 |
| 366 | 50 | 0.20 | 1 | 0.006 | 5 | 0.01 | 61 | 0.17 | 1[illegible]2 | 0.72 |
| 400 | 6 | 0.024 | 3 | 0.017 | - | - | - | - | (+) | (+) |

* * * * * * * *

Table 19

Output of the Lamp at Various Wavelengths

| Wavelength (mμ) | Energy (kcal.) | Output (W.) | Corrected (Q) |
|---|---|---|---|
| 300 | [illegible]5.5 | 10.0 | 3.[illegible] |
| 313 | 91.[illegible] | 13.6 | [illegible].6 |
| 336 | [illegible]5.0 | 2.0 | 1.7 |
| 366 | 7[illegible].0 | 21.5 | 19.[illegible] |
| 400 | 72.0 | [illegible].4 | 0.4 |

two components according to the relative optical density of each. The relative optical density is the quantity R in the Table below.

Nitrobenzene: 0.40 g.; Benzophenone: 20.0 g.

Thus R (Benzophenone) = 40 D (Benzophenone)

Table 20

The Power Absorbed by Nitrobenzene in the Sensitization by Benzophenone

| Wavelength | $D(PhNO_2)$ | $R(Ph_2C{:}O)$ | Total | Q | Power Absorbed by $PhNO_2$ |
|---|---|---|---|---|---|
| 300 | 2.44 | 60.4 | 62.8 | 3. | 0.14 |
| 313 | 1.01 | 16.8 | 17.8 | 3.6 | 0.4 |
| 336 | 0.4 | 21.2 | 21.7 | 1.7 | 0.0 |
| 366 | 0.20 | 6.8 | 7.0 | 19.3 | 0.566 |
| 400 | 0.024 | - | 0.02 | 0.4 | 0.400 |
| | | | Total: | 34.3 | 1.640 |

Thus the percentage of the total available number of quanta absorbed by nitrobenzene is $\frac{1.64}{34.3} \times 100 = 4.$ %

(b) Quenching with Biacetyl

Nitrobenzene 40 mg.; biacetyl 840 mg.

R (Biacetyl) = 1.2 D

Table 21

| Wavelength | D($PhNO_2$) | R(Biacetyl) | Total | Q | Power Absorbed by Biacetyl |
|---|---|---|---|---|---|
| 300 | 2.44 | 0.120 | 2.56 | 3.8 | 0.17[illegible] |
| 313 | 1.01 | 0.075 | 1.09 | [illegible].6 | 0.4[illegible]8 |
| 336 | 0.4[illegible] | - | 0.4[illegible] | 1.7 | - |
| 366 | 0.20 | 0.00[illegible] | 0.21 | 19.[illegible] | 0.733 |
| 400 | 0.024 | 0.022 | 0.05 | 0.4 | 0.209 |
| | | | | | |
| | | Total: | 34.3 | | 1.715 |

Percentage of total quanta absorbed by biacetyl i[illegible] 5.0%.

(c) Quenching with Octafluoronaphthalene

Nitrobenzene 504 mg.; octafluoronaphthalene 34 mg.

$R(PhNO_2) = 14.[illegible]D$

| Wavelength | $D(C_{10}F_8)$ | $R(PhNO_2)$ | Total | Q | Power Absorbed by $C_{10}F_8$ |
|---|---|---|---|---|---|
| 300 | 2.4[illegible] | 36.10 | 38.6 | 3.8 | 0.244 |
| 313 | 2.4[illegible] | 14.95 | 17.4 | [illegible].6 | 1.223 |
| 336 | 0.09 | 7.10 | 7.2 | 1.7 | 0.021 |
| 366 | 0.01 | 2.96 | 3.0 | 19.[illegible] | 0.067 |
| 400 | - | 0.35 | 0.4 | 0.4 | - |
| | | | | | |
| | | Total: | 34.3 | | 1.56 |

Percentage of total quanta absorbed by octafluoronaphthalene = 4.5%.

(d) Quenching of o-Nitrotoluene with Octafluoronaphthalene

o-Nitrotoluene 1[illegible] mg. ; octafluoronaphthalene 3[illegible] mg.

$R(C_7H_7NO_2)$ = 4.[illegible]5 D

Table 23

| Wavelength | $D(C_{10}F_8)$ | $R(C_7H_7NO_2)$ | Total | Q | Power Absorbed by $C_{10}F_8$ |
|---|---|---|---|---|---|
| 300 | 2.4[illegible] | 2[illegible].5 | 32.0 | 3.3 | 0.205 |
| 313 | 2.43 | 17.8 | 2[illegible].3 | 8.6 | 1.[illegible]50 |
| 33[illegible] | 0.09 | 7.5 | 7.6 | 1.7 | 0.021 |
| 366 | 0.[illegible]1 | 3.6 | 3.6 | 10.8 | 0.[illegible]55 |
| 400 | - | (+) | (+) | 0.4 | - |
| | | | Total: | 34.3 | 1.421 |

Percentage of total light absorbed by octafluoronaphthalene = 4.1%.

# APPENDIX 6

## Manufacturers' Data for the Output of the 500 W. Medium Pressure Mercury Arc

| Wavelength mμ | Output W. |
|---|---|
| 235 | 0.60 |
| 240 | 1.05 |
| 246 | 0.45 |
| 247 | 2.65 |
| 254 | 3.40 |
| 260 | 0.95 |
| 264 | 5.60 |
| 270 | 1.15 |
| 275 | 0.85 |
| 280 | 2.75 |
| 282 | 1.95 |
| 300 | 10.80 |
| 313 | 13.60 |
| 336 | 1.85 |
| 366 | 21.50 |
| 400 | 0.40 |
| 405 | 5.70 |
| 406 | 1.20 |
| 436 | 10.50 |
| 492 | 0.30 |
| 546 | 13.90 |
| 577 | 17.10 |

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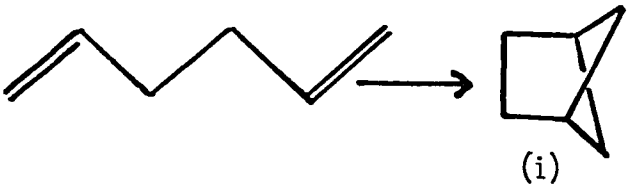
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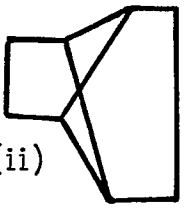
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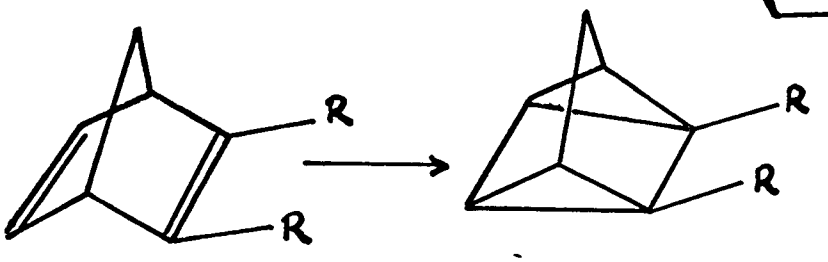
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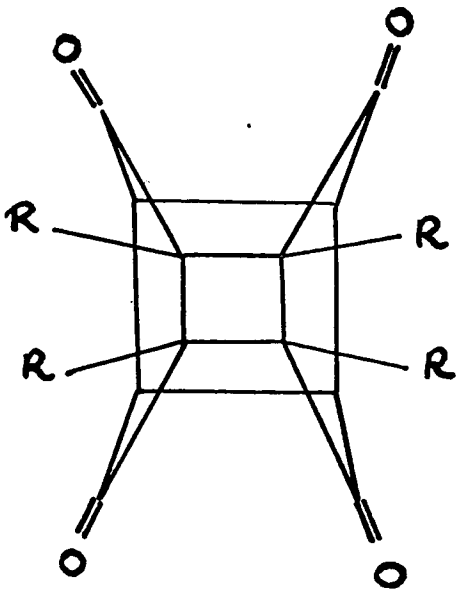
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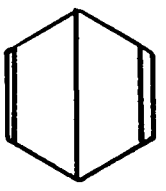
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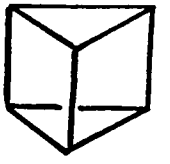

