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REACTIONS OF AZOBENZENES DEPENDENT ON PHOTOACTIVATION

A THESIS

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CONTENTS

	Page
SUMMARY	1
STATEMENT	4
ACKNOWLEDGEMENTS	5
PUBLICATIONS	6
INTRODUCTION	7
RESULTS AND DISCUSSION:	
PART I. PHOTOCHEMICAL REACTIONS IN ACETYL CHLORIDE	28
I.1 *trans*-Azobenzene	28
I.2 Reactions Leading to Di-, Tri-, Tetra-, and Penta-chloroazobenzenes	30
I.3 Substituted *trans*-Azobenzenes	42
PART II. DARK REACTION OF *CIS*-AZOBENZENE WITH ACETYL CHLORIDE	62
II.1 Reaction Products	63
II.2 Attempted Identification of the Metastable Product from this Reaction	65
II.3 Mechanism of the Photochemical Reaction	69
PART III. PHOTOINDUCED REACTIONS OF *TRANS*-AZOBENZENE WITH ACYL AND AROYL CHLORIDES	71
III.1 *ortho*/*para* Product Ratios	71
III.2 Photoproducts	79

PART IV. REACTIONS OF *CIS*- AND *TRANS*-AZOBENZENES WITH OTHER ACYL COMPOUNDS 82

PART V. QUANTUM YIELD DETERMINATIONS 87

V.1 Determination of Quantum Yields for *trans* → *cis* Isomerization of Azobenzenes in Acetic Anhydride 88

V.2 Determination of Quantum Yields for the Photoreactions of *trans*-Azobenzenes in Acetic Anhydride-Hydrochloric Acid Solution 105

EXPERIMENTAL:

General 117

Work described in Part I 119

Work described in Part II 169

Work described in Part III 174

Work described in Part IV 179

Work described in Part V 187

APPENDIX:

(a) Nucleophilic Substitution in Chloroazobenzenes 197

(b) Ultraviolet-visible spectra of *cis*- and *trans*-azobenzenes in acetic anhydride 203

(c) Tables of Mass Spectra of Reaction Products 209

REFERENCES 216

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SUMMARY

The scope of the photochemical reaction of *trans*-azobenzene with acetyl chloride (which leads to the formation of *N*,*N*'-diacetyl-4-chlorohydrazobenzene in high yield) has been investigated. Particular attention has been directed towards the elucidation of the mechanism of this reaction.

Irradiation of *trans*-azobenzene in acetyl chloride, and subsequent hydrolysis-oxidation of the photoproduct, has been shown to yield 4-chloroazobenzene (as the main product) and a small amount of 2-chloroazobenzene. A similar sequence of reactions has been extended to mono-, di-, tri-, and tetra-chloroazobenzenes. In addition, the photoreactions of several mono- and disubstituted azobenzenes with acetyl chloride have been examined. The effect of the substituents on the position of chlorination in the azobenzene molecule is discussed.

cis-Azobenzene has been shown to react with acetyl chloride in the absence of light to form *N*,*N*'-diacetyl-4-chlorohydrazobenzene and *N*'-acetyl-4-chlorohydrazobenzene as the principal products; 4-phenylaminoazobenzene and acetanilide are also formed in small amounts. In the course of the reaction a metastable dark blue product arises, and, although this could not be satisfactorily characterized, it was found to yield 4-phenylaminoazobenzene on decomposition in methanolic potassium hydroxide or in acetyl chloride. The intense blue-purple coloration, which occurs as soon as the reactants are mixed, enables *cis*-azobenzene to be readily distinguished

from its *trans* isomer. The nature of the dark reaction of *cis*-azobenzene with acetyl chloride is discussed in relation to the photoinduced reaction of *trans*-azobenzene with acetyl chloride.

Irradiation of *trans*-azobenzene in different acid chlorides and subsequent hydrolysis-oxidation of the photoproducts have been shown to give marked variations in *ortho/para* substitution ratios. Correlations indicate that the relative extents of *ortho* and *para* substitution are associated with the ionizability of the acid chlorides.

trans-Azobenzene has been converted in high yield to 4-bromoazobenzene (via *N*,*N*'-diacetyl-4-bromohydrazobenzene) by the use of a sequence of reactions analogous to those employed in converting azobenzene into 4-chloroazobenzene. Attempts to introduce a fluoro, cyano, and an iodo group into the azobenzene nucleus by analogous sequences of reactions were, however, unsuccessful.

In the case of several mono-, di-, and tetra-substituted azobenzenes, quantum yields for the following types of reactions have been determined: (a) *trans* → *cis* photoisomerization in acetic anhydride (ϕt); and (b) the photochemical reaction in the presence of acetic anhydride-hydrochloric acid solution (ϕ). In many cases the values of ϕt and ϕ are in close agreement; and this implies that the rate-determining step in the photochemical reactions of these compounds with acetyl chloride is the rate of *trans* → *cis* isomerization. The anomalous absorption spectra and rates of thermal *cis* → *trans* isomerization of some 2,6-disubstituted and 2,6,2',6'-tetrasubstituted azobenzenes are discussed.

Some nucleophilic substitution reactions of chloroazobenzenes in aqueous methanolic potassium hydroxide and in dimethyl sulphoxide containing sodium methoxide are briefly reported in an appendix.

STATEMENT

This thesis contains no material which has been accepted for the award of any other degree or diploma in any University, and to the best of my knowledge and belief contains no material previously published or written by another person, except where due reference is made in the text.

Robert John Mayfield

ACKNOWLEDGEMENTS

I wish to sincerely thank Dr. G.E. Lewis for his guidance and encouragement during supervision of this work.

I am indebted to Dr. D.P.G. Hamon for his many helpful discussions and to Mr. P.F. Donaghue for programming some of the quantum yield calculations.

This research was carried out during the tenure of a Commonwealth Postgraduate Award, which I gratefully acknowledge.

PUBLICATIONS

Part of the work described in this thesis has been published in the following papers:

"PHOTOCHEMICAL REACTIONS OF AZO COMPOUNDS. XII. DARK REACTION OF *CIS*-AZOBENZENE WITH ACETYL CHLORIDE" Lewis, G.E., and Mayfield, R.J., *Aust.J.Chem.*, 1967, *20*, 1899.

"PHOTOCHEMICAL REACTIONS OF AZO COMPOUNDS. XV. *ORTHO/PARA* SUBSTITUTION RATIOS IN THE PHOTOINDUCED REACTIONS OF *TRANS*-AZOBENZENE WITH ACID CHLORIDES" Hamon, D.P.G., Lewis, G.E., and Mayfield, R.J., *Aust.J.Chem.*, 1968, *21*, 1053.

"PHOTOCHEMICAL REACTIONS OF AZO COMPOUNDS. XVI. REACTIONS WITH ACETYL CHLORIDE LEADING TO DI-, TRI-, AND TETRA-CHLOROAZOBENZENES" Lewis, G.E., and Mayfield, R.J., *Aust.J.Chem.*, 1968, *21*, 1601.

INTRODUCTION

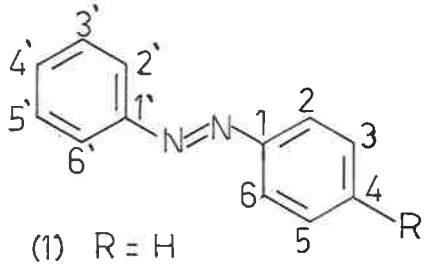
Photochemical reactions of aromatic azo compounds have been the subject of numerous studies particularly in recent years. Amongst the most extensively studied of these reactions are the well known *trans*⇌*cis* photoisomerizations first reported by Hartley[3,4] in 1937, and the more recently discovered photocatalysed cyclodehydrogenation which occurs in strongly acidic solvents and yields benzo[*c*]cinnolines.[42-48] In addition, the photoinduced rearrangements of azoxybenzenes[52-58] and the related nitrones[62,63] to *o*-hydroxyazobenzenes and oxaziranes respectively have been well documented in the literature.

Recently, work in these laboratories concerning the photochemistry of azobenzene in acidic solvents led to the discovery of a novel photochemical reaction of azobenzene with acetyl chloride.[1,2] An outline of this reaction follows.

The Photoreaction of *trans*-Azobenzene with Acetyl Chloride[1,2]

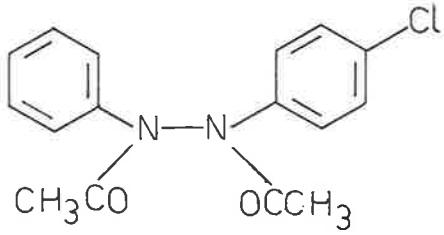
Solutions of *trans*-azobenzene (1) in acetyl chloride were found to undergo rapid decolorization on exposure to sunlight or to light from a high pressure mercury lamp. The colorless photoproduct, which was isolated in high yield, was identified as *N*,*N*'-diacetyl-4-chlorohydrazobenzene (2), the structure having been deduced from analytical, infrared, and n.m.r. spectral data and by comparison with a separately synthesised sample. When the photoproduct was

subjected to alkaline hydrolysis with subsequent oxidation of the deacetylated hydrazo compound, 4-chloroazobenzene (3) was obtained in satisfactory overall yield (73%).



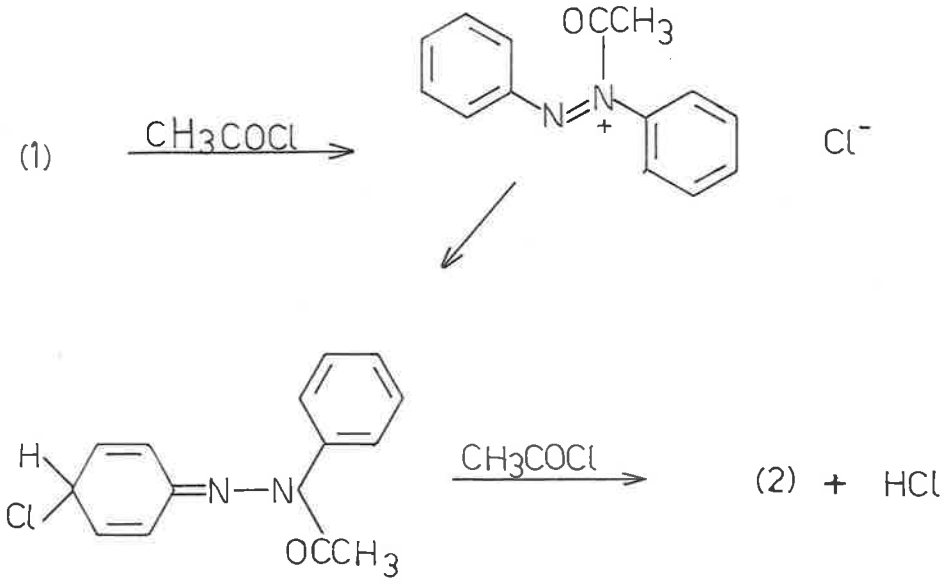
(1) R = H

(3) R = Cl



(2)

From these early studies it appeared that selective *para* chlorination was occurring. On these grounds an ionic mechanism (Scheme 1) was proposed as a plausible pathway leading to the formation of *N*,*N*'-diacetyl-4-chlorohydrazobenzene.



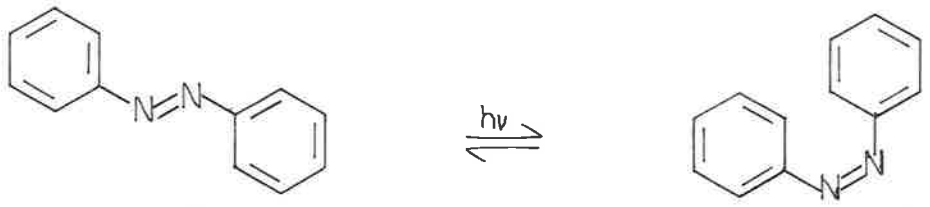
Scheme 1

Since the above sequence of reactions constituted a very convenient method of converting azobenzene to 4-chloroazobenzene, an extensive study was undertaken to determine the scope and to elucidate the mechanism of the photoreaction.

The following is an outline of the photocatalysed reactions of aromatic azo compounds and azoxybenzenes. In addition, an account of the basicities, the conjugate acids and the electronic spectra of *cis*- and *trans*-azobenzenes is given.

Photoisomerization of Azobenzenes

Solutions of *trans*-azobenzene were shown by Hartley[3,4] to undergo *trans* $\rightleftharpoons$ *cis* (1 $\rightleftharpoons$ 6) isomerization when exposed to light and to form a photostationary mixture on continued exposure. It was



(1) (6)

found that substituted azobenzenes also exhibited photoisomerization[5-10] and some of the more stable *cis* isomers were isolated from the equilibrium mixtures by chromatography.[5-7]

In recent years, many workers have studied the kinetic and theoretical aspects of the photoisomerization[11-22] and of the thermal *cis* → *trans* isomerization[6,23-27] in an effort to understand the mechanism of these reactions.

Several authors[13,23,25,28] postulated that photoisomerization involves an intermediate state common to both *cis* and *trans* isomers. However, the experimental results of Zimmerman[15] *et al.* and Fischer[16,18] were found to contradict this hypothesis.

TABLE I. Quantum Yields for Isomerization of Azobenzene in Isooctane at 25°[15]

$\lambda_{m\mu}$	ϕt	ϕc	$\phi t + \phi c$
254	0.13	0.44	0.57
313	0.11	0.41	0.52
365	0.12	0.48	0.60
405	0.22	0.53	0.75
436	0.27	0.55	0.82
546	0.24	0.40	0.64
578	0.23	0.44	0.67

Zimmerman *et al.*[15] were the first workers to accurately determine the quantum yields ϕt, for the *trans* → *cis*, and ϕc, for the *cis* → *trans* isomerizations of azobenzene. The values of ϕt and ϕc were determined at various wavelengths in iso-octane solution and are shown in Table I. The sums of ϕc and ϕt were found to be considerably less than unity, and since fluorescence from either isomer was absent, this seemed good evidence that both the *cis* and *trans* isomers could not have originated from a common excited

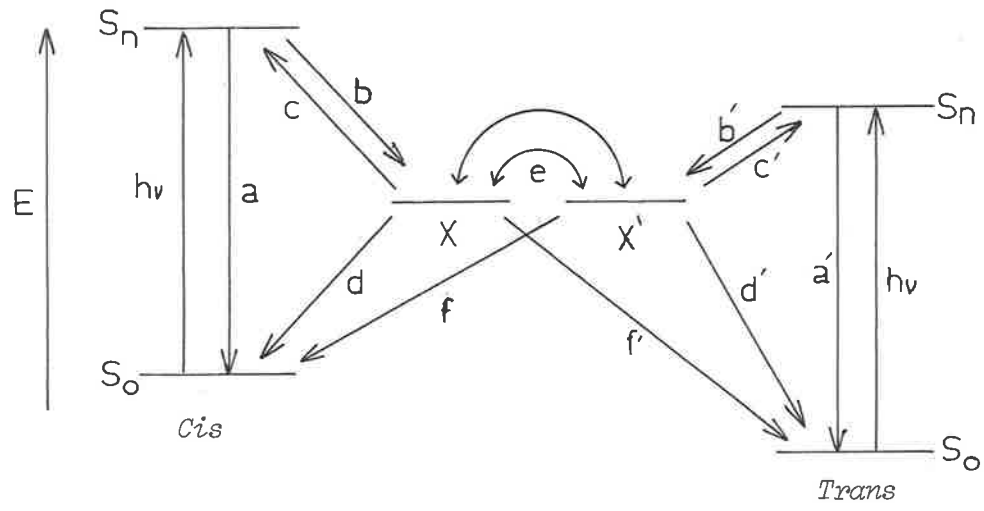
state formed by irradiation of either isomer. It was postulated that the photoisomerization takes place as an ordinary thermal reaction of an electronic excited state. The quantum yields in Table I also show that excitation of azobenzene to its lowest $n\pi^*$ singlet state results in a greater quantum yield of isomerization than does excitation to the higher lying $\pi\pi^*$ singlet state.

Fischer and Malkin[18] published results in 1962 which established that ϕc and ϕt were temperature dependent, both decreasing on lowering of temperature. This effect was found to be markedly greater for ϕt indicating that the activation energy for the *cis* → *trans* transformation was smaller than for the *trans* → *cis* transformation.

The following processes for the photoisomerization pathway have been postulated.[18]

$$\textit{Cis}^{So} \xrightarrow{h\nu} \textit{Cis}^{Sn} \longrightarrow X \left(\longrightarrow X'\right) \longrightarrow \textit{Trans}^{So}$$

$$\textit{Trans}^{So} \xrightarrow{h\nu} \textit{Trans}^{Sn} \longrightarrow X' \left(\longrightarrow X\right) \longrightarrow \textit{Cis}^{So}$$



Scheme 2

The processes a-f and a'-f' (Scheme 2) are all thermal and the intermediate states X and X' are unknown and may be of a different nature (viz. singlet and triplet).

Kearns[19] has considered this problem from the theoretical point of view, concentrating on the energy barrier to rotation about the N-N axis in the $\pi\pi^*$ and $n\pi^*$ excited states. His calculations established that an energy barrier to rotation from the planar to the perpindicular conformation existed for azobenzene in its lowest $n\pi^*$ singlet state and for both the lowest singlet and triplet states of the $\pi\pi^*$ absorption. However no energy barrier to rotation existed for the lowest $n\pi^*$ triplet state and so the most efficient process of populating the $n\pi^*$ triplet was predicted to be the best process for promoting isomerization. These theoretical considerations also offered an explanation for the temperature dependence of isomerization and so were consistent with the experimental results of Zimmerman[15] and Fischer.[18]

Recently, photosensitized isomerizations of azobenzene have been studied in an effort to shed more light on the excited states involved in the reaction.

Hammond and Jones[21] observed that diffusion controlled triplet energy transfer to azobenzene occurred and resulted in a photostationary state containing 1.5-1.8 per cent of the *cis* isomer. This gave a decay ratio[21] of 60 compared to the value of 4 obtained for the direct photoisomerization[15] (at 313 mμ) and it was concluded from these results that photoisomerization probably involves excited singlet states.