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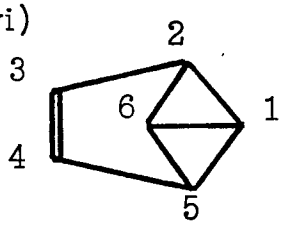

(iv): R = H
(v) : R = $CH_3$



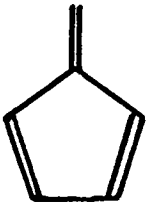
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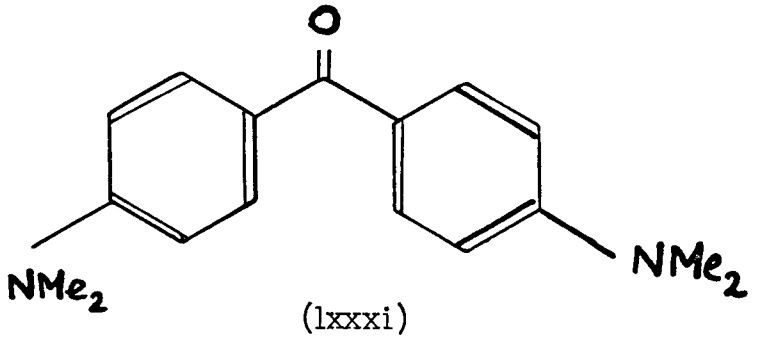
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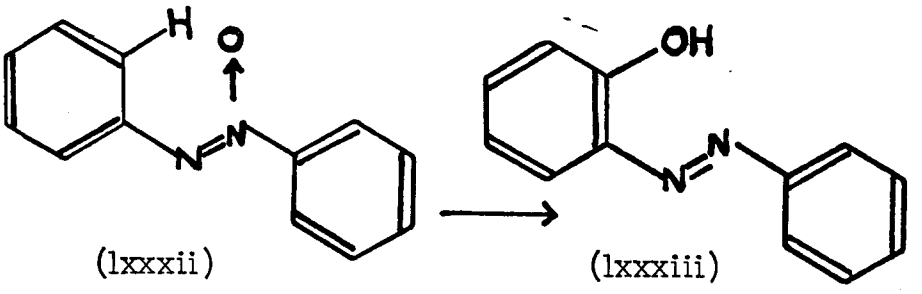

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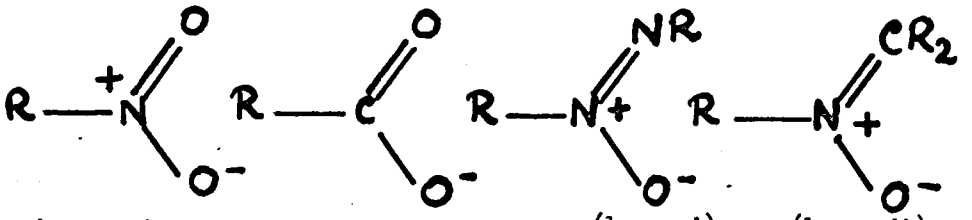
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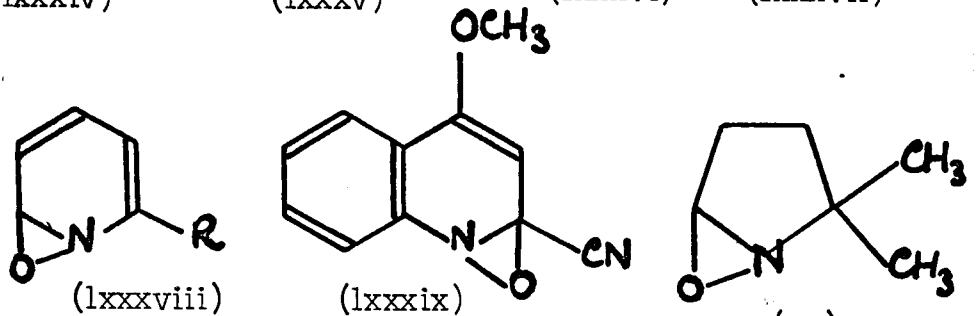
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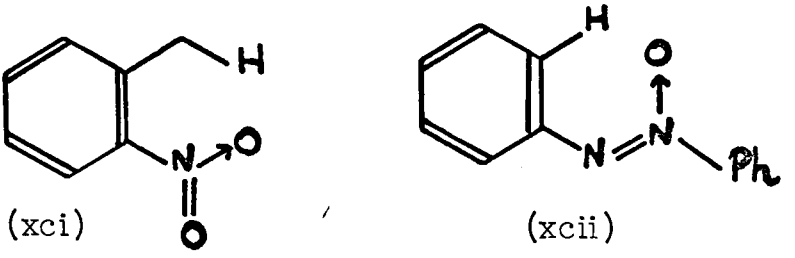
(lxxxii) (lxxxiii)



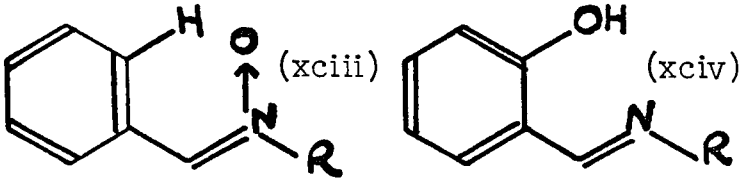
(lxxxiv) (lxxxv) (lxxxvi) (lxxxvii)



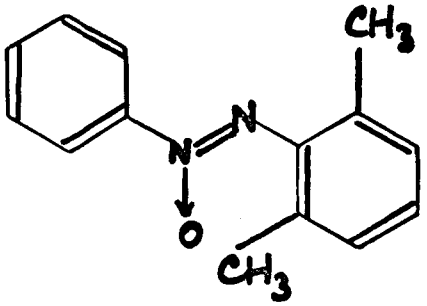
(lxxxviii) (lxxxix) (xc)



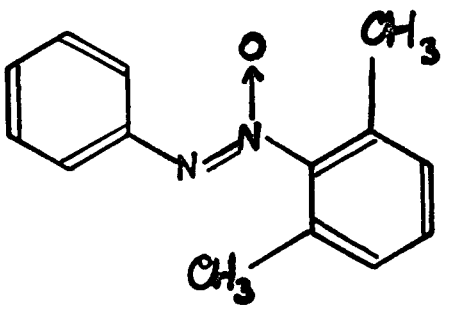
(xci) (xcii)



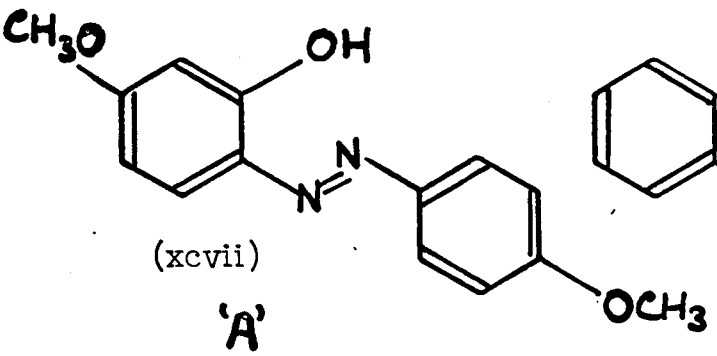
(xciii) (xciv)



(xcv)

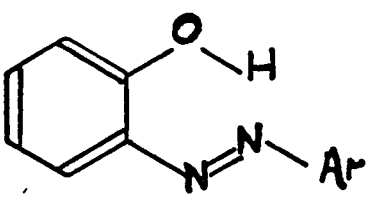


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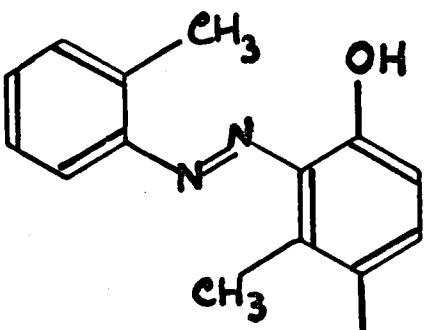