However the more recent results of Fischer[22] were in sharp contrast to those above. Using naphthalene and triphenylene as the triplet donors, photostationary states approaching 20 per cent of the *cis* isomer were obtained and this resulted in a decay ratio of 4 which was identical to the value obtained for the direct photoisomerization. These results suggest that a crossing of paths may occur in the triplet sensitized and in the direct photoisomerization

Further work is obviously needed before the mechanism for *trans* $\rightleftharpoons$ *cis* isomerizations of azobenzenes is fully understood. Lately, because of the low activation energies required for isomerization of azobenzene[6,23,24] and imines,[29,30] it has been suggested that a mechanism which does not involve rotation about the N-N or C-N axes may operate.[24,30]

Photochemical Cyclodehydrogenation of Azobenzenes

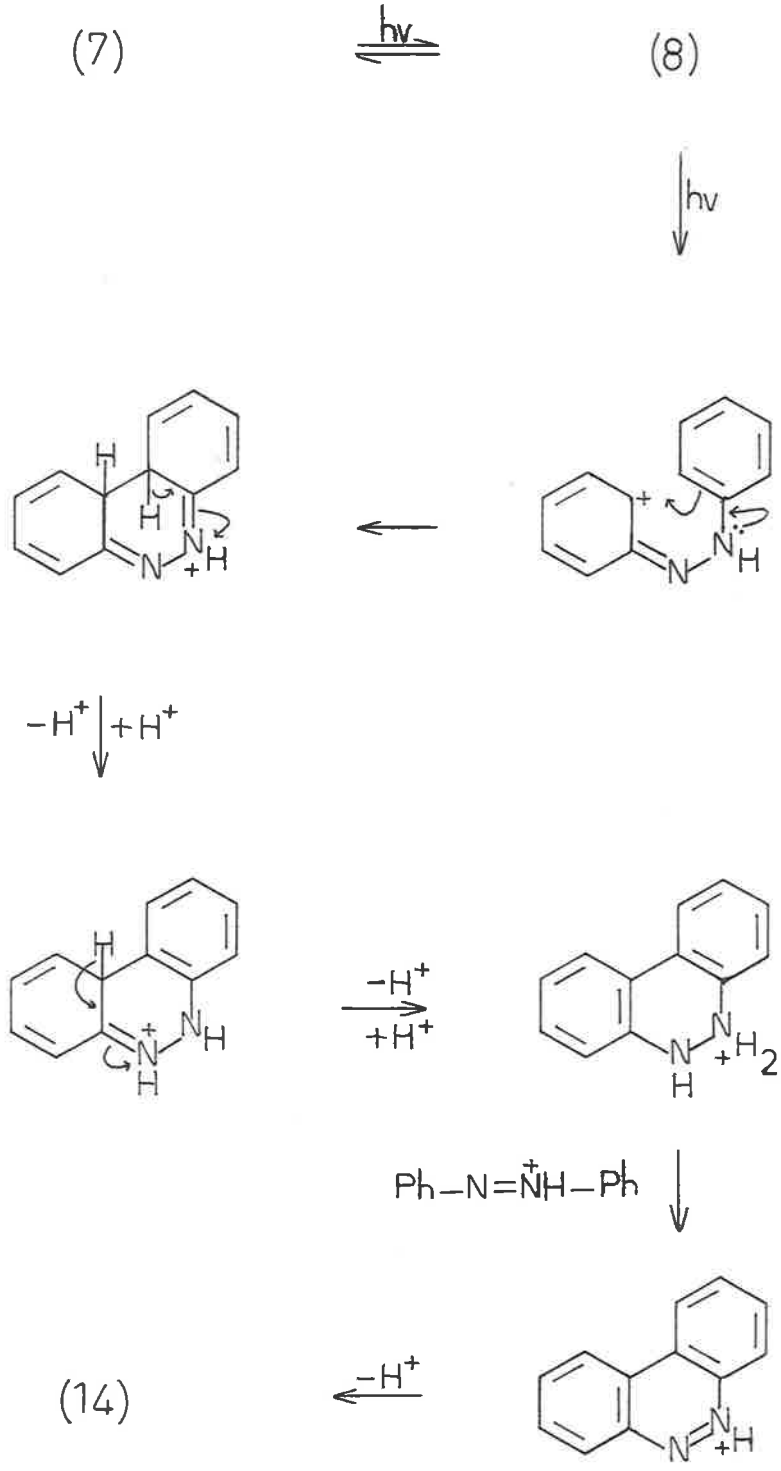
The photocatalysed cyclization of stilbene and its derivatives to phenanthrenes has been extensively studied in the last decade.[31-42] In the case of stilbene, thorough investigations have revealed that the reaction probably proceeds initially by *trans* $\rightarrow$ *cis* isomerization and then ring-closure of *cis*-stilbene[32,39] in a first excited singlet state[35,36,40] to the intermediate 4a,4b-dihydrophenanthrene.[32,41] In the presence of an oxidizing agent (O_2 or I_2) the unstable dihydro intermediate is rapidly oxidized to phenanthrene.[35]

Photochemical cyclodehydrogenation of the related azastilbenes has also been well investigated,[33,42-48] but the proposed mechanism of this photocyclization distinctly differs from that found to operate for the stilbenes.

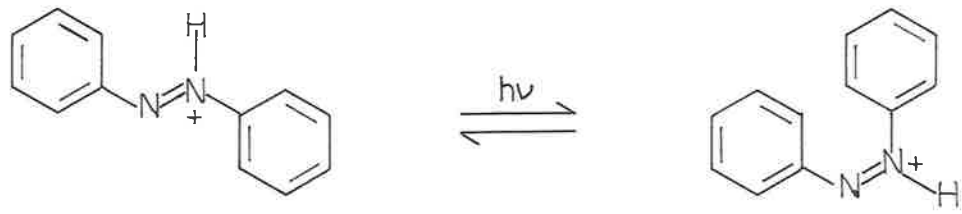
The photocyclization of azobenzene to benzo[*c*]cinnoline (14) was first reported in 1960. Lewis[43] discovered that irradiation of azobenzene in ethanolic sulphuric acid yielded benzo[*c*]cinnoline, while simultaneously, Hugelshofer *et al.*[33] reported benzo[*c*]-cinnoline formation on irradiation of azobenzene in acetic acid containing ferric chloride.

Since these initial discoveries, a large number of substituted azobenzenes have been photocyclized to benzo[*c*]cinnoline derivatives,[44-46,51] sometimes with ejection[44,45] or migration[45] of substituents from the positions of cyclization. 1-Phenylazo-naphthalene[47] and 4,4'-bis(phenylazo)biphenyl[47,48] have also been cyclized in strong acid, but a number of azonaphthalenes, 2-phenylazonaphthalene and 4-styrlazobenzene failed to cyclize.[47]

It has been demonstrated that irradiation of azobenzene in strongly acidic solution results in *trans* $\rightleftharpoons$ *cis* equilibration of the conjugate acids (7 $\rightleftharpoons$ 8) as well as cyclization.[49] Photokinetic studies recently carried out,[50] have indicated that the ring closure step involves a short-lived photoexcited state of the *cis*-conjugate acid of azobenzene. A mechanistic pathway (Scheme 3)[50] was proposed to account for the photocyclization.



Scheme 3



(7) (8)

Generally, irradiation of azobenzenes in 20-24 *N* sulphuric acid resulted in yields of cyclized product approaching 50 per cent. This phenomenon was attributed to the fact that, in the major portion of the reaction, an intermolecular disproportionation process occurred in which one molecule of azobenzene acted as a hydrogen acceptor for every molecule cyclized. Although hydrazobenzenes were not isolated from the acidic reaction mixtures, benzidine-type products were often isolated in yields comparable with those of the cyclized products.[44,45] It is believed that these originate from intermediate hydrazobenzenes by the well known acid-catalysed rearrangement.

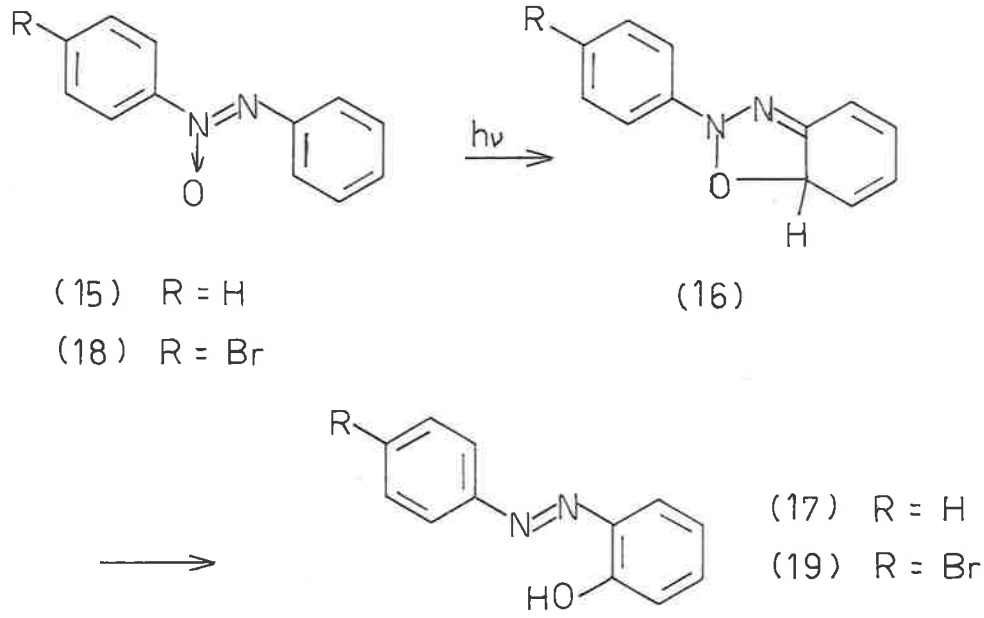
Several azobenzenes, viz. 4-amino-, 4,4'-diamino- and 4-dimethylaminoazobenzenes, failed to cyclize in 22 *N* or 98 per cent sulphuric acid. However modification of the amino group by formation of the benzal derivatives in the case of the primary amines[46] and formation of the *N*-oxide in the case of 4-dimethylaminoazobenzene[51] resulted in photocyclization to the amino benzo[*c*]cinnolines.

Photochemical Rearrangement of Azoxybenzenes and Nitrones

The photoinduced rearrangement of azoxybenzene (15) to *o*-hydroxyazobenzene (17) was first reported by Knipscheer[52,53] in 1902. In following years, several azoxy compounds were photochemically rearranged to the corresponding *o*-hydroxy compounds[54,55] in a variety of solvents. More recently, minor quantities of other rearranged products have been shown to accompany the major product.[56]

Using several unsymmetrically substituted azoxybenzenes, Badger and Buttery[55] established that oxygen migration occurred from the nitrogen to the non-adjacent phenyl ring. For example, β4-bromoazoxybenzene (18) yielded exclusively 4-bromo-2'-hydroxy-azobenzene (19). These results were confirmed by Shemyakin *et al.*[57,58] by tracer experiments with (^{15}N)-azoxybenzene[57] and (^{18}O)-azoxy compounds.[58] To account for these experimental results, the intramolecular cyclic mechanism (Scheme 4) has been proposed.[55,56]

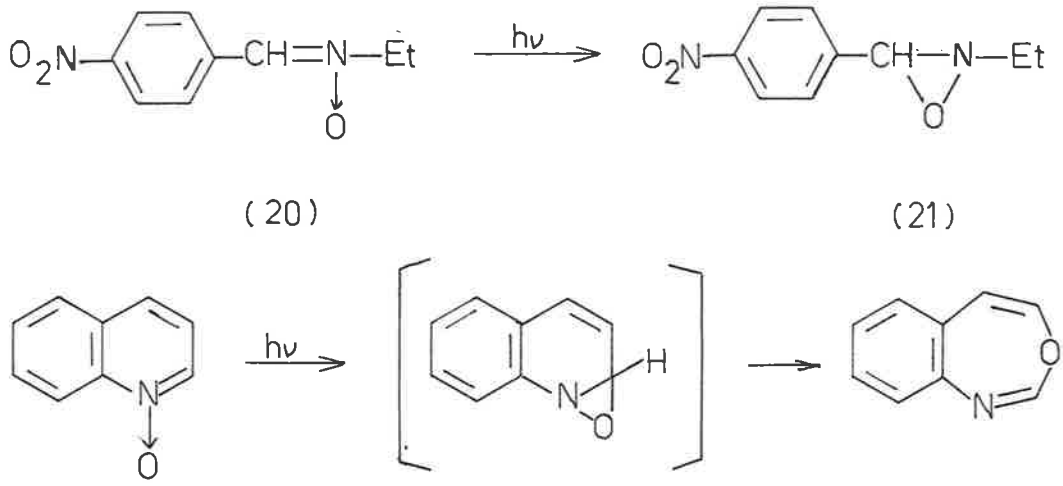
The previously unknown *cis*-azoxybenzenes have been synthesised by low temperature oxidation of the corresponding *cis*-azobenzenes[59,60] and also by photoisomerization of *trans*-azoxy benzenes.[61] Although the photoisomerisation must occur concurrently with the photo-rearrangement of azoxybenzenes, it is unlikely that the *cis* isomer is an intermediate in the rearrangement because of its unsuitable structure.



Scheme 4

Irradiation of nitrones[62,63] and *N*-oxides of aromatic bases[64-66] results in the formation of oxaziranes and oxaziridines respectively. In the case of nitrones the oxazirane is usually isolated (20 → 21),[62] but with the *N*-oxides of aromatic heterocyclic compounds the oxaziridines usually undergo further rearrangement (22 → 23 → 24).[65]

It is interesting to note that the mechanisms proposed for the foregoing photochemical reactions of azo and azoxy compounds (Schemes 1, 3, and 4) are basically related in that each reaction involves inter- or intramolecular nucleophilic substitution in the phenyl ring furthest from the quaternary nitrogen atom.



The Basicities and Conjugate Acids of *cis*- and *trans*-Azobenzenes

It is well known that the electronic absorption spectra of *cis*- and *trans*-azobenzenes undergo substantial changes on increasing the acidity of their solutions.[67-79] In many cases this spectral change is due to protonation at the azo linkage resulting in formation of the conjugate acids or, as they are commonly called, "azobenzenium ions". Extensive spectroscopic studies have been carried out on the conjugate acids[49,67-79] and the related metal halide complexes[80-84] of azobenzenes.

Earlier experiments had predicted that *cis*-azobenzene was a stronger base than the *trans* isomer.[60] This has been confirmed more recently, the basicities of both isomers having been evaluated spectroscopically in aqueous sulphuric acid,[67] ethanolic sulphuric acid[49,68-70] and acetic acid - perchloric acid[71] solvent systems. The *cis* isomer is clearly a stronger base by a factor of about 10.

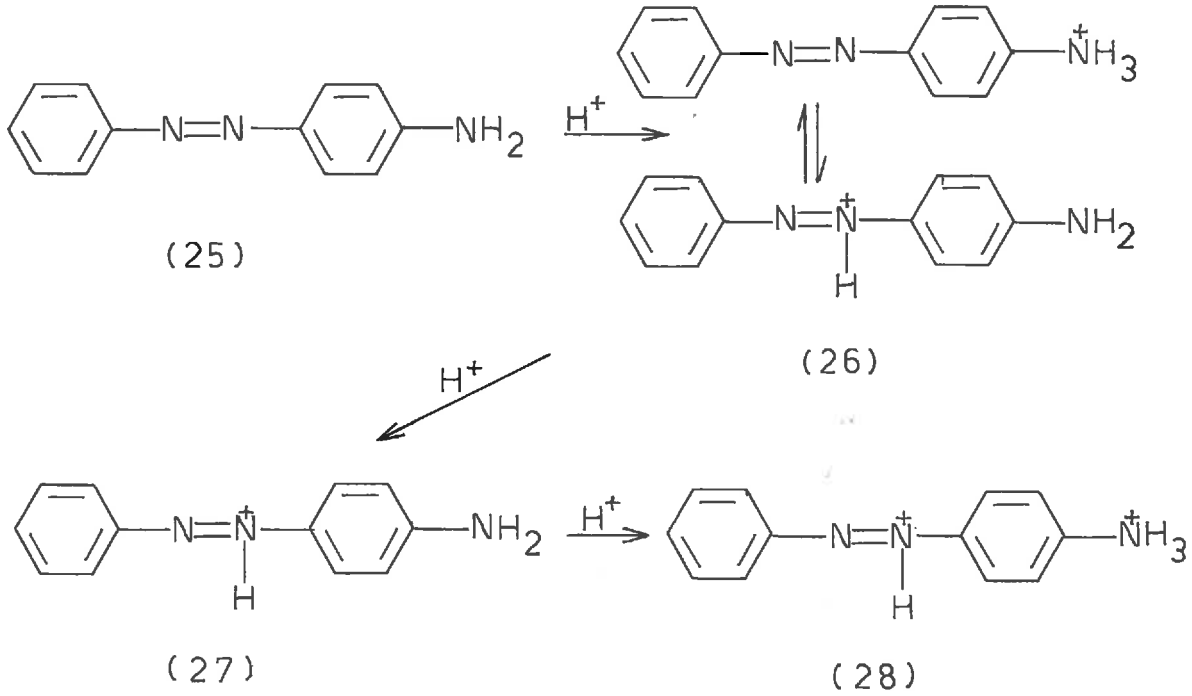
The basicities of several monosubstituted *cis*- and *trans*-azobenzenes have also been determined,[71] and in all cases except the compounds containing strongly electron-attracting (-M) groups in a *para* position, the *cis* isomer is the stronger base.

The basicity difference reflects the structural difference between these geometrical isomers. *trans*-Azobenzene is known to be essentially planar,[85] and conjugation between the π electrons of the azo linkage and phenyl rings results in some delocalization of electron density from the azo linkage. X-ray diffraction studies have shown that the C-N bond in *trans*-azobenzenes is somewhat shorter than the length of a true C-N single bond.[85] Furthermore, the orbitals of the lone pairs of electrons on the nitrogen atom lie in the nodal plane of the ring π electrons, so that bulky substituents in the *ortho* positions would be expected to hinder protonation.[67]

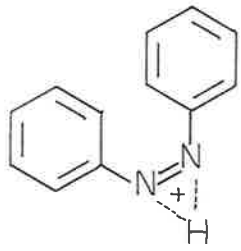
X-ray diffraction studies have shown that *cis*-azobenzene is not planar in the solid state.[86,87] In fact calculations show that the phenyl rings are turned 56° out of the nodal plane of the azo linkage π electrons because of steric repulsions between the *ortho* hydrogen atoms.[87] Recently, further calculations have indicated that the structure of *cis*-azobenzene being most consistent with its electronic spectrum, is the propeller shaped conformation in which the phenyl rings are rotated approximately 30° out of the plane.[72] The non-planar structure would result in a much smaller overlap of the azo and phenyl π orbitals and therefore give a more localized electron density (and greater basicity) at the azo linkage. X-ray

diffraction has shown that the C-N bond in *cis*-azobenzene has normal single bond length.

There has been a great deal of interest in the position of initial protonation in azobenzenes containing a second basic centre,[73-78] and the majority of work on the conjugate acids has been confined to this question. Klotz *et al.*[67] concluded that protonation of the amino group in 4-aminoazobenzene (25) preceded protonation of the azo linkage. On the other hand, Sawicki[78] has considered the tautomer concept of the proton addition and this has recently been established to be the more correct approach.[73] Increasing the acidity of solutions of 4-aminoazobenzene (25) results in three distinct kinds of spectral change; and these have been identified with the processes (25 → 26 → 27 → 28).

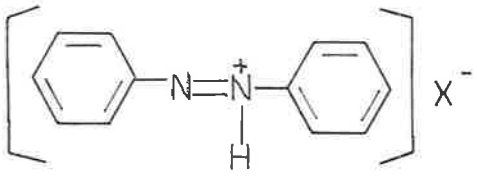


Conflicting reports on the structure of the conjugate acids of azobenzene have appeared. Jaffé *et al.*[69,70] proposed that the conjugate acids of azobenzene should be represented by a single *cis* structure (29) in which the proton is not bonded exclusively

(29) 

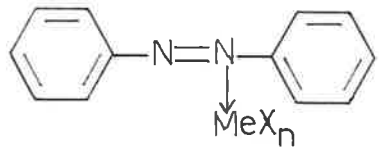
to either nitrogen atom. This proposal was based on spectroscopic studies of a large number of mono- and disubstituted azobenzenes. However, it has now been established conclusively that both *cis*- and *trans*-azobenzenes can retain their *cis* and *trans* conformations on protonation.[49,79] In fact photoisomerization of the conjugate acids has been reported and results in a *trans* $\rightleftharpoons$ *cis* equilibrium mixture containing approximately 55 per cent of the *cis* isomer.[49]

Salt-like combinations of azobenzenes with halogen acids in non-hydroxylic solvents have been known to occur for some time,[86] and more recently, several similar salts have been isolated and characterized.[80,81] Infrared studies have been carried out with azobenzenium tetrachloroborate[80] (30) and some perchlorate salts of azobenzenes[81] (31) in an effort to determine whether the proton is attached to a nitrogen atom or to the π-bond. However, the results were inconclusive.