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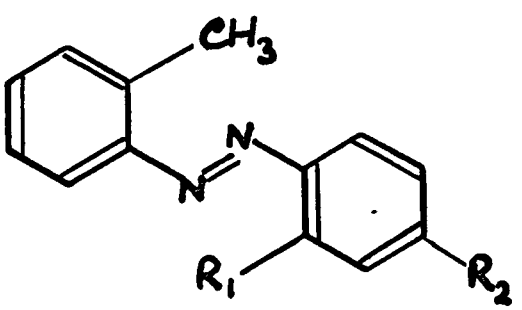
'A'



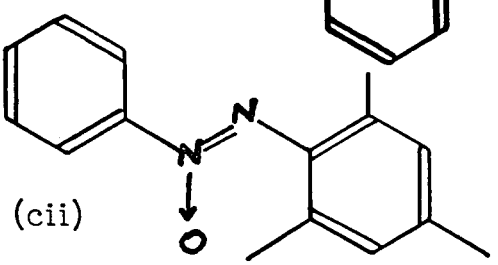
(xcviii)



(xcix)

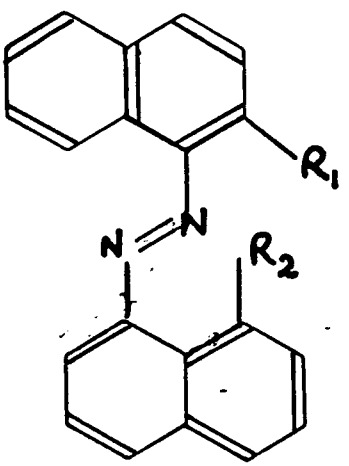


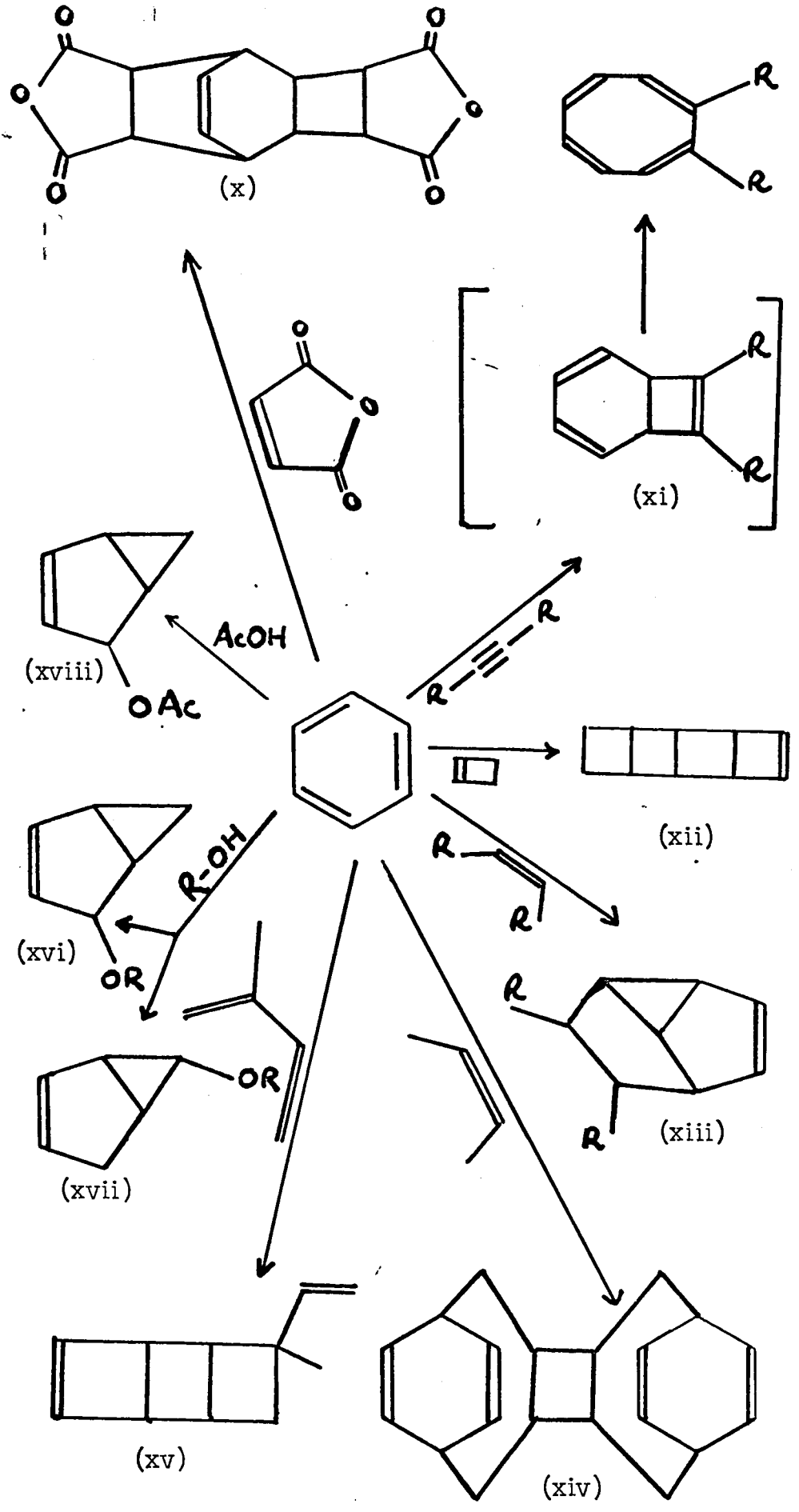
'B' (c): $R_1 = CH_3$, $R_2 = OH$
(ci): $R_1 = OH$, $R_2 = CH_3$

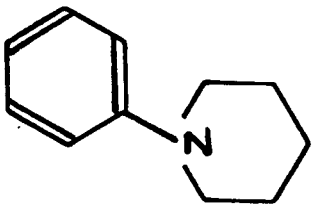


(cii)

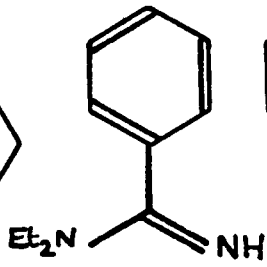
(ciii): $R_1 = OH$, $R_2 = H$
(civ): $R_1 = H$, $R_2 = OH$



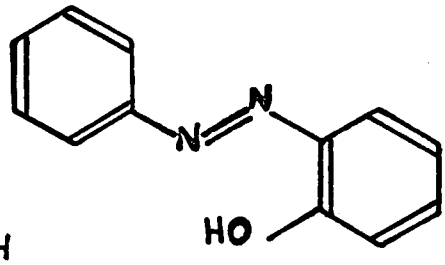

(x)
R
R
(xi)
AcOH
(xviii)
OAc
R
R
(xii)
R-OH
(xvi)
OR
R
R
OR
(xvii)
R
R
(xiii)
(xv)
(xiv)



(xix)