(30) X = BCl_4

(31) X = ClO_4



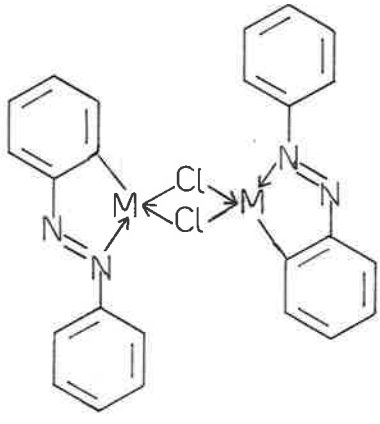
(32)

Me = Sb, Sn, Al, B, Ga, Cu

X = Cl, Br

Complexes of azobenzenes and metal halides have been isolated and characterized.[82-84] The similarity of their electronic absorption spectra[84] with those of the corresponding conjugate acids, indicates they probably have similar structures (32).

An interesting reaction between azobenzenes and palladium or platinum salts has been reported[87] and gives products having the structure (33). The reaction is not photoinduced, but may involve initial electron acceptance from a nitrogen lone pair by the metal and then nucleophilic substitution at an *ortho* position in the non-adjacent phenyl ring. Such a mechanism would closely resemble that proposed for the photorearrangement of azoxybenzene.



(33) M = Pt or Pd

Electronic Spectra of *cis*-and *trans*-Azobenzene and their Conjugate Acids

Three regions of absorption were recognised in early investigations of the electronic spectra of *cis*-[89] and *trans*-azobenzenes.[88-90] The longer wavelength absorptions occurred in the 320-370 mμ and 440-470 mμ regions and were designated the K-band and the R-band respectively. Shorter wavelength absorption occurred in the 230-270 mμ region.

More recently, analyses of azobenzene spectra have been based on electron-level diagrams calculated from molecular orbital theory and these have given a greater understanding of the spectra in terms of the underlying electronic transitions. The spectra of *cis*- and *trans*-azobenzene in 95 per cent ethanol[91] and their conjugate acids in ethanolic-perchloric acid[79] are shown in Figs. Ia and Ib respectively.

In both isomers the A-band is due to the lowest $\pi\pi^*$ transition, and for the *cis* isomer this is very much less intense besides occurring at a shorter wavelength. The π and π_1^* energy levels vary considerably with the nature of the bridge atoms joining the phenyl rings (Fig. II)[92] and this indicates that the $\pi\pi_1^*$ transition is essentially localized at the bridge atoms. On the shorter wavelength side of the A-band of both isomers two less intense and partly hidden absorption bands occur and have been assigned $\sigma\pi^*$ transitions.[72,92]

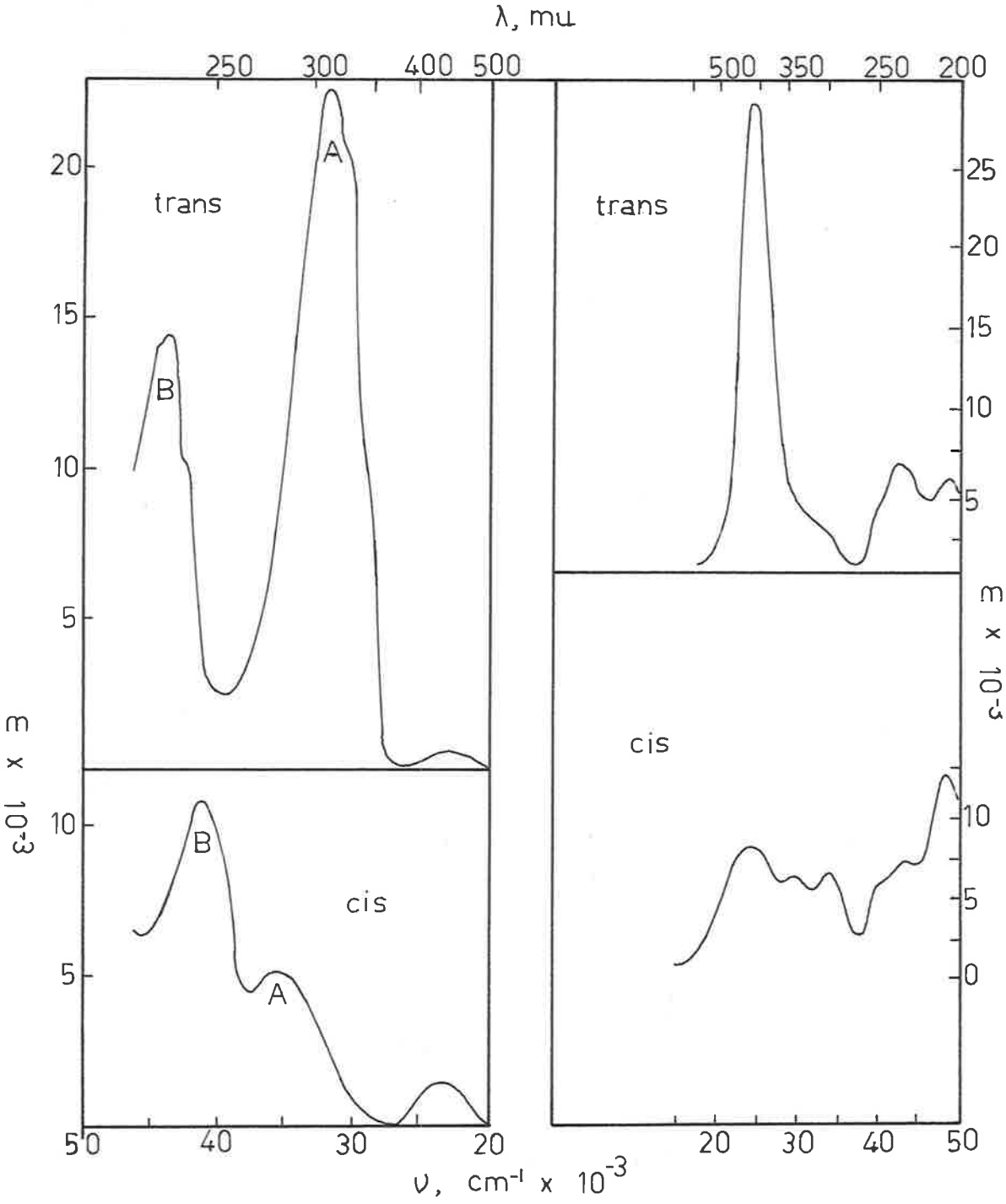


Fig. Ia - Absorption spectra of *cis*- and *trans*-azobenzene in 95% ethanol

Fig. Ib - Absorption spectra of the conjugate acids of *cis*- and *trans*-azobenzene (ethanolic perchloric acid)

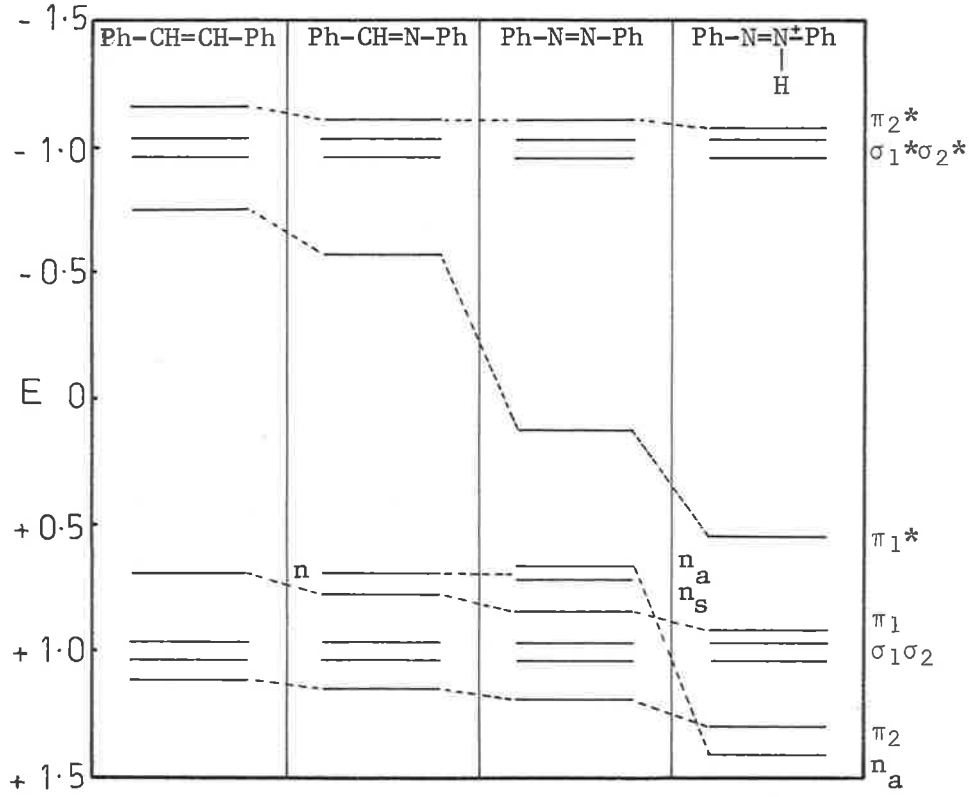


Fig. II

The shorter wavelength B-band of *cis*- and *trans*-azobenzenes is due to a $\sigma\sigma^*$ transition. This band is insensitive to the bridge bonding the phenyl rings (Fig. II) because the σ and σ^* levels are localized in the phenyl rings. Consequently the B-band of the stilbenes, benzanilines, azoxybenzenes, and conjugate acids of azobenzenes fall in the same region.

The positions of the two phenyl rings in *cis*-azobenzene must result in considerable interaction of the π electron clouds and this would be expected to complicate the energy level situation. Broadening of the $\sigma\pi^*$ band and splitting of the degenerate σ and σ^*

energy levels with corresponding small changes in transition energy does seem to be evident from the spectra of the *cis* isomer.[93]

Both *cis*- and *trans*-azobenzene have low intensity absorption bands in the 420-440 mμ region and these are associated with one or more $n\pi^*$ transitions originating in the non-bonded electrons of the azo linkage.

On protonation of *cis*- or *trans*-azobenzene, the A-band undergoes a considerable bathochromic shift to 420 mμ as well as a large intensity increase. This pronounced change of the $\pi\pi_1^*$ absorption is due to the quaternary nitrogen atom which causes a considerable lowering of the π_1^* energy level (Fig. II). The energy of the n level is compressed even more than that of the π_1^* level by protonation at the azo linkage, and correspondingly the $n\pi^*$ absorption undergoes a large hypsochromic shift to 300 mμ. As mentioned previously the B-band remains essentially unchanged on protonation of *cis*- or *trans*-azobenzene.

The $n\pi^*$ transitions in *cis*- and *trans*-azobenzenes and their conjugate acids are not very sensitive to substituent effects.[92] Generally electron-attracting substituents cause small hypsochromic shifts while electron-donating substituents have the opposite effect. In the case of the $\pi\pi^*$ transitions, mesomerically electron-donating substituents (OH, OR, NR_2) cause considerable bathochromic shifts while electron-attracting substituents have little effect. As expected, replacement of the benzene rings with naphthalene rings in azobenzenes results in a large bathochromic shift of the $\pi\pi^*$ absorption.[90]

RESULTS AND DISCUSSION

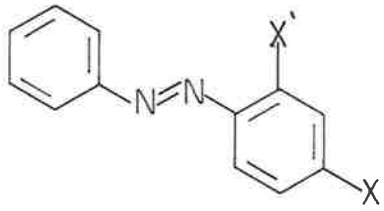
I. PHOTOCHEMICAL REACTIONS IN ACETYL CHLORIDE

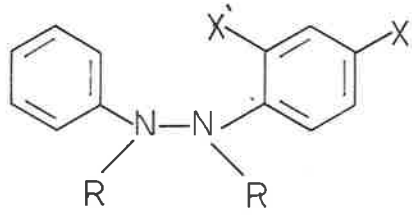
1. *trans*-Azobenzene

The photoinduced reaction of *trans*-azobenzene (1) with acetyl chloride is known to give *N*,*N*'-diacetyl-4-chlorohydrazobenzene (2) in high yield[1,2] and the ionic mechanism proposed for this reaction has already been described (Scheme 1). Deacetylation of the photoproduct (2) can be accomplished by alkaline hydrolysis, and oxidation of the intermediate 4-chlorohydrazobenzene (34) results in a good overall yield of 4-chloroazobenzene (3).[1,2] Since this sequence of reactions (1 → 2 → 34 → 3) constituted a convenient synthetic route for 4-chloroazobenzene, a large scale reaction was carried out in the following manner.

A solution of azobenzene (1) in acetyl chloride was irradiated until the solution was completely decolorized. The crude product remaining after removal of the excess acetyl chloride was subjected to hydrolysis and aerial oxidation in aqueous methanolic potassium hydroxide. Examination of the final product revealed a mixture of 4-chloroazobenzene (3) and 2-chloroazobenzene (35) in 83% and 12% overall yields respectively. Most of the 4-chloro isomer crystallized from the crude reaction mixture and was isolated in the pure state (73% overall yield) by filtration and subsequent recrystallization. The combined filtrate and mother liquors were evaporated to dryness and shown by comparative infrared spectroscopy to be an approximately equimolar mixture of 2- and 4-chloroazobenzenes. Attempts to separate the isomers (3) and (35) by preparative scale procedures were only

partially successful, but when the mixture was subjected to gas chromatography two separate peaks were observed. An analytical gas chromatography technique was devised in which runs with a series of standard mixtures made from the pure 2- and 4-chloro compounds were used to prepare a calibration curve. In this manner, the molar ratio of 2- and 4-chloroazobenzene in the combined filtrate - mother liquor residue was shown to be 1.2:1 (corresponding to 12% and 10% overall yields respectively).





	X	X'
(1)	H	H
(3)	Cl	H
(35)	H	Cl

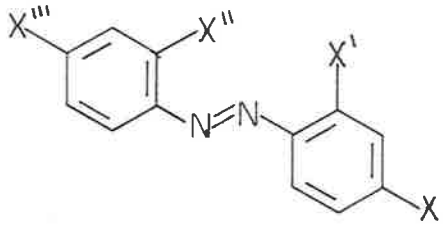
	R	X	X'
(36)	Ac	H	Cl
(2)	Ac	Cl	H
(34)	H	Cl	H

Since 2-chloroazobenzene (35) was isolated in 12% overall yield from the hydrolysed photochemical reaction mixture it was concluded that a similar amount of *N*,*N*'-diacetyl-2-chlorohydrazobenzene (36) was probably formed as a photoproduct. However attempts to separate the *N*,*N*'-diacetyl isomers (2) and (36) were unsuccessful.

2. Reactions Leading to Di-, Tri-, Tetra-, and Penta-chloroazobenzenes

By using a sequence of reactions analogous to those used in converting azobenzene to 2- and 4-chloroazobenzenes, mono-, di-, tri-, and tetra-chloroazobenzenes were converted to di-, tri-, tetra-, and penta-chloroazobenzenes respectively.

4-Chloroazobenzene (3) was irradiated in acetyl chloride until the solution was completely decolorized. After removal of the excess acetyl chloride by evaporation, the photoproduct was obtained as a colorless glass which slowly crystallized when allowed to stand in light petroleum for several weeks. However, separation into its components was unsuccessful, and the mixture was subjected directly to hydrolysis and aerial oxidation in methanolic potassium hydroxide. The final mixture of products was resolved into 4,4'-dichloroazobenzene (37), 2,4-dichloroazobenzene (38) and 2,4'-dichloroazobenzene (39) by a combination of crystallization and column chromatography. Compound (37) was the major product and was readily isolated in the pure state by crystallization from the crude reaction mixture. The isomers (38) and (39) were separated by column chromatography.



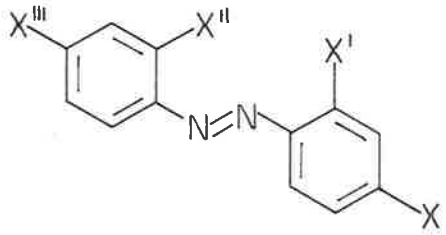
	X	X'	X''	X'''
(3)	Cl	H	H	H
(35)	H	Cl	H	H
(37)	Cl	H	H	Cl
(38)	Cl	Cl	H	H
(39)	H	Cl	H	Cl
(40)	H	Cl	Cl	H

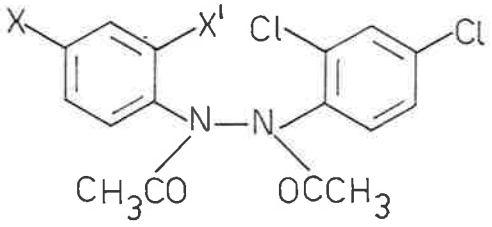
Compounds (37), (38) and (39) were identified by direct comparisons with authentic samples. 4,4'-Dichloroazobenzene (37) was available from earlier work,[94] 2,4-dichloroazobenzene (38) was prepared by condensation of 2,4-dichloroaniline with nitrosobenzene[95] and 2,4'-dichloroazobenzene (39) was prepared by condensation of *o*-chloroaniline with *p*-chloronitrosobenzene.

The photoinduced reaction of 2-chloroazobenzene (35) with acetyl chloride was carried out in a similar manner, but as in the foregoing case, the product could not be resolved into its constituents. Alkaline hydrolysis and oxidation of the crude photoproduct gave a mixture of dichloroazobenzenes, and this was shown by comparative gas chromatography to consist of 2,4-dichloroazobenzene (38), 2,4'-dichloroazobenzene (39), and 2,2'-dichloroazobenzene (40). Analytical gas chromatography showed that the ratio of the 2,4-, 2,4'- and 2,2'-dichloro isomers in the mixture was 6.25:9:1. Authentic samples of compounds (38) and (39) were available from the previous reaction. An authentic sample of 2,2'-dichloroazobenzene was prepared by reduction of *o*-chloronitrobenzene with zinc and alkali.[117]

The only product formed on irradiation of 4,4'-dichloroazobenzene (37) in acetyl chloride was obtained as a white crystalline solid and subsequently identified as *N*,*N*'-diacetyl-2,4,4'-trichlorohydrazobenzene (41). The structure was confirmed by elementary analysis and infrared spectroscopy, coupled with the fact that hydrolysis and oxidation in the usual manner afforded 2,4,4'-trichloroazobenzene (42). A small quantity of 2,4'-dichloro-4-methoxyazobenzene (43) was also isolated from the final reaction mixture,

and in a separate experiment this product was shown to be slowly formed from 2,4,4'-trichloroazobenzene when the latter was boiled in aqueous methanolic potassium hydroxide solution (see appendix).