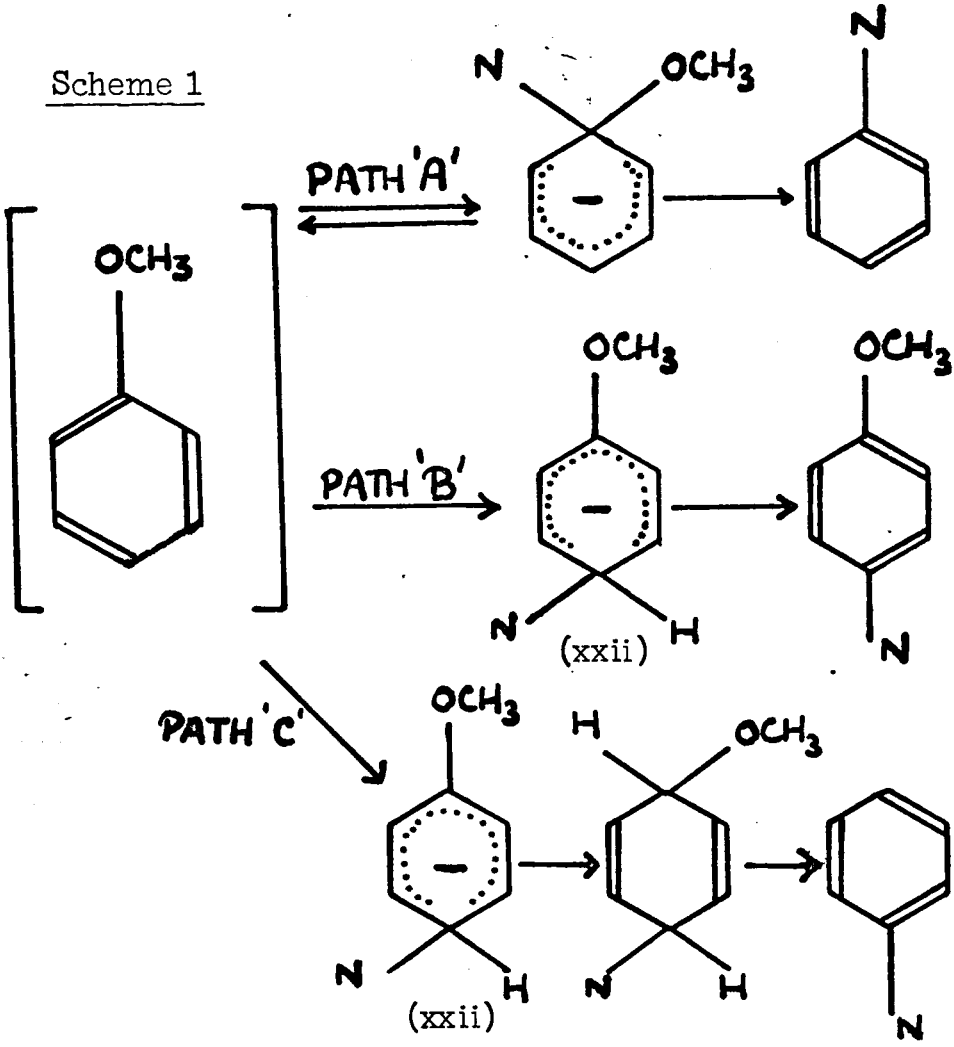


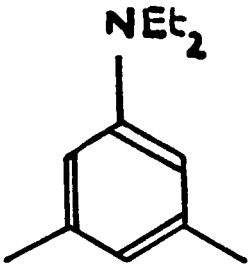
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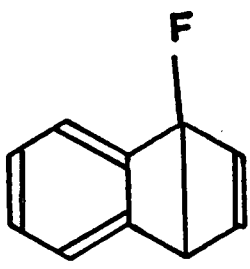
(xxi)

Scheme 1

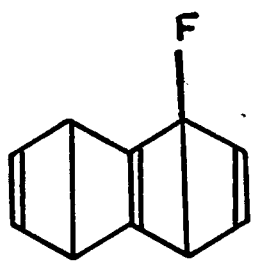


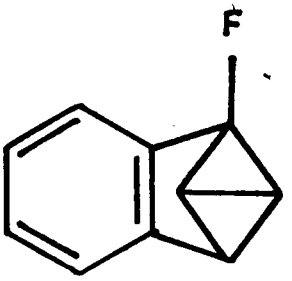
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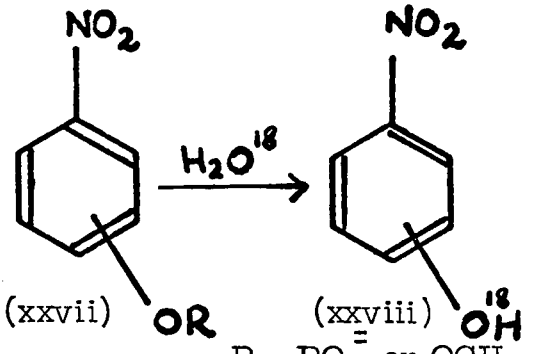
(xxiv)



(xxv)

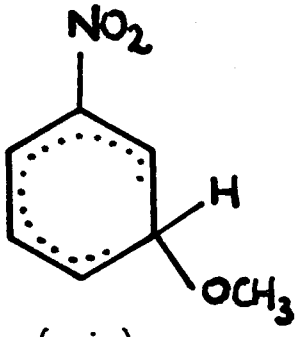



(xxvi)

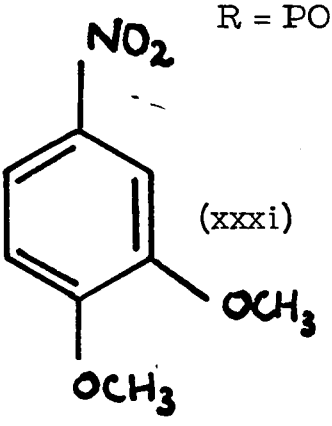



(xxvii) (xxviii)

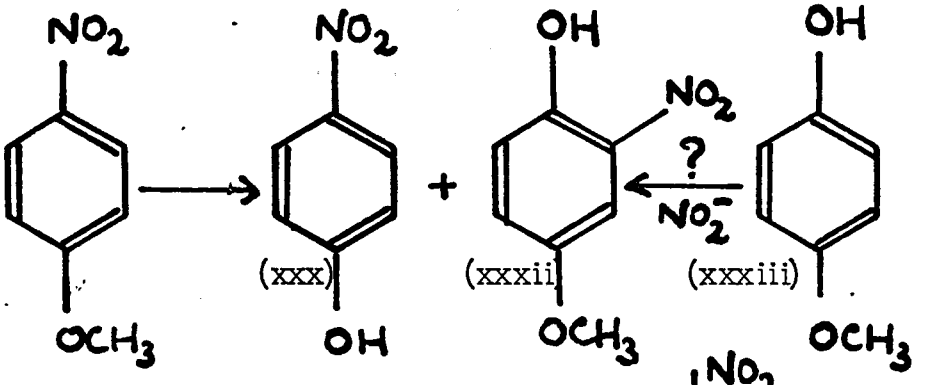
R = $PO_4^{=}$ or $OCH_3$



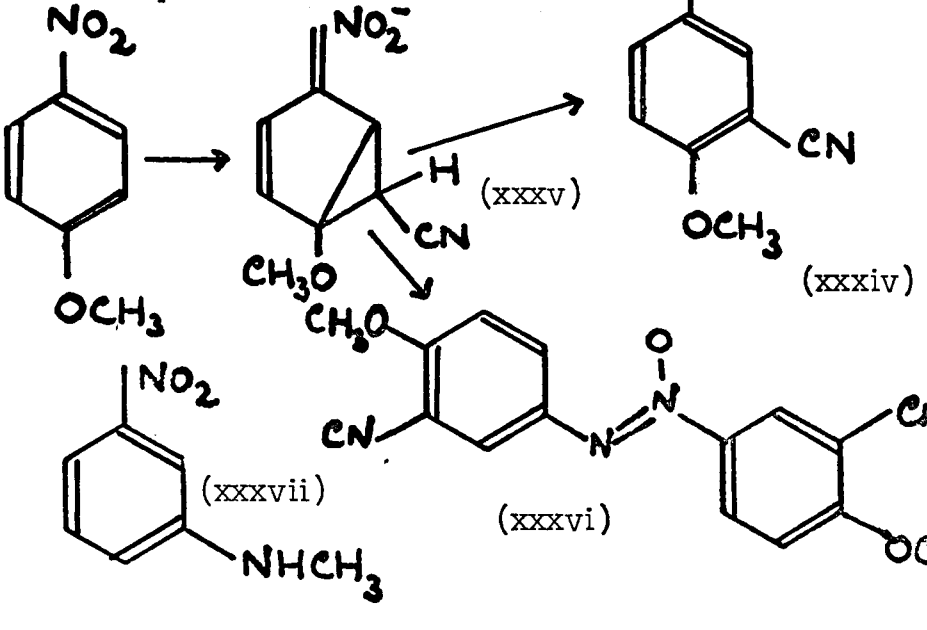

(xxix)




(xxxi)

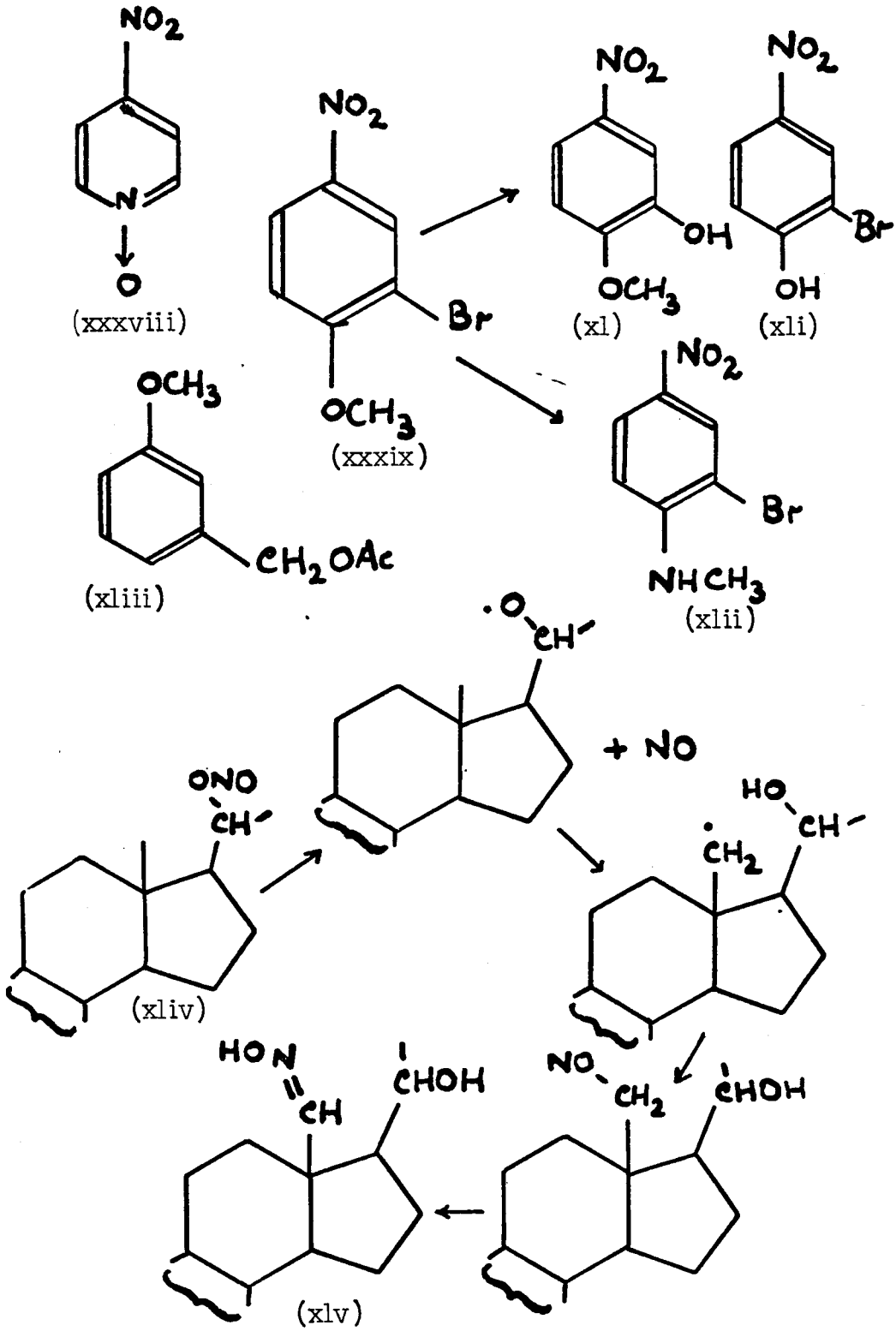


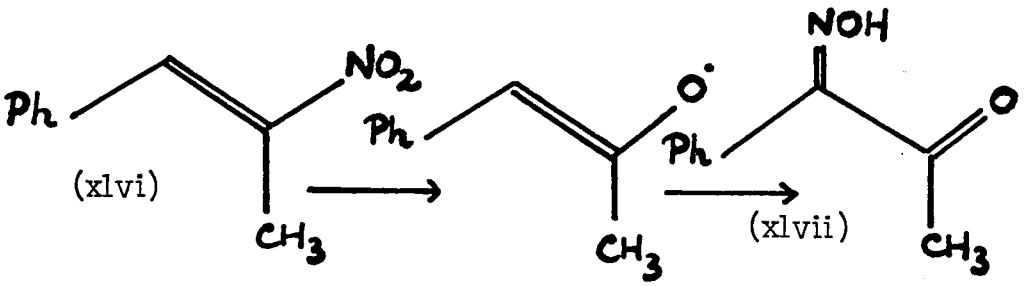

(xxx) (xxxii) (xxxiii)

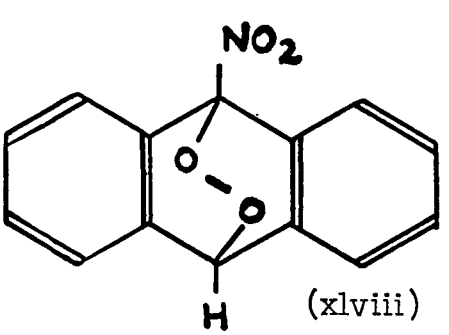



(xxxv) (xxxiv)

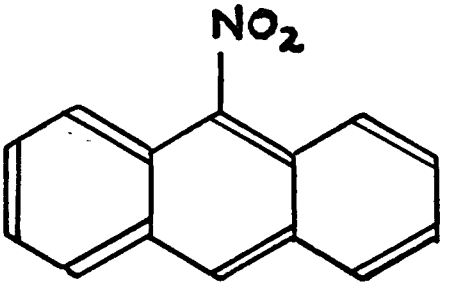
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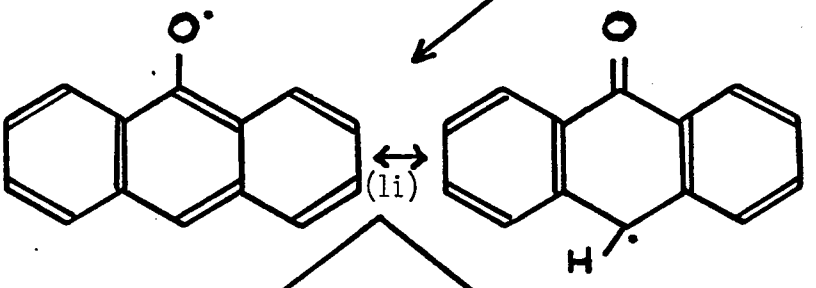

NO2
N
O
(xxxviii)
NO2
Br
OCH3
(xxxix)
NO2
OH
OCH3
(xl)
NO2
Br
OH
(xli)
OCH3
CH2OAc
(xliii)
NO2
Br
NHCH3
(xlii)
O
CH
+ NO
ONO
CH
(xliv)
HO
CH
CH2
NO
CH2
CHOH
HON
CH
CHOH
(xlv)

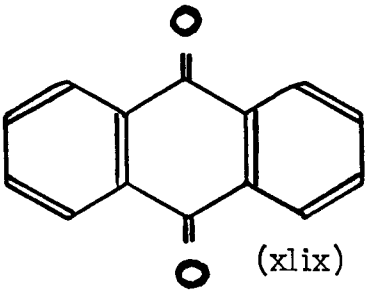


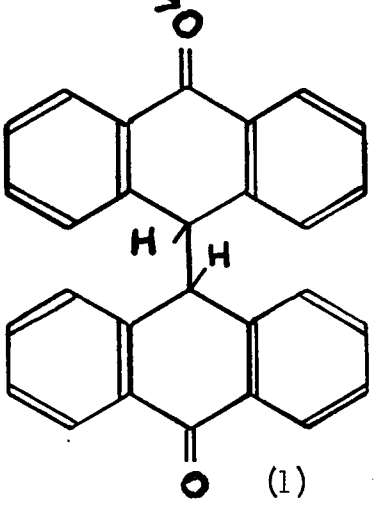

(xlviii)