	X	X'	X''	X'''
(37)	Cl	H	H	Cl
(38)	Cl	Cl	H	H
(42)	Cl	Cl	H	Cl
(43)	OCH_3	Cl	H	Cl
(44)	Cl	Cl	Cl	H

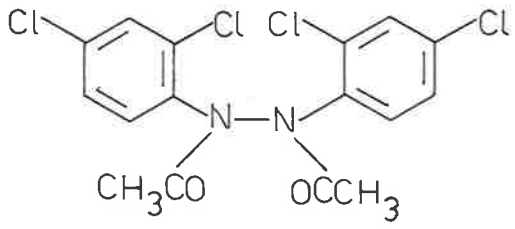
	X	X'
(45)	H	Cl
(41)	Cl	H

The structures of products (42) and (43) were confirmed by direct comparisons with authentic samples. 2,4,4'-Trichloroazobenzene was synthesised by condensation of *p*-chloronitrosobenzene with 2,4-dichloroaniline whereas 2,4'-dichloro-4-methoxyazobenzene (43) was prepared by coupling *p*-chlorophenyldiazonium chloride with *m*-chlorophenol and then methylating the resulting hydroxyazo compound with dimethyl sulphate. The n.m.r. spectrum ($CDCl_3$) of (43) was determined; and chemical shifts (relative to tetramethylsilane) are shown in Table II.

Irradiation of 2,4-dichloroazobenzene (38) in acetyl chloride and subsequent recrystallization of a small portion of the crude photoproduct gave pure *N*,*N*'-diacetyl-2,4,4'-trichlorohydrazobenzene (41). The structure was confirmed by comparison with the previously characterized sample. Alkaline hydrolysis and subsequent oxidation of the unpurified photoproduct afforded 2,4,4'-trichloroazobenzene (42) (as the major product), 2,2',4-trichloroazobenzene (44), and 2,4'-dichloro-4-methoxyazobenzene (43). Products (42) and (43) were identified by comparisons with the previously characterized samples, whereas the structure of compound (44) was confirmed by comparison with an available authentic sample.[96] Isolation of 2,2',4-trichloroazobenzene (44) in small yield indicated that some of the corresponding *N*,*N*'-diacetyl compound (45) was formed in the photochemical reaction.

Irradiation of 2,4,4'-trichloroazobenzene (42) in acetyl chloride gave only one photoproduct and this was shown to be *N*,*N*'-diacetyl-2,4,2',4'-tetrachlorohydrazobenzene (46). The structure of (46) was established on the basis of elementary analysis, the infrared spectrum, and the fact that alkaline hydrolysis and oxidation in the usual manner afforded 2,4,2',4'-tetrachloroazobenzene (47). Minor quantities of 2,4,2'-trichloro-4'-methoxyazobenzene (48) and 2,4,4'-trichloro-2'-methoxyazobenzene (49) were also isolated from the hydrolysis reaction mixture. However in a separate experiment, 2,4,2',4'-tetrachloroazobenzene was shown to be slowly

converted to the methoxy isomers (48) and (49) when boiled in aqueous methanolic potassium hydroxide (see appendix).



(46)

	X'	X
(42)	H	Cl
(47)	Cl	Cl
(48)	Cl	OCH_3
(49)	OCH_3	Cl
(50)	Cl	OH
(51)	OH	Cl

An authentic sample of 2,4,2',4'-tetrachloroazobenzene was used to confirm the structure of the hydrolysis product (47) and was prepared by zinc/alkali reduction of 2,4-dichloronitrobenzene. In the case of product (48), the structure was confirmed by elementary analysis, the infrared and n.m.r. spectra (Table II) and by demethylatio with aluminium trichloride to 2,4,2'-trichloro-4'-hydroxyazobenzene (50). Compound (50) was separately synthesised from 2,4-dichlorophenyldiazonium chloride and *m*-chlorophenol and was shown to be identical with the demethylated product. Elementary analysis established that the methoxy compound (49) was isomeric with 2,4,2'-trichloro-4'-methoxyazobenzene. Demethylation of (49) produced a

trichlorohydroxyazo compound, the hydroxy group of which, had features characteristic of hydrogen bonding as in *o*-hydroxyazo compounds.[97,56] For example, the infrared spectrum showed a broad absorption in the 3100-2500 cm^{-1} region and the n.m.r. spectrum showed a sharp singlet at τ -2.95 (1 proton). On these grounds the structures (51) and (49) were assigned to the trichlorohydroxyazo and the corresponding methoxy compound respectively.

TABLE II. Chemical Shifts of Methoxy Protons and the Adjacent Aromatic Protons of Some Chloromethoxyazobenzenes

Compound 43; Solvent CCl_4

Signal	Chemical Shift (p.p.m.)	Proton Count	J (c/s)	Assignment
Singlet	3.85	3	-	$-O-CH_3$
Doublet of	6.76	1	J_{ortho} 8.9	5-H
doublet			J_{meta} 2.75	
Doublet	6.97	1	J_{meta} 2.6	3-H

Compound 48; Solvent $CCl_4/CDCl_3$ 2:1

Singlet	3.86	3	-	$-O-CH_3$
Doublet of	6.79	1	J_{ortho} 8.8	5'-H
doublet			J_{meta} 2.5	
Doublet	6.99	1	J_{meta} 2.5	3'-H

Compound 49; Solvent CCl_4

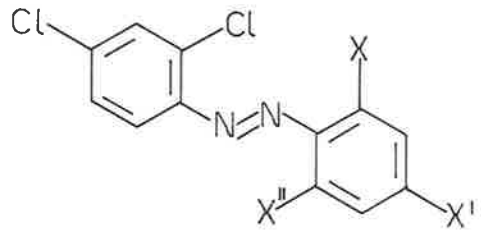
Singlet	4.02	3	-	$-O-CH_3$
Doublet and	*c*.6.94	2	J_{ortho} *c*.9	5'-H
Singlet			J_{meta} 2.3	
Singlet	7.01	$1\frac{1}{2}$	-	3'-H ($\frac{1}{2}$ 5'-H)

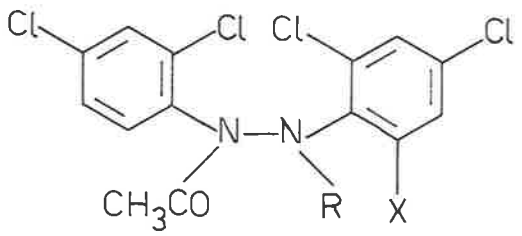
Compound 56; Solvent $CCl_4/CDCl_3$ 5:1

Singlet	3.86	3	-	$-O-CH_3$
Singlet	6.95	2	-	3' and 5'-H

The photoinduced reaction of 2,4,2',4'-tetrachloroazobenzene (47) with acetyl chloride, unlike the previous reactions, was very slow and resulted in a complex mixture of products. Even after exposing to sunlight for 80 hours the solution retained much of the original color intensity. After removal of the excess acetyl chloride, column chromatography was employed in an attempt to resolve the remaining mixture into its components. Although three separated fractions were eluted from the column, the first two still proved to be mixtures. The first fraction was found to be a mixture of 2,4,6,2',4'-pentachloroazobenzene (52) and 2,4,2',4'-tetrachloroazobenzene (47) in the ratio of 84:16, the latter compound probably being unchanged starting compound. The second fraction appeared to be a mixture of *N*-acetyl-2,4,2',4'-tetrachlorohydrazobenzene (53)

and *N*'-acetyl-2,4,6,2',4'-pentachlorohydrazobenzene (54) while the third and only pure fraction was *N*,*N*'-diacetyl 2,4,6,2',4'-pentachlorohydrazobenzene (55).





	X	X'	X''
(47)	Cl	Cl	H
(52)	Cl	Cl	Cl
(56)	Cl	OCH_3	Cl
(48)	Cl	OCH_3	H
(49)	OCH_3	Cl	H

	R	X
(53)	H	H
(54)	H	Cl
(55)	Ac	Cl

The structure of 2,4,6,2',4'-pentachloroazobenzene was established by elementary analysis and the infrared and mass spectra. Synthesis of this compound by condensation of 2,4,6-trichloronitrosobenzene with 2,4-dichloroaniline was unsuccessful.

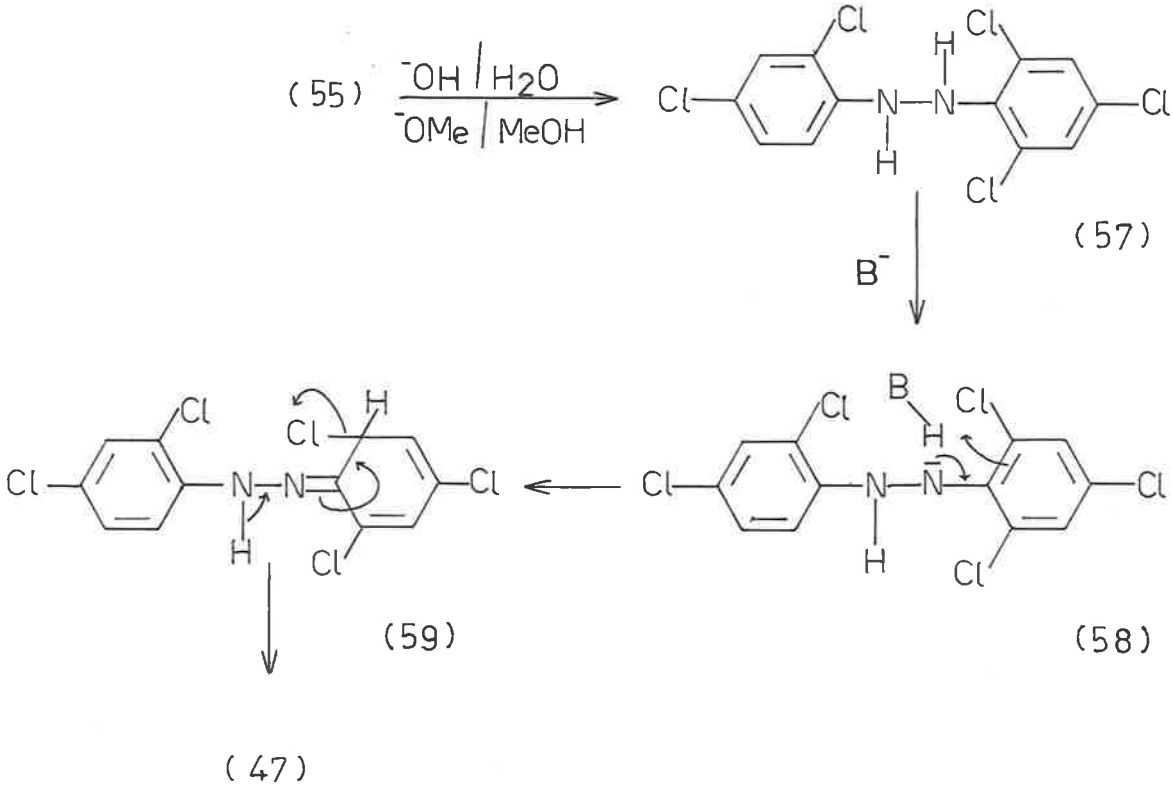
Separation of the *N*-acetyl compounds (53) and (54) was completely unsuccessful and accordingly their structures were not confirmed. However, the mass spectrum of the mixture showed probable molecular ions at *m/e* 396 (M) and 362 (M') with the isotope peaks having the correct relative abundance for five and four chloro groups respectively. Peaks at *m/e* 354 and 320 corresponding to M-42 and

M'-42 respectively were also present (showed metastables) and this further substantiated that *m/e* 396 and 362 were the respective molecular ions of (54) and (53). The infrared spectrum of the mixture exhibited a sharp N-H absorption at 3255 cm^{-1} and a sharp carbonyl absorption at 1655 cm^{-1} indicating the presence of only monoacetyl compounds.

The structure of *N*,*N*'-diacetyl-2,4,6,2',4'-pentachlorohydrazobenzene (55) was confirmed on the basis of elementary analysis and the infrared and mass spectra.

Hydrolysis and subsequent oxidation of the pure *N*,*N*'-diacetyl compound (55) in the usual manner gave a mixture of products, the major constituents of which, were identified by comparative gas and thin-layer chromatography or by isolation with column chromatography. The main products were 2,4,6,2',4'-pentachloroazobenzene (52) and 2,4,2',4'-tetrachloroazobenzene (47) and analytical gas chromatography showed they were formed in the ratio of 73:37. Small quantities of 2,4,2'-trichloro-4'-methoxyazobenzene (48), 2,4,4'-trichloro-2'-methoxyazobenzene (49) and 2,4,2',6'-tetrachloro-4'-methoxyazobenzene (56) were also isolated from the reaction mixture. Isomers (48) and (49) were identified by comparative gas chromatography; and the identity of compound (56) was established by elementary analysis and the infrared and n.m.r. spectra (Table II). As described previously, the methoxy compounds are formed by nucleophilic displacement during alkaline hydrolysis, this fact having been confirmed by separate experiments (see appendix).

The formation of 2,4,2',4'-tetrachloroazobenzene (47) in the above hydrolysis/oxidation reaction was completely unexpected. Examination of the *N*,*N*'-diacetylpentachloro compound (55) ruled out the possibility of contamination by *N*,*N*'-diacetyl-2,4,2',4'-tetrachlorohydrazobenzene (46), since the melting point of the former, besides being sharp, was also considerably higher than that of the latter. A reaction pathway from (55) to (47) consistent with the reaction conditions is shown in Scheme 5, but this has not been confirmed by separate examination of (57) under similar reaction conditions.



Scheme 5

Oxidation of hydrazobenzene to azobenzene in basic media has been shown to proceed via the dianion resulting from removal of both hydrazo protons.[98] In the above case, removal of a proton from the nitrogen atom adjacent to the trisubstituted phenyl ring would be facilitated by the three electron-attracting chloro groups (-I effect). An alternative oxidative pathway involving steps (58 → 59 → 47) could then occur and result in loss of a chloride ion. In the presence of a cage effect one would expect the *ortho* chloro group to be lost preferentially.

The mixture of monoacetyl compounds (53) and (54) were also subjected to alkaline hydrolysis, but since conversion to the azo compounds occurred so readily, aerial oxidation of the reaction mixture was not required. The major products were 2,4,6,2',4'-pentachloroazobenzene (52) and 2,4,2',4'-tetrachloroazobenzene (47) and they were shown to be in the ratio of 80:20 by analytical gas chromatography.

Further experiments were carried out in an attempt to identify the precursor of the 2,4,6,2',4'-pentachloroazobenzene isolated directly from the photochemical reaction products. *N*,*N*'-Diacetyl-2,4,6,2',4'-pentachlorohydrazobenzene (54) was irradiated for 50 hours in acetyl chloride but recovered unchanged at the end of this period. In a similar experiment, the mixture of monacetyl compounds (53) and (54) was irradiated for 25 hours in acetyl chloride. At the end of this period, the solution had developed a distinct orange color. The colored products were isolated and shown to consist of

a mixture of 2,4,6,2',4'-pentachloroazobenzene (52) and 2,4,2',4'-tetrachloroazobenzene (47) in the ratio of 95:5. A similar experiment carried out in the absence of light failed to yield colored products, and therefore, the formation of compound (52) in the photochemical reaction may be accounted for by a secondary photochemical process involving the product (54).

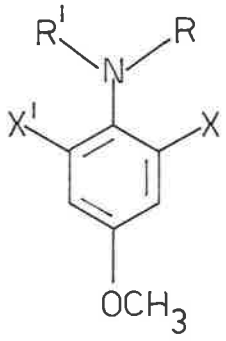
3. Substituted *trans*-Azobenzenes

The photoinduced reactions of several substituted azobenzenes in acetyl chloride solution was studied in order to determine whether substituents attached to the aromatic ring had any effect on the position of substitution by the incoming chloro group. Such directive effects of substituents, if encountered, might give important information concerning the mechanism of the photoreaction.

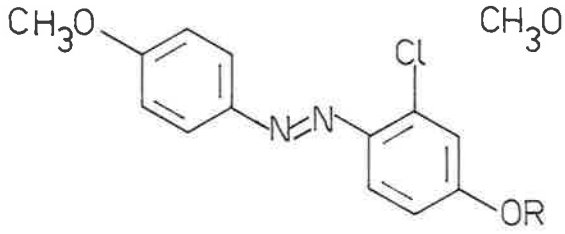
The mixtures of isomeric *N*,*N*'-diacetylhydrazobenzenes formed in many of the photoreactions of substituted azobenzenes with acetyl chloride could not be resolved by column chromatography, and consequently, the photoproducts were not characterized in these cases. However, when the photoproducts were deacetylated by the hydrolysis/oxidation procedure, the mixture of isomeric azo compounds so formed could, in many cases, be partially resolved and quantitatively analysed by gas chromatography.

A solution of 4,4'-dimethoxyazobenzene (60) in acetyl chloride was irradiated until the initially red colored solution had almost completely faded. Examination of the crude reaction mixture by thin-layer chromatography revealed that several photoproducts had been formed and accordingly an attempt was made to separate these products by column chromatography. The compounds obtained in order of elution from the column were *N*,*N*-diacetyl-2,6-dichloro-4-methoxyaniline (61), *N*,*N*-diacetyl-2-chloro-4-methoxyaniline (62), *N*-acetyl-2-chloro-4-methoxyaniline (63) and *p*-acetanisidide (64). Compounds (63) and (64) were the major products of the reaction. In addition

to the above compounds, a small quantity of an unidentified glass was isolated from the final fractions eluted from the column. When subjected to the hydrolysis/oxidation procedure, however, 2-chloro-4,4'-dimethoxyazobenzene (65) and *p*-anisidine (66) were obtained. This indicated that the original unidentified material consisted of a mixture of *N*,*N*'-diacetyl-2-chloro-4,4'-dimethoxyhydrazobenzene (67) and *p*-acetanisidide (64).

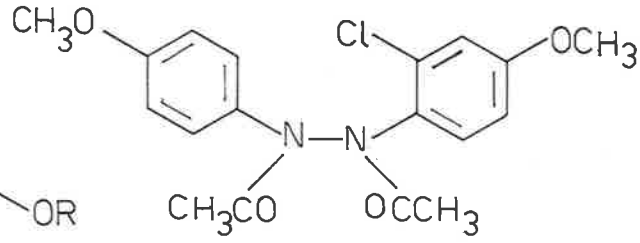


	R	R'	X	X'
(61)	Ac	Ac	Cl	Cl
(62)	Ac	Ac	Cl	H
(63)	Ac	H	Cl	H
(64)	Ac	H	H	H
(66)	H	H	H	H



(65) R = CH_3

(68) R = H



(67)

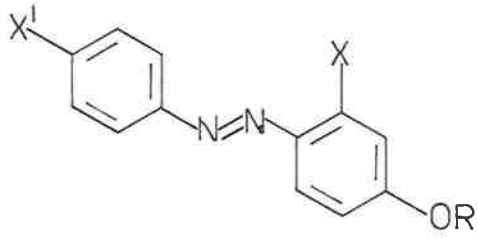
The photoproducts (61), (62) and (63) were characterized by the infrared, n.m.r. (Table III) and mass spectra, whereas the products (64) and (66) were identified by direct comparison with authentic samples. Confirmation of the structure of compound (65) was accomplished by comparison with an authentic sample synthesised by coupling *p*-methoxydiazonium chloride with *m*-chlorophenol followed by methylation of the resulting 2-chloro-4-hydroxy-4'-methoxyazobenzene (68) with dimethyl sulphate.