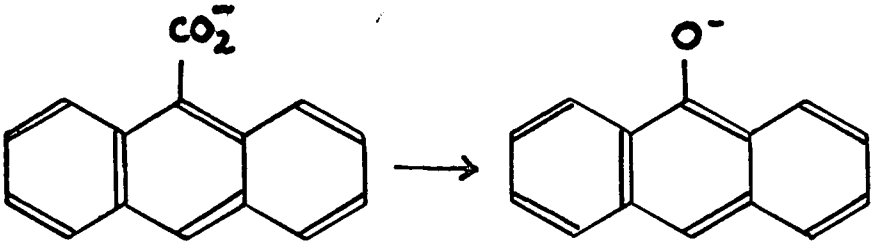



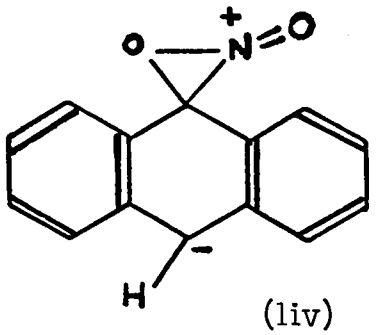

(xlix)



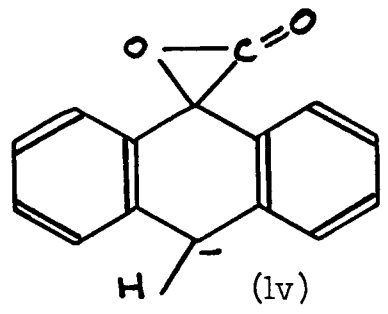

(l)



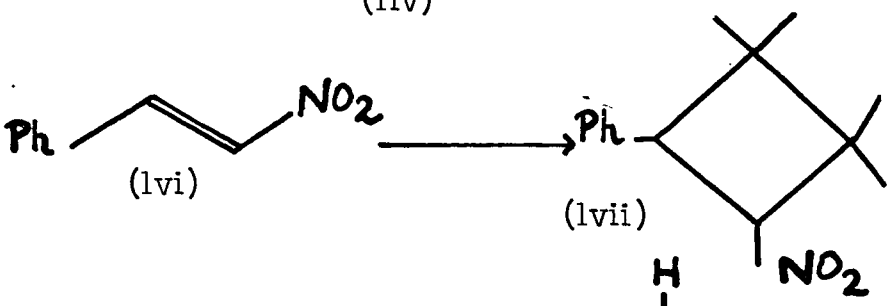

(lii) (liii)



(liv)

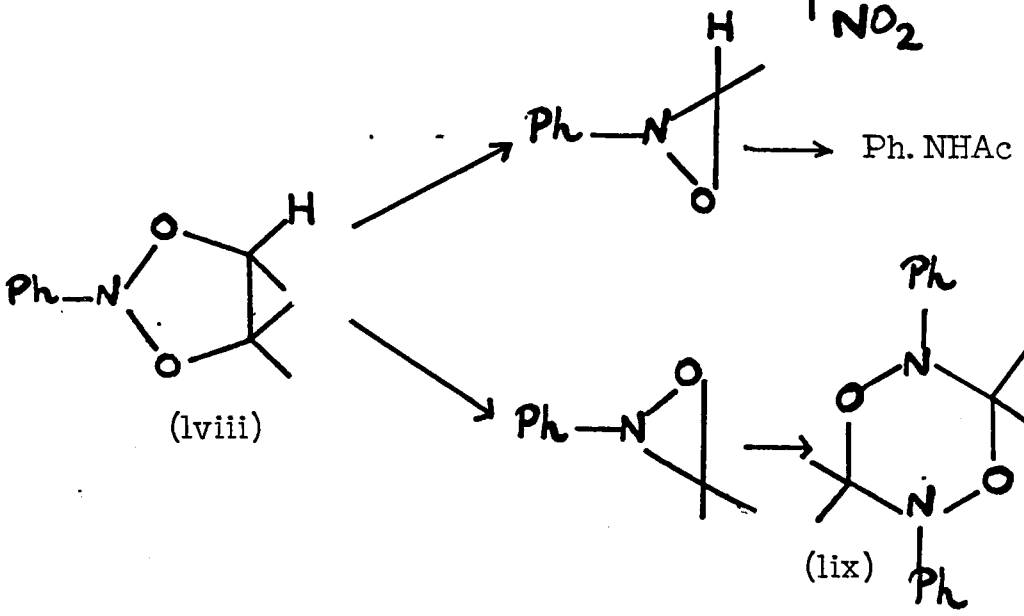


(lv)



(lvi)

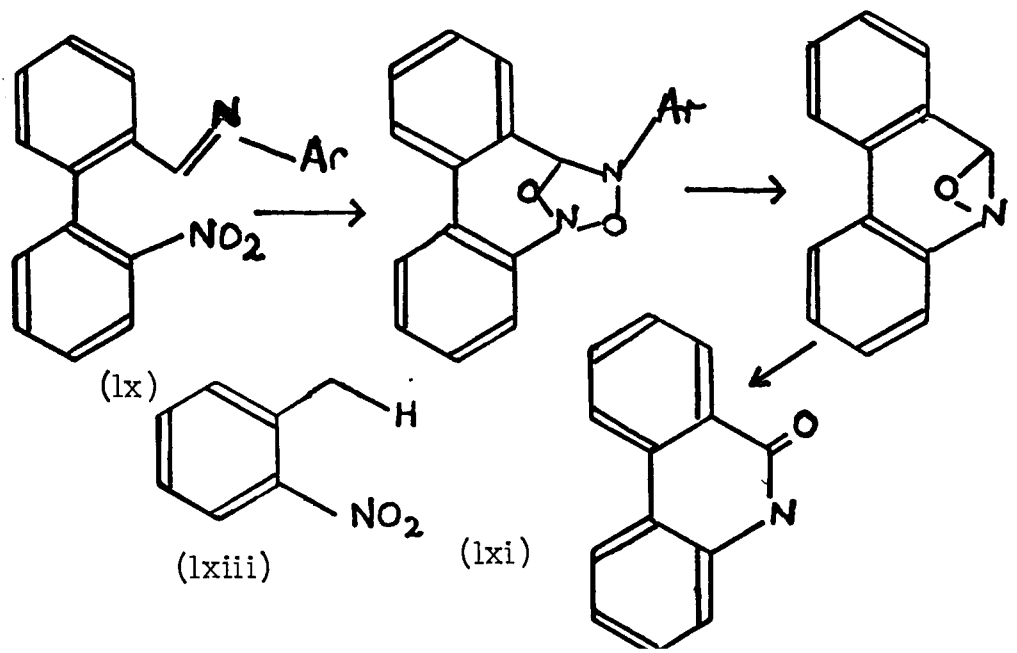
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(lviii)



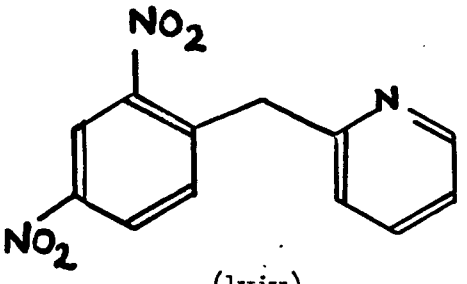
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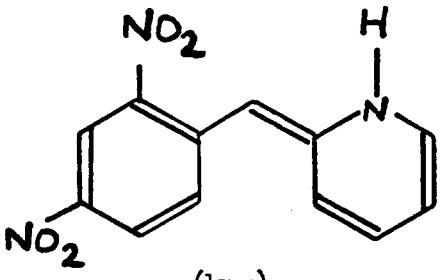
(lx)

(lxiii)