The amides (61-64) probably were formed as a result of homolytic or heterolytic fission of the N-N bond of *N*,*N*'-diacetyl-2-chloro-4,4'-dimethoxyhydrazobenzene (67). This suggested mode of formation is supported by the knowledge that the N-N bonds of tetraphenylhydrazines[99] and tetraphenyl-1,2-diazetidinones[100] are readily cleaved when they have electron-donating (*p*-CH_3O- and *p*-$(CH_3)_2N$-) groups attached to the aromatic rings. In both of these cases good evidence exists that the process involves homolytic fission.[99,100]

The process resulting in the formation of *N*,*N*-diacetyl-2,6-dichloro-4-methoxyaniline is not known, but the possibility of an Orton rearrangement[101] cannot be discounted, especially since they can be light catalysed[102,103] and the required N-chloroamide could be formed during cleavage of the N-N bond of the *N*,*N*'-diacetyl compound.

Irradiation of 4-methoxyazobenzene (69) in acetyl chloride solution gave a mixture of photoproducts which was separated by column chromatography. The minor products eluted firstly from the

column were *N*,*N*-diacetyl-2,6-dichloro-4-methoxyaniline (61), *N*,*N*-diacetyl-2-chloro-4-methoxyaniline (62) and acetanilide (70). The major product was obtained as a colorless glass, the infrared spectrum of which showed two carbonyl and no N-H stretching absorptions. Alkaline hydrolysis of the major product followed by oxidation afforded a mixture of chloromethoxyazobenzenes. Two peaks were observed when this isomeric mixture was subjected to gas chromatography. It was subsequently shown that 2-chloro-4-methoxyazobenzene (71) constituted more than 95% of the mixture. The minor constituent, although not identified, was possibly the isomeric 4-chloro-4'-methoxyazobenzene (72).



(70)

	R	X	X'
(69)	CH_3	H	H
(71)	CH_3	Cl	H
(72)	CH_3	H	Cl
(73)	H	Cl	H

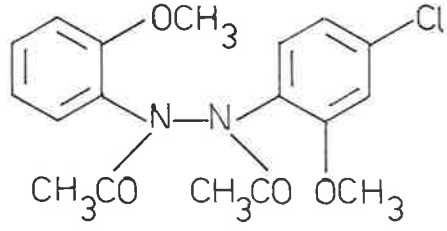
Compounds (61) and (62) were shown to be identical with two compounds isolated from the corresponding photochemical reaction of 4,4'-dimethoxyazobenzene. As previously suggested, they probably originated through cleavage of the N-N bond of the

N,*N*'-diacetyl compounds. The structure of 2-chloro-4-methoxyazobenzene was confirmed by comparison with an authentic sample synthesized by coupling phenyldiazonium chloride with *m*-chlorophenol and methylation of the resulting hydroxyazo compound (73).

The crude product isolated from the photoinduced reaction of 2,2'-dimethoxyazobenzene (74) with acetyl chloride, was chromatographed on silica gel. Apart from small quantities of unidentified oils, the only products eluted from the column were *N*-acetyl-4-chloro-2-methoxyaniline (75) and *N*,*N*'-diacetyl-4-chloro-2,2'-dimethoxyhydrazobenzene (76), the latter product being isolated as a white crystalline solid in 83% yield. Alkaline hydrolysis and oxidation of compound (76) in the usual manner yielded 4-chloro-2,2'-dimethoxyazobenzene (77) as the only product.

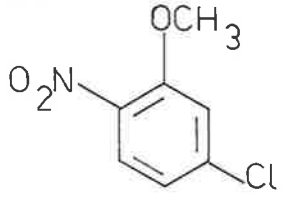
(74) X = H

(77) X = Cl

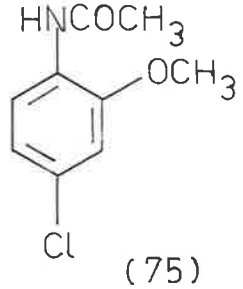


(76)

Compound (75) was characterized on the basis of infrared and mass spectra whereas the structures of the major photoproduct (76) and the hydrolysis product (77) were established by elementary analysis, infrared, n.m.r. (Table III) and mass spectra. An attempted independent synthesis of a separate sample of 4-chloro-2,2'-dimethoxyazobenzene by sodium hydroxide fusion of 3-chloro-6-nitroanisole (78) with *o*-anisidine was unsuccessful. A small quantity of compound (78) was prepared in several steps from *m*-chlorophenol.



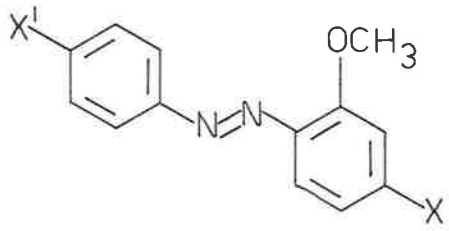
(78)



(75)

Chromatography of the photoproduct formed on irradiation of 2-methoxyazobenzene (79) in acetyl chloride resulted in elution of only one broad band and this fraction afforded a colorless glass. After hydrolysis/oxidation of the chromatographed material, a mixture of chloromethoxyazobenzenes was obtained, and attempts were made to isolate the isomers and estimate the isomer ratio. Preparative gas chromatography resulted in partial separation of the isomers, and several recrystallizations of the fraction corresponding to the peak with the longer retention time, afforded 4-chloro-2'-methoxyazobenzene (80) in the pure state. Comparative infrared spectroscopy using authentic samples of (80) and (81) showed that the fraction corresponding to the peak having the

shorter retention time consisted mainly of 4-chloro-2-methoxy-azobenzene (81). However, compound (81) could not be obtained pure by recrystallization of this fraction. Analytical gas chromatography showed that the ratio of (80) to (81) in the original reaction mixture was 68:32.



	X	X'
(79)	H	H
(80)	H	Cl
(81)	Cl	H

In order to confirm the structures of (80) and (81), the authentic compounds were separately synthesised. 4-Chloro-2-methoxyazobenzene was prepared by sodium hydroxide fusion of aniline and 3-chloro-6-nitroanisole (78); and the 4-chloro-2'-methoxy isomer was synthesised in a similar manner from *p*-chloroaniline and *o*-anisidine.

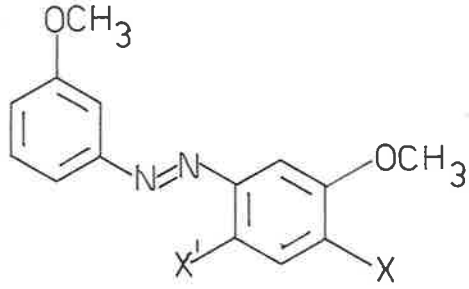
The product obtained after irradiation of 3,3'-dimethoxy-azobenzene (82) in acetyl chloride was passed through a column of silica gel. Only one broad band was eluted from the column and collected in two approximately equal fractions. The material isolated from each fraction was separately subjected to the hydrolysis/oxidation procedure and the products examined in each case. One hydrolysis mixture afforded almost pure 4-chloro-3,3'-dimethoxyazobenzene (83) in about 37% overall yield whereas the

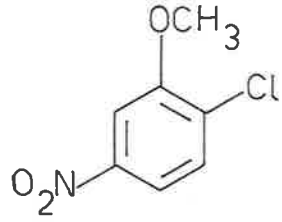
other gave a mixture of at least three compounds. Preparative gas chromatography isolated one compound from the mixture and this was identified as 3,3'-dimethoxyazobenzene (82) by direct comparison with authentic material. However, further separation of the mixture was not achieved, even after gas chromatography with several analytical columns, and an estimate of the isomer ratio was not obtained.

Compound (83) and 6-chloro-3,3'-dimethoxyazobenzene (84) were synthesised and their n.m.r. spectra determined (Table III). The chemical shift of the 3-methoxy group in compounds (83) and (84) was found to vary slightly with the position of the chloro group (Table III), but the change was too small for integration of the methoxy peaks to be used as an estimate of isomer ratios in the inseparable mixture.

Synthesis of isomers (83) and (84) was accomplished by sodium hydroxide fusions of *m*-anisidine with 2-chloro-5-nitroanisole (85) and 4-chloro-3-nitroanisole (86) respectively. Compounds (85) and (86) were prepared in several steps from *o*-anisidine and *p*-anisidine respectively.

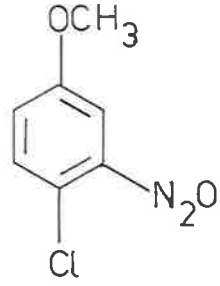
Irradiation of 3-methoxyazobenzene (87) in acetyl chloride gave a photoproduct which was eluted from a column of silica gel as one broad band. After the usual procedure of hydrolysis and oxidation of the photoproduct, a mixture of compounds was obtained and shown to consist of 4-chloro-3'-methoxyazobenzene (88), 4-chloro-3-methoxyazobenzene (89) and 3-methoxyazobenzene (87). The latter





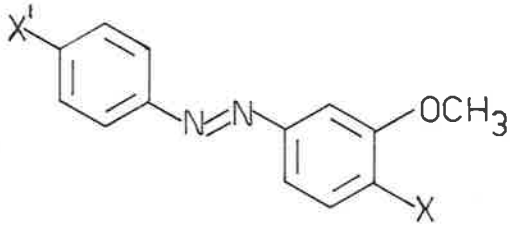
(85)

	X	X'
(83)	Cl	H
(84)	H	Cl
(82)	H	H



(86)

compound was separated by preparative gas chromatography and characterized by direct comparison with the starting material. Analytical gas chromatography using a calibration curve prepared from known mixtures of the authentic compounds established that the ratio of (89) to (88) was 45:55.



	X	X'
(87)	H	H
(88)	H	Cl
(89)	Cl	H

For identification purposes, isomers (88) and (89) were resolved by fractional crystallization and the structures confirmed by direct comparison with authentic samples. 4-Chloro-3'-methoxy-

azobenzene was prepared by sodium hydroxide fusion of *p*-chloroaniline with *m*-anisidine and 4-chloro-3-methoxyazobenzene was prepared in a similar manner from aniline and 2-chloro-5-nitroanisole (85).

In the foregoing reactions of 3-methoxyazobenzene and 3,3'-dimethoxyazobenzene, the small amounts of starting material isolated from the final reaction mixtures were clearly not unchanged compounds, since the photoproducts were purified before the hydrolysis/oxidation procedure was carried out. Apparently during hydrolysis of the photoproducts, loss of a chloro group can occur, and a reaction pathway for such a process has been previously described (Scheme 5). The presence of non-chlorinated products in the final reaction mixtures of the *o*- and *p*-methoxyazobenzenes was not observed, and would not be expected on the basis of the mechanism proposed for their formation, since the mesomeric electron-donating effect of *o*- and *p*-methoxyl groups would not facilitate proton removal from the intermediate hydrazo compound.

TABLE III. Chemical Shifts of Some Photoproducts and Azo Compounds

Compound No.	Signal	Chemical Shift (p.p.m.)	Proton Count	Assignment
61 (CCl_4)	Singlet	2.14	6	$-N(COCH_3)_2$
	Singlet	3.75	3	$-O-CH_3$
	Singlet	6.86	2	3-H, 5-H

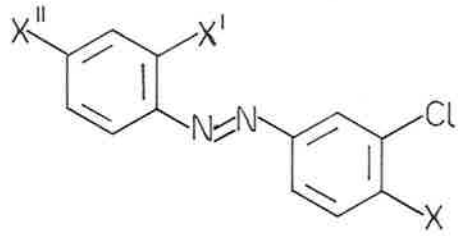
62	(CCl_4)	Singlet	2.17	6	$-N(COCH_3)_2$
		Singlet	3.73	3	$-O-CH_3$
		Multiplet	6.7-7.4	3	aromatics
76	(CCl_4)	Singlet	1.75	6	2 x $N-COCH_3$
		Singlet	3.27	3	$2'-O-CH_3$
		Singlet	3.32	3	$2-O-CH_3$
		Multiplet	6.6-7.9	7	aromatics
81	(CCl_4)	Singlet	3.92	3	$-O-CH_3$
		Multiplet	6.7-7.9	8	aromatics
84	($CCl_4/CDCl_3$	Singlet	3.78	3	$3'-O-CH_3$
	4:1)	Singlet	3.83	3	$3-O-CH_3$
		Multiplet	6.7-7.6	7	aromatics
83	(CCl_4)	Singlet	3.80	3	$3'-O-CH_3$
		Singlet	3.90	3	$3-O-CH_3$
		Multiplet	6.7-7.6	7	aromatics
88	(CCl_4)	Singlet	3.80	3	$3'-O-CH_3$
		Multiplet	6.8-7.9	8	aromatics

The photoinduced reaction of 3-chloroazobenzene (90) with acetyl chloride was examined for comparison with the corresponding reactions of 2- and 4-chloroazobenzenes which have been described.

The crude photoproduct was subjected directly to hydrolysis and oxidation, and attempts were made to separate the resulting mixture of isomeric dichloroazobenzenes. A small quantity of 3,4'-dichloroazobenzene (91) was separated by fractional crystallization, but preparative techniques failed to resolve other constituents of the mixture. Gas chromatography with several analytical columns also failed to resolve the major reaction products, but did separate a minor product which was probably 2,3'-dichloroazobenzene (92).

The expected major products of the above reaction were 3,4'- and 3,4-dichloroazobenzene (91 and 93) and these were synthesised. As expected, gas chromatography of various mixtures of the authentic compounds (91) and (93) resulted in only one symmetrical peak.

The basis of another attempted separation of (91) and (93) was nucleophilic displacement of the *p*-chloro group of the 3,4-dichloro isomer by methoxide ion. Presence of an adjacent chloro group in compound (93) was expected to facilitate displacement, so that under mild reaction conditions, (91) would remain unchanged. However, initial experiments with the authentic compounds showed that some replacement did occur with 3,4'-dichloroazobenzene even under mild reaction conditions, and further attempts to separate the mixture were abandoned.



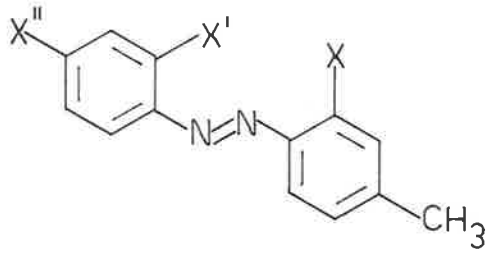
	X	X'	X''
(90)	H	H	H
(91)	H	H	Cl
(92)	H	Cl	H
(93)	Cl	H	H

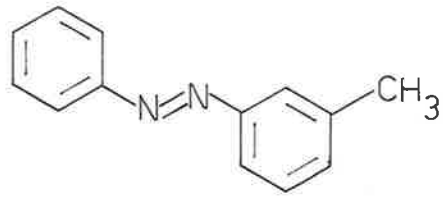
Authentic samples of compounds (91) and (92) were synthesised by sodium fusions of *m*-chloronitrobenzene with *p*-chloroaniline and *o*-chloroaniline respectively. Condensation of nitrosobenzene with 3,4-dichloroaniline afforded 3,4-dichloroazobenzene (93).

The crude photoproduct isolated from the photoinduced reaction of 3-methylazobenzene (94) with acetyl chloride was subjected to hydrolysis and aerial oxidation. Attempts to resolve the isomeric products in the final reaction by gas chromatography and preparative techniques were, however, completely unsuccessful. Consequently no reaction products were characterized. Determination of the isomer ratio in the final mixture was attempted by n.m.r. spectroscopy, since it appeared that methyl protons of the different isomers would exhibit different chemical shifts. However, the n.m.r. spectrum of the mixture showed only a single peak for the methyl protons.

In a similar experiment with 4-methylazobenzene (95), the mixture of compounds resulting from hydrolysis and oxidation of the photoproducts was successfully resolved by gas chromatography.

The principal constituents of the mixture were 4-chloro-4'-methylazobenzene (96) and 2-chloro-4-methylazobenzene (97) and these were readily separated by fractional crystallization. Analytical gas chromatography showed that the ratio of (97) to (96) in the mixture was approximately 73:27. Although a sample of 2-chloro-4'-methylazobenzene (98) exhibited an identical retention time to compound (97), on the basis of the known *ortho/para* ratio in the photoinduced reaction of azobenzene with acetyl chloride (*c.* 1:8) a relative yield of only *c.* 3% of compound (98) would be expected.





(94)

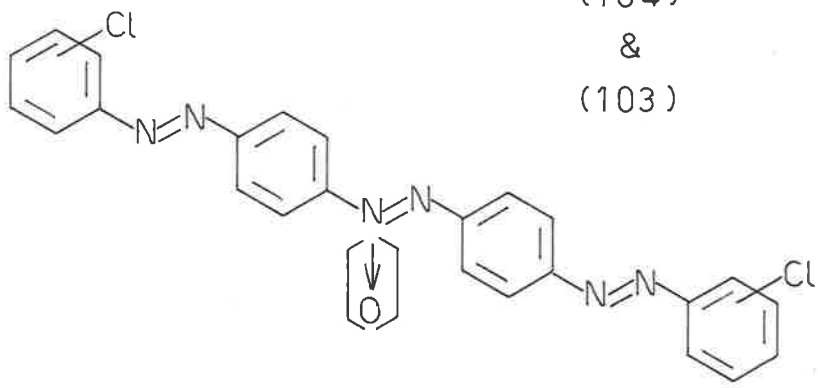
	X	X'	X''
(95)	H	H	H
(96)	H	H	Cl
(97)	Cl	H	H
(98)	H	Cl	H

The structures of compounds (96) and (97) were confirmed by direct comparison with authentic samples prepared in the following manner. 4-Chloro-4'-methylazobenzene was prepared by sodium hydroxide fusion of *p*-chloroaniline with *p*-nitrotoluene and 2-chloro-4-methyl-

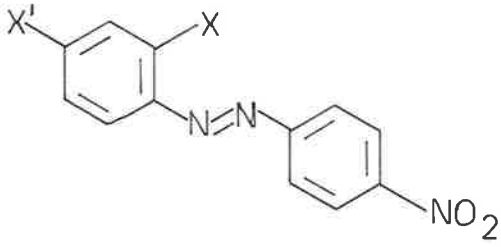
azobenzene by condensation of nitrosobenzene with 3-chloro-*p*-toluidine. Compound (98) was synthesised by fusion of *o*-chloroaniline, *p*-nitrotoluene and sodium hydroxide.

Irradiation of 3- and 4-nitroazobenzenes (99 and 100) in acetyl chloride afforded in each case a pale yellow glass. Chromatography of each photoproduct resulted in one broad band being eluted from the columns and the isolated products showed infrared spectra typical of *N*,*N*'-diacetylhydrazobenzene compounds. Alkaline hydrolyses of the photoproducts proceeded rapidly; insoluble material precipitating from the reaction media after only several minutes warming. It was subsequently shown, however, that the precipitate in each case was an ether-insoluble orange solid of reasonably high molecular weight. A small quantity of ether-soluble material was also isolated from the final reaction mixture. Only the products derived from 4-nitroazobenzene by the above reaction sequence were examined further.

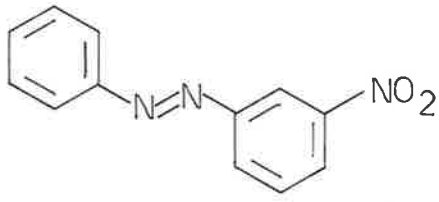
Chromatography of the ether-soluble material afforded a mixture of 4-chloro-4'-nitroazobenzene (101) and 2-chloro-4'-nitroazobenzene (102). A small amount of an orange solid was isolated from the final fractions eluted from the column. Compounds (101) and (102) were readily resolved by fractional crystallization and were characterized by comparisons with separately synthesised samples. The orange solid appeared to be a mixture of isomeric bis(chloro-*p*-phenylazo)azobenzenes (103). The mass spectrum of this mixture exhibited a peak at *m/e* 458 (molecular ion) with isotope peaks (M+2 and M+4) having the correct relative abundance for two chloro groups and thus was consistent with structure (103).



(104)
&
(103)



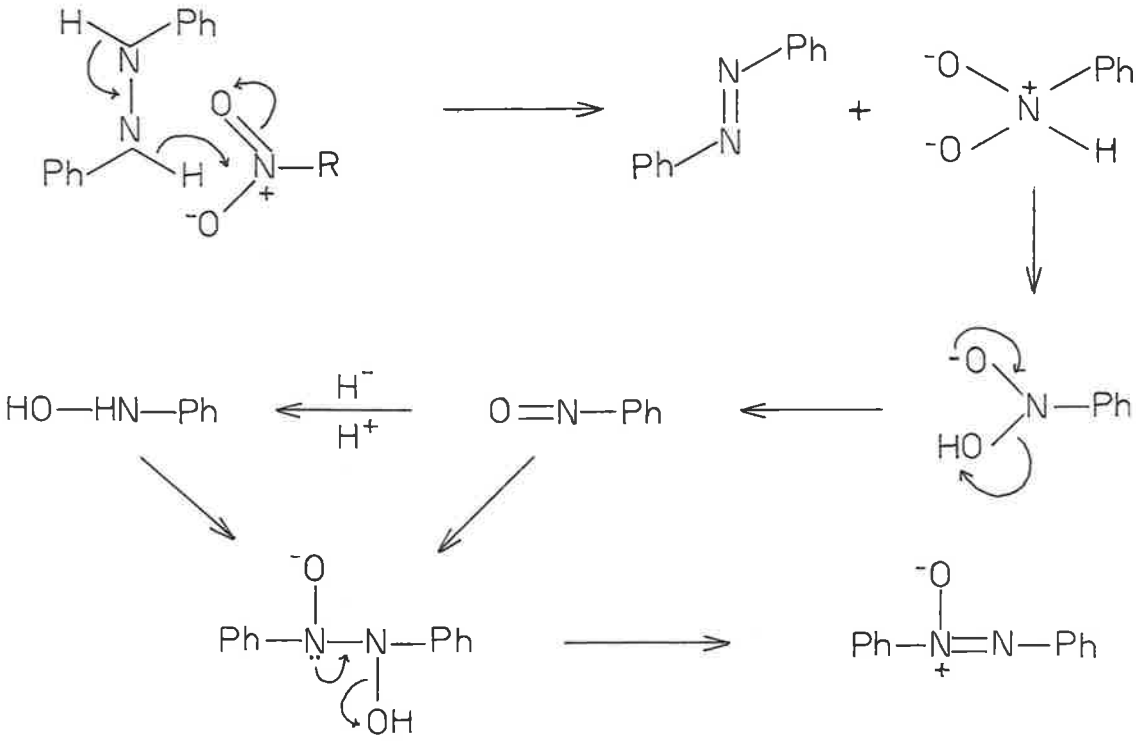
	X'	X
(100)	H	H
(101)	Cl	H
(102)	H	Cl



(99)

The mass spectrum of the ether-insoluble material isolated from the hydrolysis reaction mixture was also determined. This showed a peak at *m/e* 474 (molecular ion) with isotope peaks (M+2 and M+4) corresponding to two chloro groups present in the molecule. The spectrum also exhibited a strong peak at *m/e* 458 (M-16) and this indicated that the material was probably a mixture of isomeric bis(chloro-*p*-phenylazo)azoxybenzenes (104).

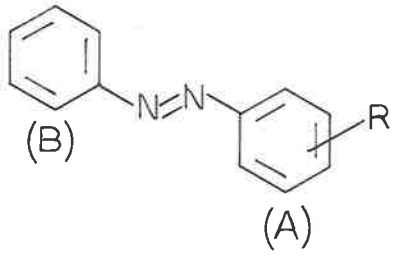
A plausible pathway leading to the formation of compounds (103) and (104), and involving simultaneous oxidation of a hydrazo group and reduction of a nitro group is shown in Scheme 6. Formation of azoxybenzenes by reduction of nitrobenzenes with reducing sugars in alkaline media is a well known reaction.[105,106] Much controversy has arisen over the mechanism of this reaction, but it seems likely that the azoxy compound is formed by a sequence of reactions analogous to those shown in Scheme 6. In this case of course, hydride transfers would occur from the reducing sugar. The fact that nitrosobenzenes and phenylhydroxylamines readily condense in alkaline solution to give azoxybenzenes[104] (and small amounts of azobenzenes) supports the proposed route (Scheme 6) to compounds (103) and (104).



Scheme 6

In the foregoing reactions, relative yields of the isomeric products were determined in several cases for monosubstituted azobenzenes and a summary of these is shown in Table IV. Besides the relative isomer yields, the total proportion of product arising from chlorination in either phenyl ring is shown and this gives an estimation of the directive effect of the substituents on the position of chlorination.

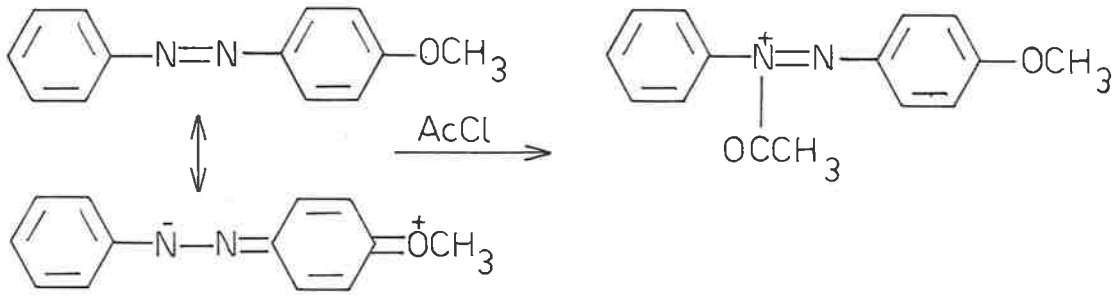
TABLE IV. Positions of Chlorination and the Corresponding Product Yields for the Monosubstituted Azobenzenes.



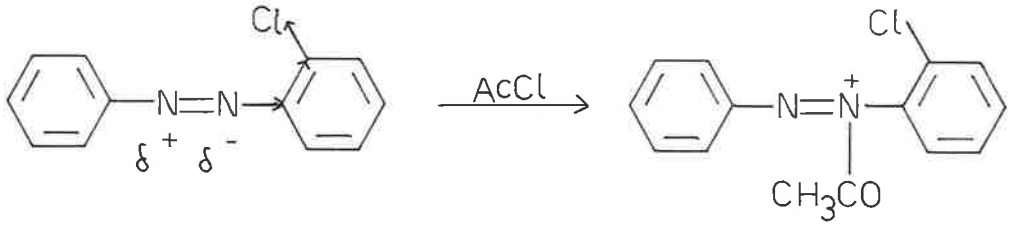
Substituent (R)	Ring (A)			Ring (B)		
	ortho	para	Total	ortho	para	Total
2-chloro-(35)	-	39	39	6	55	61
4-chloro-(3)	41	-	41	5	54	59
4-methyl-(95)	73	-	73	0	27	27
2-methoxy-(79)	-	32	32	0	68	68
3-methoxy-(87)	0	45	45	0	55	55
4-methoxy-(69)	>95	-	*c.*95	0	<5	*c.*5

Substituents attached to the azobenzene molecule would be expected to result in unequal distribution of electronic charge at the nitrogen atoms of the azo linkage due to inductive and mesomeric electronic effects (as shown by 105 and 106). If a cationic species (viz. 105b or 106b) is initially formed as postulated, then acetylation would occur preferentially at the nitrogen atom having the highest electron density. From the known mesomeric electron-donating character of the *p*-methoxy group one would expect initial acetylation of 4-methoxyazobenzene to give predominantly the cation (105b). In this case, chlorination would be expected to occur predominantly in ring A (at the *ortho* positions); and this is in fact observed (see Table IV). On the other hand, the inductive effect (-I) of a 2-chloro group should result in a majority of the cation (106b) and thus preferential chlorination in ring B (at the *para* position). This effect is also observed. Furthermore, the mesomeric electron-donating power of *p*-methoxy, *p*-methyl and *p*-chloro groups lies in the order $CH_3O > CH_3 > Cl$ and accordingly the percentage chlorination in the substituted ring (ring A) was found to lie in the same order.

Of the compounds shown in Table IV only the result obtained from 2-methoxyazobenzene is inconsistent with the above reasoning. Overall, the results are therefore consistent with the ionic mechanism (Scheme 1) which has been proposed for the photoreaction of azobenzene with acetyl chloride.



(105) (105b)



(106) (106b)

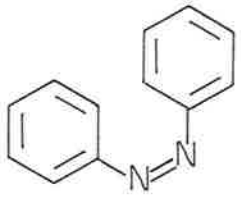
II. DARK REACTION OF *CIS*-AZOBENZENE WITH ACETYL CHLORIDE

An account of the photoinduced reaction between *trans*-azobenzene and acetyl chloride has been given, the products obtained from the reaction having been shown to be *N*,*N*'-diacetyl-4-chloro-hydrazobenzene and a small amount of the 2-chloro isomer. In the postulated ionic mechanism of the photochemical reaction, a photoexcited state of *trans*-azobenzene was assumed to be the reactive species, since a separate experiment determined that no perceptible reaction occurred between *trans*-azobenzene and acetyl chloride at room temperature in the absence of light. However, irradiation of neutral or acidic solutions[4,49] of *trans*-azobenzene is known to give *trans* $\rightleftharpoons$ *cis* equilibrium mixtures, and it was therefore necessary to investigate whether a dark reaction between *cis*-azobenzene and acetyl chloride could occur.

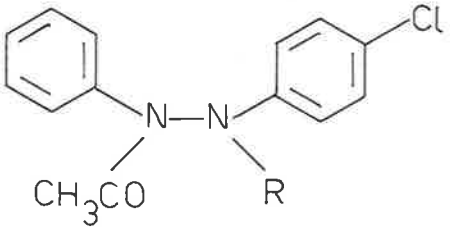
When *cis*-azobenzene and acetyl chloride were mixed a rapid reaction occurred resulting in evolution of hydrogen chloride, giving an intensely blue-purple colored solution. When the reaction mixture was allowed to stand, the blue-purple color slowly faded until after *c*. 20 minutes only a red color remained. No further color change occurred when the red solution was allowed to stand in darkness for several days or when it was exposed to sunlight. Since pure *trans*-azobenzene gives simply an orange solution in acetyl chloride (which fades on exposure to light), the coloration formed by the *cis* isomer in acetyl chloride constitutes a very sensitive test for distinguishing *cis*-azobenzene from the *trans* isomer.

1. Reaction Products

In one experiment, *cis*-azobenzene (6) and excess acetyl chloride were mixed and well stirred for one minute before water was added to destroy all excess acetyl chloride. The resulting purple acidic solution was partly neutralized (to pH 5-6) and extracted with ether, the purple material remaining in the aqueous phase. Chromatography of the residue obtained after evaporation of the ether gave *N*,*N*'-diacetyl-4-chlorohydrazobenzene (2: 40% yield), *N*'-acetyl-4-chlorohydrazobenzene (107: 34% yield), 4-phenylaminoazobenzene (108; 5% by weight of the *cis*-azobenzene employed) and *trans*-azobenzene (1: 12% yield). When the remaining purple aqueous solution was rendered alkaline, a dark blue color developed, and the blue material was readily extracted into ether at this stage. Evaporation of the ether gave a significant quantity (12% by weight of the *cis*-azobenzene employed) of a blue-black resinous compound.

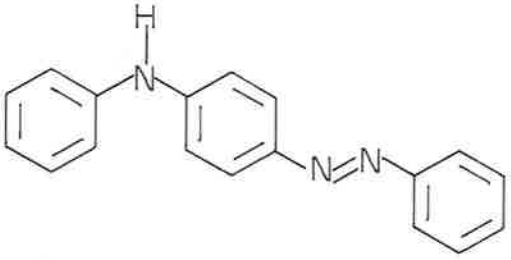


(6)



(2) R = $COCH_3$

(107) R = H



(108)

Compounds (2) and (107) were only partially separated by column chromatography and complete separation was accomplished by fractional crystallization. They were characterized by the infrared spectra and by the fact that alkaline hydrolysis followed by aerial oxidation afforded 4-chloroazobenzene as the only product. In addition, the position of the acetyl group of compound (107) was established by cleavage of the N-N bond with phenylhydrazine[107] and identification of the resulting fragments. Acetanilide and *p*-chloroaniline were isolated by column chromatography thus characterizing compound (107) as the *N'*-acetyl isomer. 4-Phenylaminoazobenzene and *trans*-azobenzene were identified in each case by direct comparison with authentic samples.

In another experiment, *cis*-azobenzene and acetyl chloride were mixed and the solution was allowed to stand in the absence of light for 170 hours. No trace of the blue-purple coloration remained after this period, and on extraction of the reaction mixture the only product isolated, in addition to those (2, 107, 108 and 1) already found, was acetanilide (70; 3% by weight of the *cis*-azobenzene employed).

2. Attempted Identification of the Metastable Products from this Reaction

Thin-layer chromatography of the blue-black resin obtained from the reaction of *cis*-azobenzene with acetyl chloride indicated that it consisted mainly of one blue compound mixed with very minor quantities of several other colored compounds. Progressive decomposition of the resinous material occurred on standing in acidic or basic solutions, by boiling in light petroleum, or just on standing in air for several days. The decomposition products from the above reactions were examined by thin-layer chromatography, and in each case a yellow compound having an identical R_F value to authentic 4-phenylaminoazobenzene appeared as one of the many products. Furthermore, when redissolved in acetyl chloride or boiled with methanolic potassium hydroxide, the blue compound afforded mainly 4-phenylaminoazobenzene. From the alkaline hydrolysis, a good yield (*c.* 50% by weight) of 4-phenylaminoazobenzene was obtained after its separation from the many minor products by column chromatography. These observations indicated that the 4-phenylaminoazobenzene isolated from the dark reaction of *cis*-azobenzene with acetyl chloride originated by decomposition of some of the blue-black compound before extraction of the reaction products.

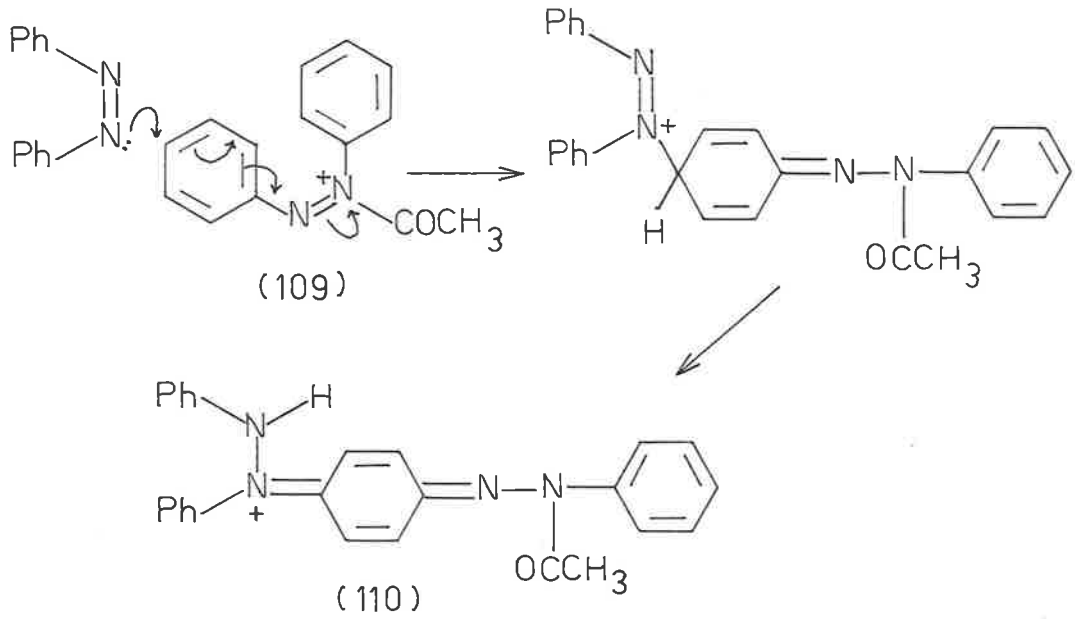
Attempts to crystallize the resin resulted in slow decomposition. Nevertheless the n.m.r. and infrared spectra of a freshly prepared sample were determined. The infrared spectrum

(Nujol) showed bands at 1680-1650, 1595 and 1365 cm^{-1} and the n.m.r. spectrum (deuterochloroform) exhibited a sharp singlet at τ 7.80, two peaks at τ 2.7-2.8 assigned to the aromatic protons and a very broad peak at τ 3.0-3.3. A solution of the compound in 1 *N* hydrochloric acid showed a broad absorption band at λ_{max} 550 mμ, whereas ethanol and chloroform solutions exhibited broad absorption at λ_{max} 580 and 620 mμ respectively.

Although the structure of the blue compound has not been established, the presence of an acetyl group in the molecule may be inferred from the bands at 1680-1650 and 1365 cm^{-1} in the infrared spectrum and the singlet at τ 7.80 in the n.m.r. spectrum. The electronic absorption spectrum of the compound in acidic solution is similar to that of the conjugate acid of 4-phenylaminoazobenzene,[108] but in neutral solution, the absorption spectrum of 4-phenylamino-azobenzene as the free base differs completely from that of the blue compound.

The structure of the blue compound, consistent with the above observations, is considered to be one incorporating two molecules of azobenzene and an acetyl group. A possible pathway leading to such a structure is shown in Scheme 7, and involves nucleophilic attack by a *cis*-azobenzene molecule on the cation (109). In this manner a compound having a quinonedi-imine structure similar to (110) may be formed, and by comparison with dyestuffs having similar structures, such a compound would be expected to be intensely colored. If the metastable blue compound is formed by a process similar to that shown in Scheme 7, then *cis*-azobenzene

must be competing with chloride ion as a nucleophile in the reaction, and consequently, the yield of blue compound should depend on the *cis*-azobenzene concentration in the reaction mixture. Indeed, the yield of blue compound was found to depend on the volume of acetyl chloride employed in the reaction. For example, when acetyl



Scheme 7

chloride was slowly added dropwise to *cis*-azobenzene, the yield of blue material was considerably greater than when *cis*-azobenzene was simply added to excess acetyl chloride.