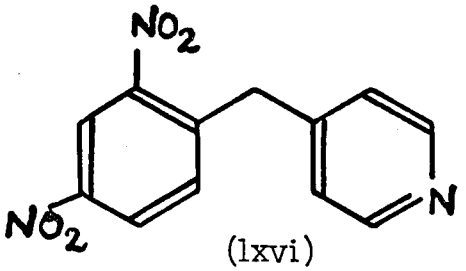
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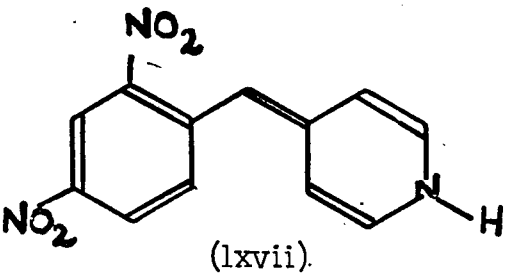
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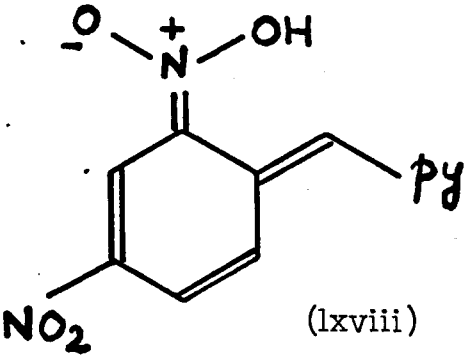
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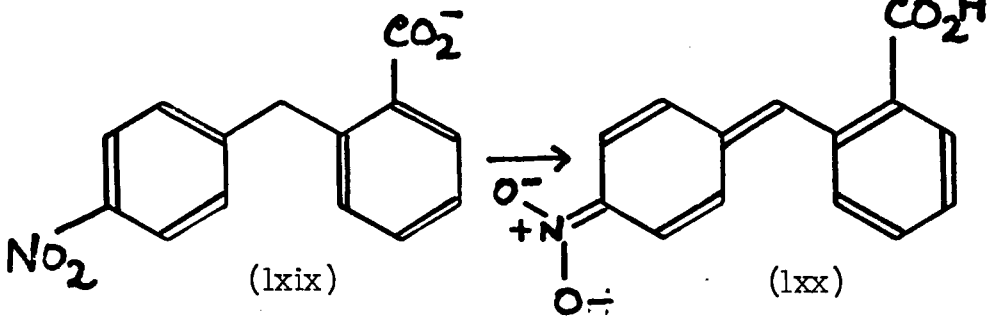
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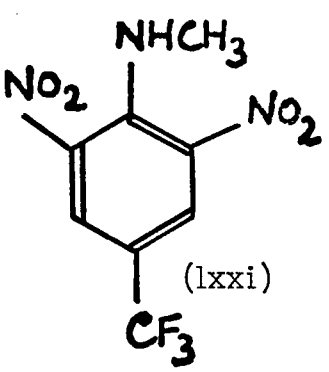
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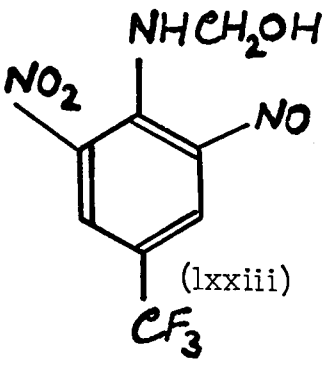
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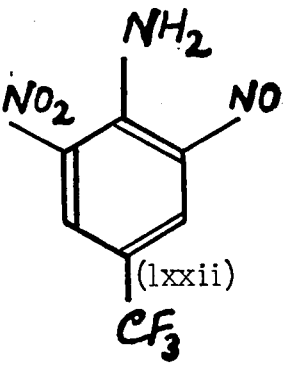
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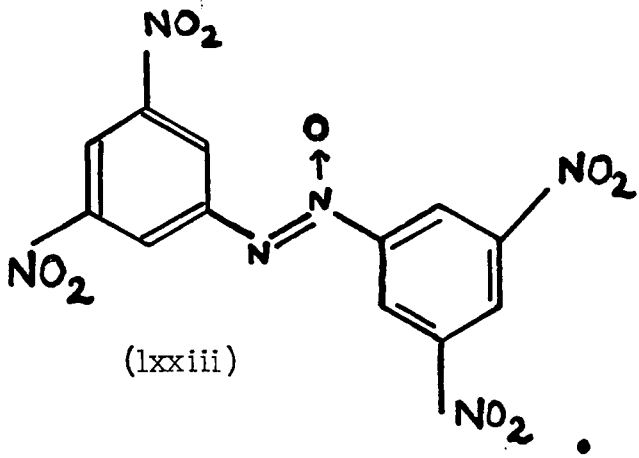
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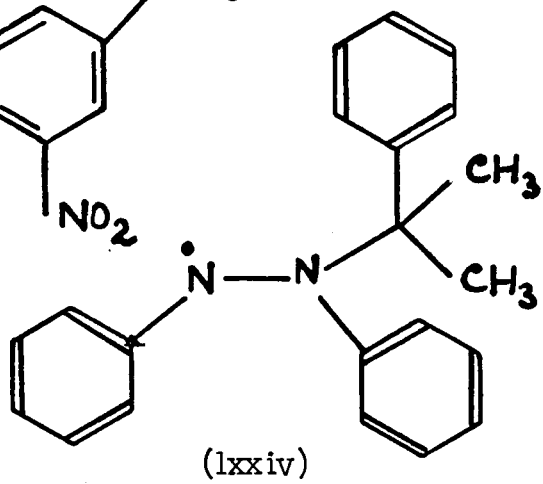
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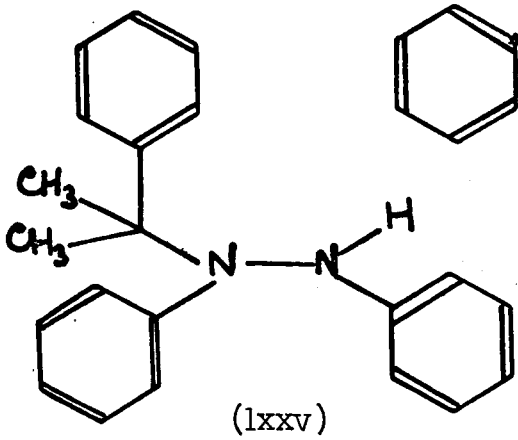
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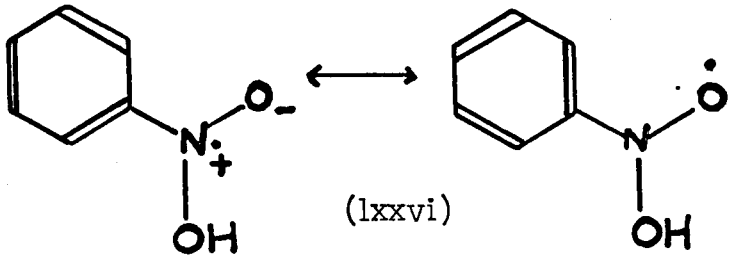
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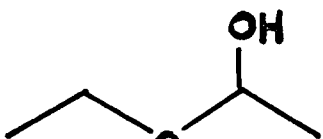
(lxxiv)



(lxxv)



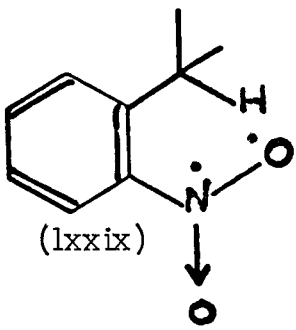
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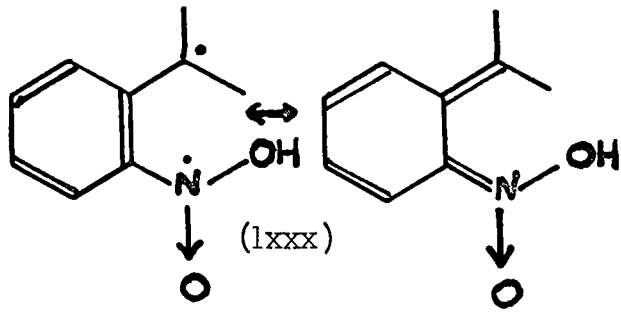
(lxxvii)



(lxxviii)



(lxxix)



(lxxx)

## SUMMARY

The work described in this thesis concerns the photochemistry of substituted aromatic compounds. In a previous study by the present author of the photonucleophilic substitution of monosubstituted benzenes the scope of the photo-substitution was investigated, but the mechanism was unclear. This work has been continued and the mechanism established. A radical process is excluded, and it is found that the reaction proceeds by attack of a nucleophile on the excited state of the aromatic compound, probably to give a sigma bonded intermediate (1), which decomposes to the substituted product.

A series of kinetic experiments established that the nucleophile participates in the rate determining step, but for alkoxide ions the order of the reaction in alkoxide ion is not unity. This is interpreted as being due to association of the ions to ion pairs and greater aggregates in the non-polar alcoholic solvent.