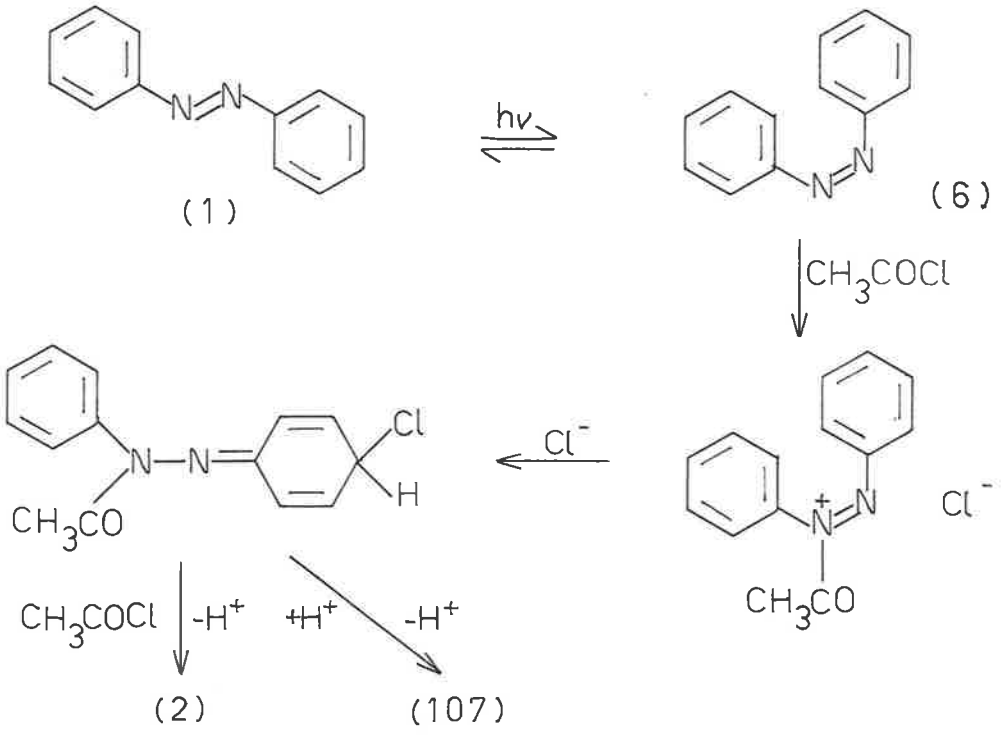
The fact that no blue coloration is observed during the course of the photochemical reaction of *trans*-azobenzene with acetyl chloride is attributed to the very small concentration of *cis*-azobenzene present at any one time in the reaction mixture. Presumably, any *cis*-azobenzene formed by photoisomerization of

the *trans* isomer reacts immediately with the large excess of acetyl chloride so that an accumulation of the *cis* isomer cannot occur.

Formation of 4-phenylaminoazobenzene and aniline from compound (110) can be envisaged by cleavage of one of the N-N bonds. Although attempts to identify aniline in the decomposition products of the blue compound were unsuccessful, a small quantity of acetanilide was isolated from the reaction of *cis*-azobenzene with acetyl chloride in which the blue coloration was allowed to fade before the products were extracted.

3. Mechanism of the Photochemical Reaction

The reaction of *cis*-azobenzene with acetyl chloride in the absence of light yielded *N*,*N*'-diacetyl-4-chlorohydrazobenzene (2) and *N*'-acetyl-4-chlorohydrazobenzene (107) as the major products, the former being identical to the compound obtained from the photo-induced reaction of *trans*-azobenzene with acetyl chloride. These results indicate that the photochemical reaction involves initial *trans* ⇌ *cis* photoisomerization followed by a non-photochemical reaction of *cis*-azobenzene with acetyl chloride. A mechanistic pathway (Scheme 1) has already been proposed for the photochemical reaction and may now be reasonably extended (Scheme 8) to include the photoisomerization step. This scheme also allows one plausibly to account for the formation of *N*'-acetyl-4-chlorohydrazobenzene.



Scheme 8

Formation of compound (107) in the reaction of *cis*-azobenzene with acetyl chloride can be attributed to the appreciable quantity of hydrogen chloride rapidly evolved during the reaction, since protons could readily compete with acetyl chloride (or acetylium ions) in attacking the nitrogen atom adjacent to the substituted phenyl group. In the photochemical reaction of *trans*-azobenzene with acetyl chloride, the *N*,*N*'-diacetyl compounds are formed exclusively because of the low concentration of hydrogen chloride in the reaction mixture. Besides being carried out in a considerably larger volume of acetyl chloride, the photochemical reaction occurs at a much slower rate (presumably at the rate of *trans* → *cis* isomerization), and the hydrogen chloride concentration cannot accumulate to an extent which would result in an appreciable quantity of *N*'-acetyl-4-chlorohydrazobenzene being formed.

III. PHOTOINDUCED REACTIONS OF *TRANS*-AZOBENZENE WITH ACYL AND AROYL CHLORIDES

1. *ortho/para* Product Ratios

Irradiation of *trans*-azobenzene in acetyl chloride followed by alkaline hydrolysis and oxidation of the photoproducts has already been shown to give 4-chloroazobenzene (3) and 2-chloroazobenzene (35) in 83% and 12% overall yields respectively. However, experiments in which benzene was employed as an inert solvent in the photochemical step revealed that the above sequence of reactions affords an *ortho/para* (35/3) product ratio considerably larger than when only acetyl chloride is used as solvent. The *ortho/para* ratio has also been found to be markedly dependent on the acid chloride used in the photochemical step. For example, when acetyl chloride was replaced by trichloroacetyl chloride in the photochemical reaction, hydrolysis and oxidation of the photoproducts yielded 2-chloroazobenzene (35) as the principal product.

In order to further investigate the effect of various acid chlorides (with and without benzene as solvent) on the relative extents of *para*- and *ortho*-chlorination *trans*-azobenzene was irradiated in the presence of several different acyl and aroyl acid chlorides. Separation of the mixture of photoproducts was in each case found to be impracticable. The photoproducts were therefore subjected directly to the hydrolysis/oxidation procedure. The final reaction mixture contained 2- and 4-chloroazobenzene (with some unchanged azobenzene in a few cases), and the product ratio (35/3) was determined by analytical gas chromatography.

TABLE V. Acid Chlorides as Solvent Reactants: Yields and Ratio of 2- and 4-Chloroazobenzene

(15 ml of acid chloride used with 0.002 mole of *trans*-azobenzene)

Acid Chloride	Irradiation Period hr.	Combined Yield %	Product Ratio (35/3)
Acetyl	2	95	0.18
Trichloroacetyl	35	40	19.0
Trimethylacetyl	20	- *	0.22
Oxalyl	3	76	0.64
Benzoyl	7	72	0.59
p-Methoxybenzoyl	7	- *	0.30

* These combined yields could not be accurately determined.

TABLE VI. Results with Benzene as Solvent

(15 ml benzene; 0.002 mole of *trans*-azobenzene)

Acid Chloride	Quantity (mole)	Irradiation Period hr.	Combined Yield %	Product Ratio (35/3)
Acetyl	0.010	2	90	0.47
	0.006	2	91	0.59
	0.004	2	91	0.61
Trichloroacetyl	0.010	35	51	13.3
	0.005	35	51	13.3
Trimethylacetyl	0.010	20	- *	0.33
Oxalyl	0.010	5	44	4.0
Benzoyl	0.010	10	88	2.0
	0.005	10	81	2.2
p-Nitrobenzoyl	0.010	20	85	3.2
3,5-Dinitrobenzoyl	0.010	10	74	3.3
	0.005	10	60	4.3
p-Methoxybenzoyl	0.010	20	- *	1.6

* These combined yields could not be accurately determined.

In Table V details of the photoreactions of *trans*-azobenzene with pure acid chlorides are given whereas Table VI contains details of the photoreactions in which benzene was used as solvent. Since both *p*-nitrobenzoyl and 3,5-dinitrobenzoyl chlorides are solids, only reactions in benzene as solvents were investigated in these cases. In all of the photoreactions, solutions which were equimolar with respect to *trans*-azobenzene were irradiated in sunlight for the period indicated.

The rate at which the photoreactions proceeded varied considerably with the acid chloride used. Reactions with trichloroacetyl, trimethylacetyl, *p*-nitrobenzoyl, and 3,5-dinitrobenzoyl chlorides were particularly slow and this phenomenon was attributed to the intense colorations which developed soon after irradition of the solutions was commenced. Presumably the colored solutions absorbed much of the light required for the photoreaction, thus considerably reducing the rate. *p*-Nitro- and 3,5-dinitrobenzoyl chlorides gave purple solutions, the colors of which were similar to that formed during the reaction of *cis*-azobenzene with acetyl chloride. However, in the latter reaction the purple color rapidly faded, whereas in the photochemical reactions with the nitrobenzoyl chlorides no such fading of the purple color occurred, even after long periods of standing.

The photoreactions of *trans*-azobenzene with trimethylacetyl and *p*-methoxybenzoyl chlorides were also very slow, but in these cases the slow rate was probably due to the unreactive nature of the acid chlorides. Determination of the combined yield of 2- and

4-chloroazobenzenes was unsuccessful for these reactions since a considerable amount of unchanged azobenzene remained in the final reaction mixture. However, the product ratios (35/3) were satisfactorily measured by analytical gas chromatography. The unreactive nature of the *p*-methoxybenzoyl and trimethylacetyl chlorides is attributed to the electron-donating character of the *p*-methoxy and methyl substituents.

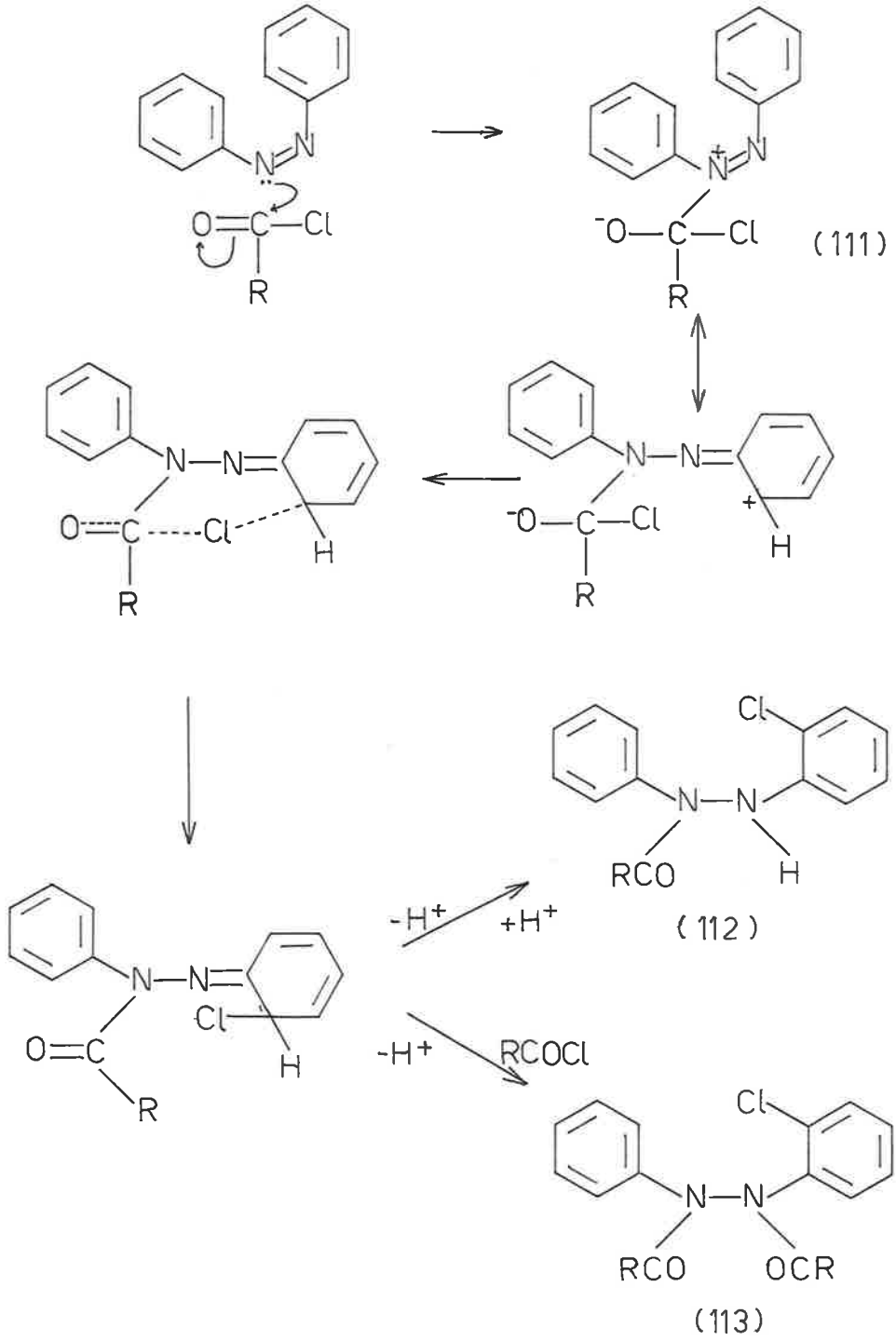
From the results in Tables V and VI it is apparent that dilution of the acid chlorides with benzene results in a substantial increase of the *ortho/para* (35/3) ratio. One exception is trichloroacetyl chloride, but since the *ortho/para* ratio is already very high in this case, the difference is probably not significant. Replacement of benzene with cyclohexane as the solvent in the photochemical reaction gave almost identical results thus indicating that benzene simply acts as an inert solvent which reduces the polarity of the reaction medium.

Results in Tables V and VI show that the nature of the substituent attached to the acid chloride also determines the *ortho/para* ratio. Electron-attracting substituents result in high *ortho/para* ratios whereas electron-donating groups have the opposite effect. For example, trichloroacetyl and oxalyl chlorides afford considerably more 2-chloroazobenzene than does acetyl chloride, and similarly, *p*-nitro and 3,5-dinitro-benzoyl chlorides give a greater yield of the 2-chloro isomer than does benzoyl chloride. On the other

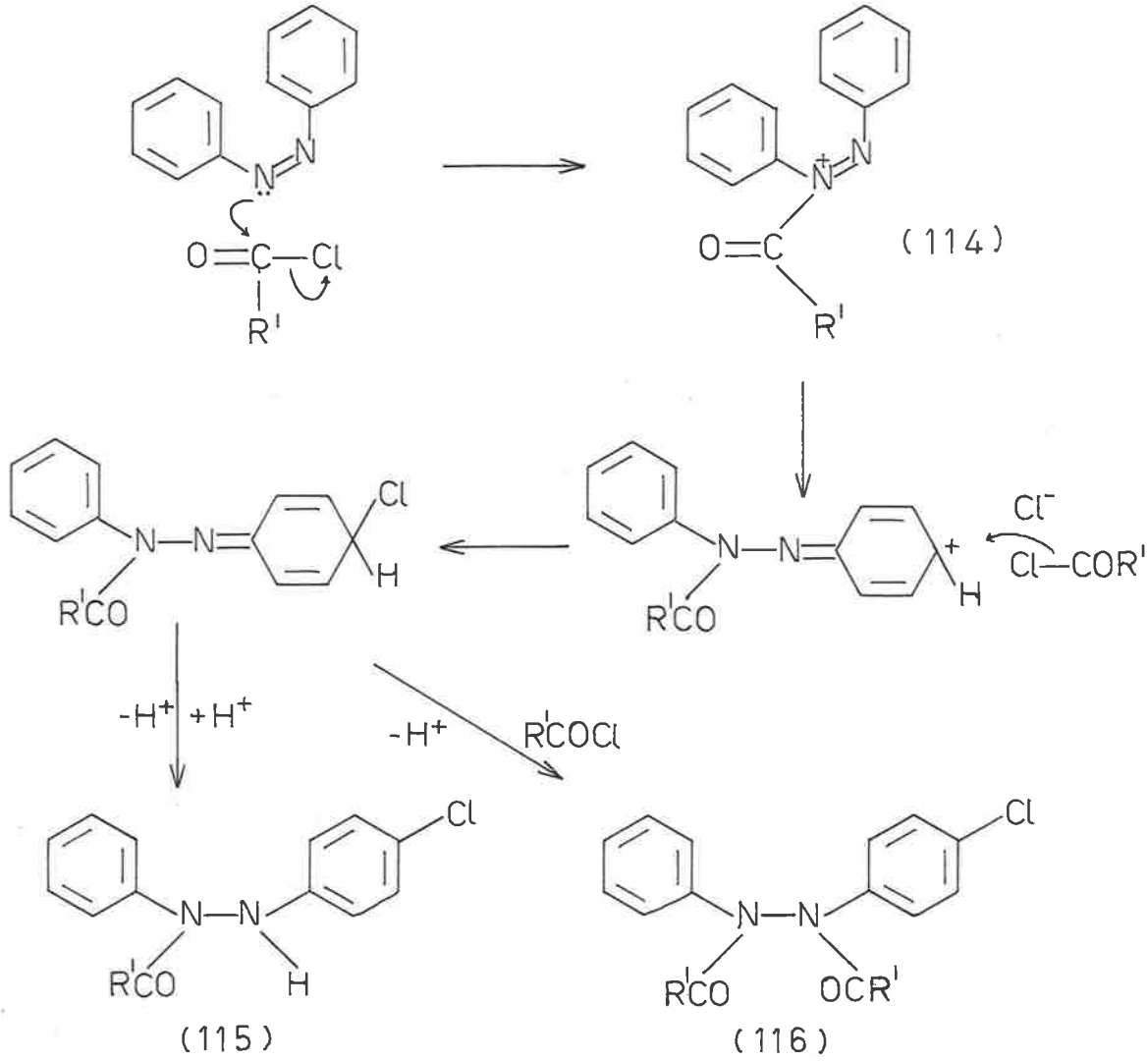
hand *p*-methoxybenzoyl and trimethylacetyl chlorides give lower *ortho/para* ratios than does benzoyl and acetyl chlorides respectively.

From the foregoing results it seems that the *ortho/para* product ratio is associated with the ionizability of the acid chloride employed in the photoreaction. Electron-attracting groups attached to acid chlorides should inhibit ionization, and it was found in such cases that a high *ortho/para* ratio resulted. Similarly, dilution of the photochemical medium with benzene would decrease the solvent polarity and thus suppress ionization of the acid chlorides. Again it was found this resulted in a high *ortho/para* ratio. These observations suggest that two competing mechanisms may operate: (a) one when ionization of the acid chloride is restricted, resulting in exclusive *ortho* substitution by an intramolecular mechanism (as shown in Scheme 9), and (b) another when ionization of the acid chloride is not restricted so that *p*-chlorination predominates (as in Scheme 10). The nature of the substituents attached to the acid chloride and the polarity of the solvent are assumed to be the factors which determine which of the above mechanisms predominate.

Formation of cations (111) and (114) probably involves a bimolecular reaction between the acid chloride and *cis*-azobenzene (formed by photoisomerization of the *trans* isomer). Good evidence for this is shown by the fact that the photoreactions carried out in



Scheme 9



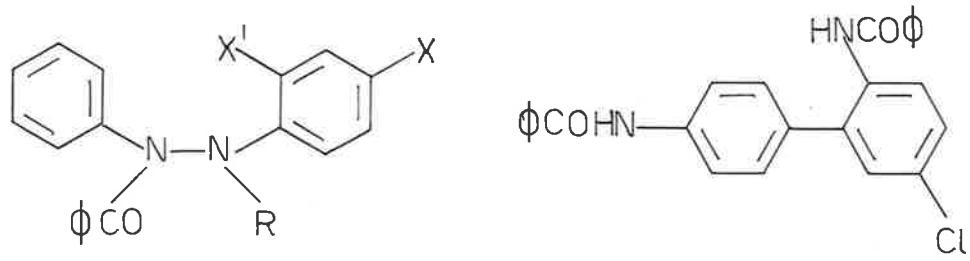
Scheme 10

trimethylacetyl and *p*-methoxybenzoyl chlorides only proceeded slowly and not to completion. These two acid chlorides would have been the only ones expected to form cations (111) and (114) by an "S_N1-like" reaction, in which case they would have reacted faster and to completion.