A correlation was noted between the photochemical lability of substituents (where these are leaving groups in the context of nucleophilic substitution) and the development of a partial positive charge on the carbon atom bearing the substituent in the $\pi,\pi^*$ excited state of the aromatic compound, as calculated using an H. M. O. approximation. An attempt was made to apply the same consider-

ations to photonucleophilic substitution in the disubstituted benzene series. Although calculations indicated which compounds might be expected to be photochemically reactive, experimental difficulties precluded the formulation of substitution rules.

In the monosubstituted naphthalene series the fluoronaphthalenes underwent photonucleophilic substitution readily, but the methoxynaphthalenes gave complex mixtures of unstable substances. In the case of 1-fluoronaphthalene a novel photochemical transformation product of the starting material, 3, 4-benz-2-fluoro-tricyclo-$(3,1,0,0^{2,6})$-hex-3-ene (11), was isolated. This is the first example of a benz-benzvalene.

Irradiation of nitrobenzene with diethylamine was found to give, not the substituted product, N, N-diethylaniline, but reduction products, mainly aniline. A study of the reaction was made, and it was found that photo-reduction of aromatic nitrocompounds is a general phenomenon, in solvents bearing hydrogen atoms capable of abstraction. Interposition of a Pyrex glass filter between the lamp and the photolyte causes coupled species, initially the azoxycompound, to be formed as major products, when a basic solvent is used. However, the azoxycompound is not usually isolated, for it is transformed photochemically both to the o-hydroxyazocompound and, by photosensitization by the

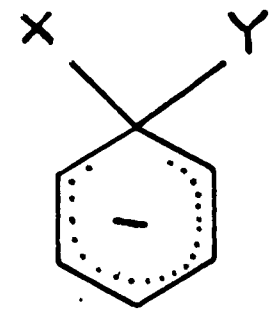
starting material, to the azocompound.

Mechanistic studies on the photo-reduction of nitrobenzene indicate that reduction occurs by hydrogen abstraction processes, rather than by oxygen atom transfer or electron transfer. Although nitrosobenzene and phenylhydroxylamine have not been isolated from the reaction mixtures, their presence has been inferred, and it is suggested that they are removed from the solution, before they attain isolable concentrations, by reduction by the first formed intermediate $C_6H_5NO_2H$. This intermediate is seen as arising by hydrogen abstraction from the solvent by excited nitrobenzene in a triplet $\pi, \pi^*$ state. Although hydrogen abstraction is not a reaction generally associated with $\pi, \pi^*$ states, H. M. O. calculations on nitrobenzene indicate that in this state an electron-deficiency develops on the oxygen atoms of the nitro group, giving them something of the character of an alkoxy radical.

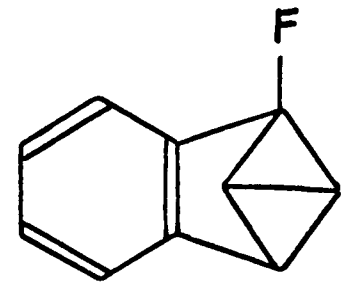
Photochemical studies on azoxycompounds shew that the well-known rearrangement to give the o-hydroxyazocompound (iii - iv) proceeds faster in polar solvents, perhaps suggesting an ionic process rather than a hydrogen atom abstraction/radical recombination. Sensitization encourages photo-reduction to the azocompound; this indicates that rearrangement is probably a reaction of the singlet

state, whereas photo-reduction involves the triplet. The situation therefore parallels that found for nitrocompounds, where photo-reduction proceeds via the triplet state and the rearrangement of o-methylnitrobenzenes to o-nitrosobenzyl alcohols (v - vi) is a function of the singlet state.

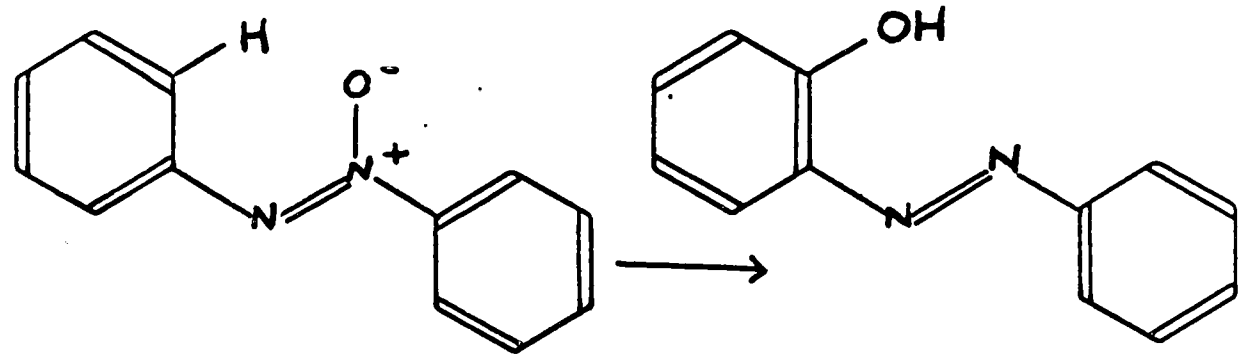
Furthermore, just as the normal photo-reaction of o-nitro-benzyl compounds (reduction) is faster than the oxygen transfer rearrangement, so in the azoxycompounds, oxygen transfer to a phenyl ring is a process much preferred to oxygen atom transfer to an ortho methyl group (vii - viii).



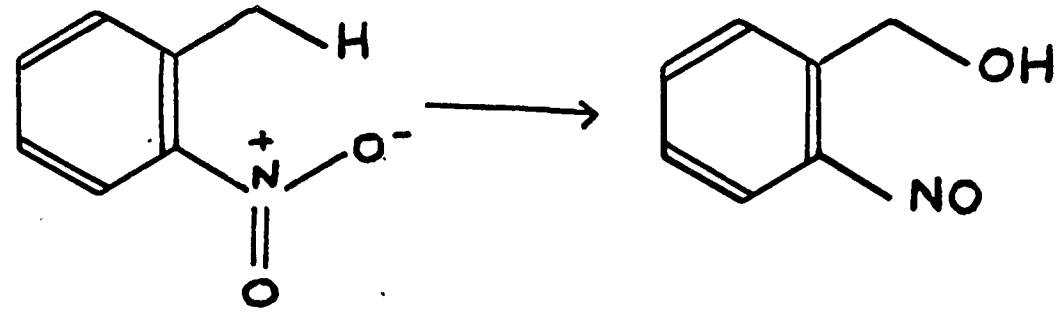

(i)



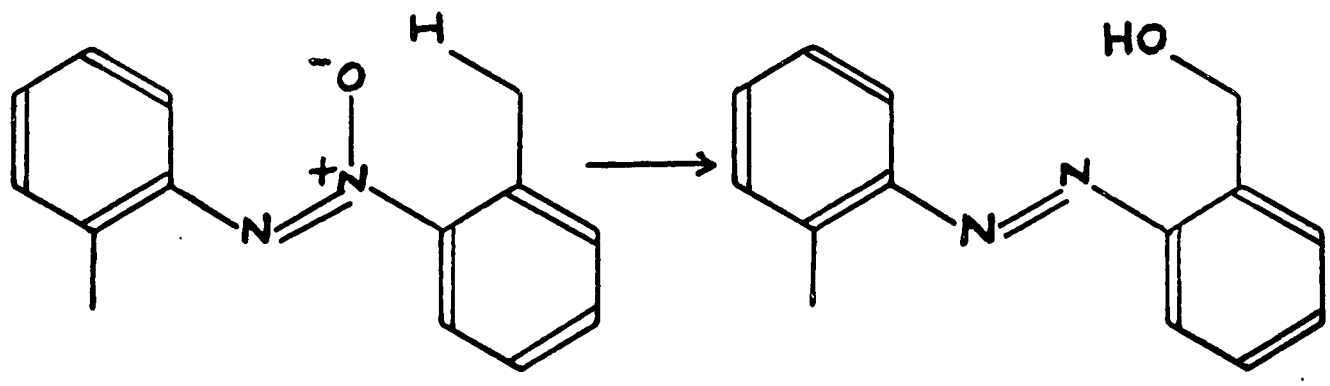

(ii)




(iii) (iv)




(v) (vi)




(vii) (viii)