2. Photoproducts

In several of the photoreactions of *trans*-azobenzene with acid chlorides, the mixtures of photoproducts were examined by infrared spectroscopy. Most of the products exhibited one band in the N-H stretching region (*c.* 3,300 cm^{-1}) of the infrared; and from this observation it appeared that a considerable amount of mono-acylated or mono-aroylated compounds were formed in the photoreactions. Since alkaline hydrolysis/oxidation of the photoproducts afforded mixtures of varying proportions of 2- and 4-chloroazobenzenes, it was concluded that the photoproducts consisted of mixtures of the compounds (112), (113), (115) and (116) as shown in Schemes 9 and 10.

An attempt was made to separate the mixtures of compounds obtained from the photoreactions of *trans*-azobenzene and benzoyl chloride with and without benzene as solvent. Chromatography of the photoproducts isolated from the reaction carried out in pure benzoyl chloride afforded a small amount of *N*,*N*'-dibenzoyl-5-chloro-2,4'-diaminodiphenyl (117) and a large quantity of a colorless glass which slowly crystallized on standing. The latter product was a mixture, but several recrystallizations resulted in *N*,*N*'-dibenzoyl-4-chlorohydrazobenzene (118) being isolated in 29% overall yield. The infrared spectrum of the mother liquors indicated the remaining mixture consisted of mono- and di-benzoylated products.



(117)

	X	X'	R
(118)	Cl	H	ϕCO
(119)	H	Cl	H
(120)	Cl	H	H
(121)	Cl	H	H (ϕCO = 3,5-$(NO_2)_2$ϕCO)

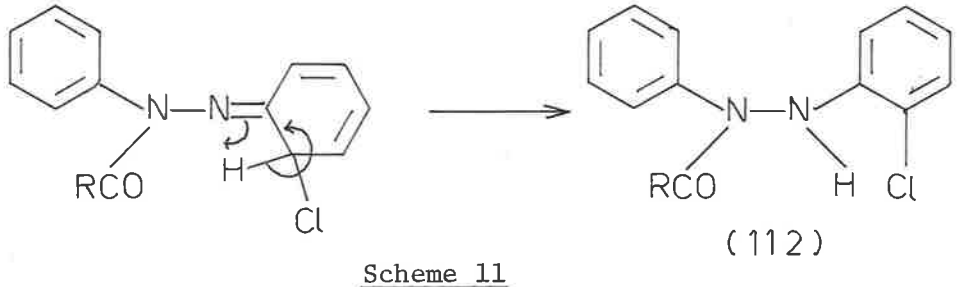
Chromatography of the products obtained from the photoreaction with benzene as solvent resulted in the partial separation of *N'*-benzoyl-2-chlorohydrazobenzene (119) and *N'*-benzoyl-4-chlorohydrazobenzene (120), final purification being effected by recrystallization. A substantial amount of unseparated products was also eluted from the column, and the infrared spectrum indicated this consisted mainly of monobenzoylated compounds.

During the course of crystallization of *N'*-benzoyl-2-chlorohydrazobenzene the solution developed a distinct orange color and further investigation revealed that the colored material was 2-chloroazobenzene. Furthermore, when the products from the photoreaction of *trans*-azobenzene with 3,5-dinitrobenzoyl chloride (ether as solvent) were subjected to chromatography, the only products eluted from the column were ethyl 3,5-dinitrobenzoate,

2-chloroazobenzene and *N*'-3,5-dinitrobenzoyl-4-chlorohydrazobenzene (121). 2-Chloroazobenzene was not originally present as a photoproduct and hence decomposition of the 2-chloro isomer of (121) apparently must have occurred during the chromatography. These observations indicate that *N*'-aroyl-2-chlorohydrazobenzenes slowly decompose in solution to give 2-chloroazobenzene. No such instability was found to occur with the corresponding 4-chloro isomers.

Formation of the mono-acylated or mono-aroylated products in the foregoing photoreactions probably involves a process similar to that already suggested for formation of the monoacetylated compound in the dark reaction of *cis*-azobenzene with acetyl chloride. The photoreactions carried out with benzene as solvent contained only a several-fold molar excess of acid chloride, so that the hydrogen chloride concentration could have become sufficiently high for protons to compete effectively with the acid chloride in attacking the nitrogen adjacent to the chlorinated phenyl group.

Mono-acylated or mono-aroylated products could also be formed by the concerted process shown in Scheme 11. On this basis, one would expect the majority of *o*-chlorinated photoproducts to be mono-acyl or mono-aroyl compounds.



Scheme 11

IV. REACTIONS OF *CIS*- AND *TRANS*-AZOBENZENES WITH OTHER ACYL COMPOUNDS

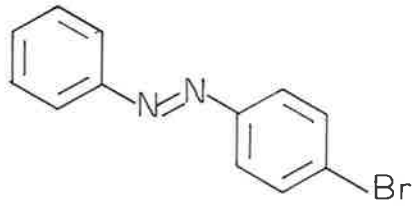
Photoreactions of *trans*-azobenzene with acid chlorides have been shown to constitute a useful method for introducing a chloro substituent into the *ortho* or *para* position of the azobenzene nucleus. Similar results have also been obtained from the reaction of *cis*-azobenzene with acetyl chloride in the absence of light. Using similar experiments with other acyl compounds, attempts were made to introduce fluoro, bromo, iodo, and cyano groups into the azobenzene molecule.

An attempt was made to prepare 4-fluoroazobenzene by employing a sequence of reactions essentially similar to those used in the photochemical preparation of 4-chloroazobenzene. Unfortunately the propionyl fluoride employed in the photochemical step could not be obtained completely free of acid chloride impurity (it was synthesised from benzoyl chloride, propionic acid, and potassium hydrogen fluoride). The reaction mixture developed an intense purple coloration during the course of the photoreaction and this indicated that some *cis*-azobenzene had accumulated within the solution. The photoproducts were subjected to the hydrolysis/oxidation procedure and examination of the final reaction mixture revealed 4-chloroazobenzene (3) and 4-phenylaminoazobenzene (108) as the only products. The fact that no 4-fluorazobenzene was obtained from the above reaction sequence (even though a small amount of acid chloride impurity was present) reveals the essentially unreactive

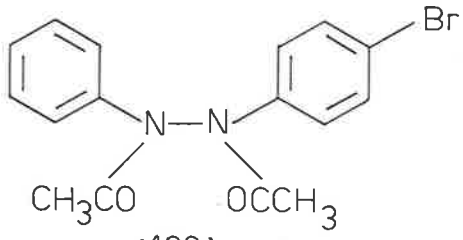
nature of acid fluorides in the photochemical reaction with *trans*-azobenzene. The purple material and the 4-phenylaminoazobenzene observed in the above reaction were presumably formed by a process similar to that suggested for their formation in the reaction of *cis*-azobenzene with acetyl chloride.

In order to examine further the apparent unreactive nature of acid fluorides in the photochemical reaction, a dark reaction of *cis*-azobenzene was carried out in acetic anhydride-hydrofluoric acid solution. As expected, chromatography of the reaction products only afforded unchanged azobenzene and some 4-phenylaminoazobenzene.

Irradiation of *trans*-azobenzene in acetic anhydride containing hydrobromic acid resulted in rapid decoloration of the solution. The photoproduct was obtained as a colorless glass, but a small sample was crystallized from light petroleum, and this afforded pure *N*,*N*'-diacetyl-4-bromohydrazobenzene (122). Alkaline hydrolysis and oxidation of the bulk of the crude photoproduct gave 4-bromoazobenzene (123), which after recrystallization, was obtained in 80% overall yield. Examination of the mother liquors by gas chromatography revealed that no 2-bromoazobenzene was present. From these results, it is evident that a bromo group may be introduced into the azobenzene nucleus as readily as a chloro group.



(123)

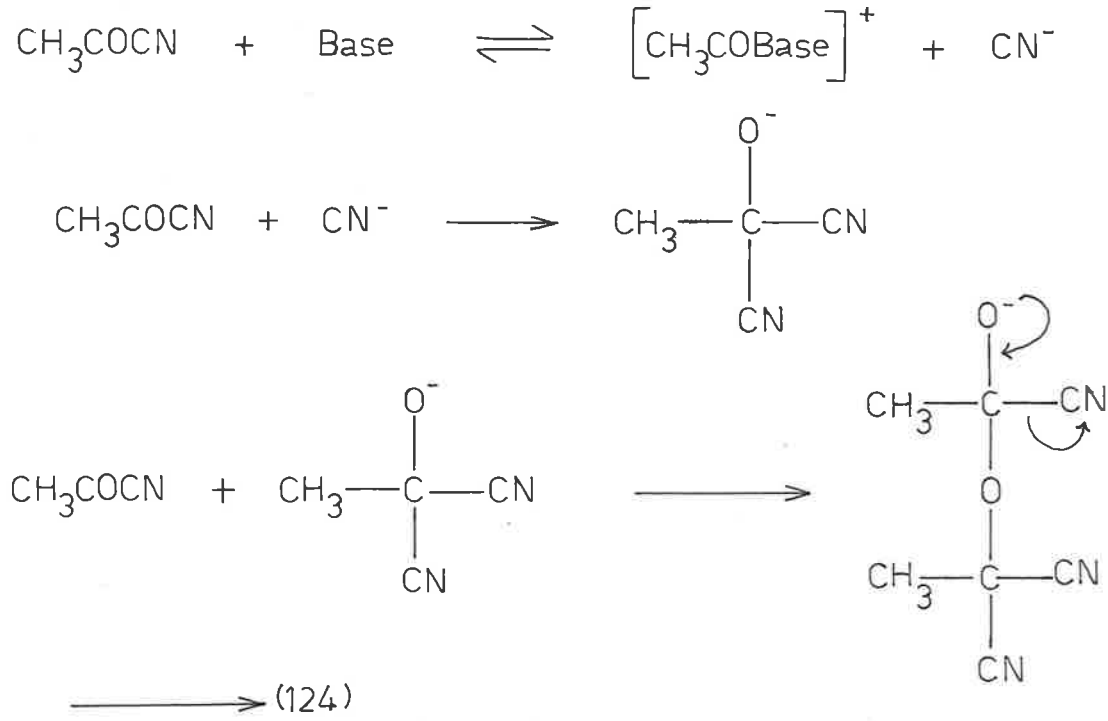


(122)

In an attempt to form 4-iodoazobenzene, *trans*-azobenzene was dissolved in an iodine free solution of hydroiodic acid and acetic anhydride. However, before irradiation was commenced, the solution rapidly darkened (free iodine) and a yellow solid separated from the solution. Although the reaction was not further investigated, it seems not unlikely that it could have involved initial reduction of azobenzene by the hydroiodic acid.

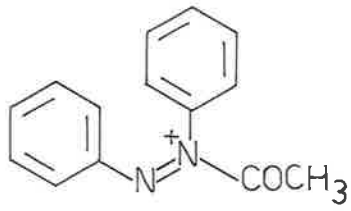
Another attempt to introduce iodine into the azobenzene nucleus was made by mixing *cis*-azobenzene with aluminium tri-iodide in acetic anhydride solution. Again a considerable amount of iodine was formed during the reaction. The reaction product was isolated as a viscous oil, the infrared spectrum of which, exhibited bands in the N-H and carbonyl stretching regions. Alkaline hydrolysis and oxidation of the product, however, only afforded azobenzene, and it was concluded that the reaction had only produced a mixture of *N*-acetyl- and *N*,*N*'-diacetyl-hydrazobenzenes. It was evident from this result that initial reduction of *cis*-azobenzene to hydrazobenzene had occurred.

The photoinduced reaction of *trans*-azobenzene with acetyl cyanide was also investigated. Chromatography of the crude photoproduct from this reaction afforded unchanged azobenzene, a large quantity of α,α-dicyanoethyl acetate (124) and small amounts of several unidentified oils. Base catalysed dimerization of acetyl cyanide to give (124) is known to occur,[109] (Scheme 12) and presumably in the photoreaction, *cis*-azobenzene is sufficiently basic to catalyse the dimerization.



Scheme 12

In a similar experiment, *trans*-azobenzene was irradiated in a 20% (v:v) solution of hydrogen cyanide in acetic anhydride. The main products isolated were shown to be unchanged azobenzene, α,α-dicyanoethyl acetate (124) and 4-phenylaminoazobenzene (25% by weight of the *trans*-azobenzene employed). Since 4-phenylaminoazobenzene is obtained in reasonable yield from this reaction it appears that the cation (109) or a similar 1:1 addition complex is formed from *cis*-azobenzene and acetyl cyanide (by step 1 in Scheme 12). However, the concentration of cyanide ion is probably too low (due to the competing dimerization) for nucleophilic attack to occur on the cation (109).



(109)

In the final reactions of this series, the reaction of *cis*-azobenzene with acetic anhydride in the absence of light and the photoreaction of the *trans* isomer with acetic anhydride were examined. Although in both cases the solutions darkened considerably during the course of the reactions, intense colorations did not form. Examination of the final reaction mixtures revealed unchanged starting materials and very small amounts of unidentified colored products. Apparently, acetic anhydride alone cannot form the cation (109) with *cis*-azobenzene.

V. QUANTUM YIELD DETERMINATIONS

The reaction of *cis*-azobenzene with acetyl chloride in the absence of light to give products similar to those derived from the photochemical reaction of *trans*-azobenzene with acetyl chloride strongly suggests that the photoreaction proceeds initially by *trans* → *cis* photoisomerization. It seemed possible that the *cis*-azobenzene so formed could then rapidly react with the acetyl chloride in a non-photochemical reaction. In order to examine the above scheme more critically, quantum yields were determined for: (a) the photochemical reactions of several *trans*-azobenzenes with acetyl chloride and (b) *trans* → *cis* isomerization of the same azobenzenes in acetic anhydride. The quantum yields found for (a) and (b) were then compared.

The overall quantum yield of a photochemical reaction may be defined by[154]

$$\phi = \frac{\text{Molecules of product formed per unit vol. per unit time}}{\text{Quanta of light absorbed by the reactant per unit vol. per unit time}}$$

Quantum yields for the photoreactions (a) and (b) could then be determined by measuring the rates of reaction in conjuction with the corresponding rates of absorption of light quanta. The intensity of the light incident upon the solutions at the various wavelengths studied for the photochemical reactions was determined by potassium trisoxalatoferrate actinometry.[153] This involved irradiation of actinometer solutions under conditions identical to those employed for the photoreactions.

1. Determination of Quantum Yields for *trans* → *cis* Isomerization of Azo Compounds in Acetic Anhydride

Work by Zimmerman *et al.*[15] has established that quantum yields for photoisomerization of azobenzene in both directions (*cis* ⇌ *trans*) are dependent on wavelength and not on concentration or the intensity of the incident light. However, it has been shown that the quantum yields are temperature dependent especially in the case of *trans* → *cis* isomerization.[16,18] The experiments described below were carried out at room temperature which varied over a small range (16-25°). Other workers have shown[13,50] that the errors introduced into the quantum yield values by a small temperature variation of this nature are very small and well within the limits of experimental error.

The photoreactions shown in Tables VII, VIII, IX, and X were all commenced with solutions of the pure *trans* isomer, although it has been shown[15] that the composition of the stationary state is independent of the initial composition of the solution being irradiated. Photoisomerization of the azobenzenes in acetic anhydride was followed spectroscopically by observing the rates of change of optical densities. In this manner it was possible to express the experimental results in terms of the fraction of *cis* isomer as a function of time (Fig. III). However before this could be done it was necessary to determine the extinction coefficients of the pure *cis* and *trans* isomers at the wavelength at which the reaction was being followed.

The method of Zimmerman *et al*[15] was employed for calculation of the quantum yields. Symbols used in the rate equations are defined as follows:

v = volume of reaction solution (l);

l = 1 cm = path length through solution (cm);

t = time of irradiation (min);

ϕt and ϕc = the respective quantum yields for *trans* → *cis* and *cis* → *trans* isomerizations;

D = optical density of the reaction solution at any time, t;

ε = extinction coefficient of any *cis* ⇆ *trans* mixture;

εt and εc = the respective extinction coefficients of the *trans* and *cis* isomers;

I_o = amount of light entering the reaction solution (einsteins min^{-1});

c_o = total concentration of azo compound at any time, t;

y = fraction of *cis* isomer present at any time, t;

y_∞ = fraction of *cis* isomer at the photostationary state;

z = $(y_\infty - y)$

$$F = \frac{D}{(1 - e^{-D})}$$

The rate equation for *cis* ⇌ *trans* photoisomerization in a cell, which is completely evenly illuminated with monochromatic light, can be written as follows,[15] provided that Beer's Law is obeyed and that the quantum yields in both directions are independent of I_o and c_o:

$$\frac{dy}{dt} = \frac{I_o l}{vF} [\phi t \varepsilon t(1-y)] - \frac{I_o l}{vF} (\phi c \varepsilon c y) - ky \qquad .....(1)$$

The first and second terms refer to the photochemical rates in both directions and the third term is the thermal *cis* → *trans* rate. Setting $\frac{dy}{dt} = o$ for $t = \infty$, solving for ϕc and substituting into equation (1) gives

$$\frac{dy}{dt} = \frac{A}{F} (y_\infty - y) - ky \left(\frac{F_\infty}{F} - 1\right) \qquad .....(2)$$

where $A = \frac{I_o l \phi t \varepsilon t}{v y_\infty}$. Since the second term in (2) can be neglected[15] it follows that

$$\frac{dz}{dt} = - \frac{A}{F} z \qquad .....(3)$$

By placing

$$I(z) = \int F \frac{dz}{z}$$

then

$$I(z) = -At + \text{constant} \qquad .....(4)$$

and A (and thus ϕt) may be solved by plotting I(z) against time. However, in order to determine I(z) the function F must be solved in terms of z as follows:

$$\varepsilon = \frac{D}{c_o} = y\varepsilon c + (1-y)\varepsilon t \qquad .....(5)$$

and hence

$$D = c_o [\varepsilon t + (\varepsilon c - \varepsilon t)y]$$

and it follows that

$$D = c_o [\varepsilon t + (\varepsilon c - \varepsilon t)(y_\infty - z)] \qquad .....(6)$$

Expansion of (6) gives

$$D = \varepsilon t c_o + c_o y_\infty (\varepsilon c - \varepsilon t) - c_o z (\varepsilon c - \varepsilon t) \qquad .....(7)$$

The function F can be represented by a power series[15]

$$F(D) = 1 + \frac{D}{2} + \frac{D^2}{12} - \frac{D^4}{720} + \ldots \qquad .....(8)$$

and substitution of (7) into (8) followed by integration results in I(z) being solved. The following valid approximations hold:

(a) If $\underline{D < 0.02}$ then $F = 1$

and $I(z) = \int \frac{dz}{z} = \log_e z$ .....(9)

(b) If $\underline{0.02 < D < 0.2}$ then $F = 1 + \frac{D}{2}$

Putting $D = k_1 - k_2 z$ where $k_1 = \varepsilon t c_o + c_o y_\infty (\varepsilon c - \varepsilon t)$

and $k_2 = c_o(\varepsilon t - \varepsilon c)$ (see equation 7)

then

$$I(z) = \int \frac{dz}{z} + \frac{k_1}{2} - \frac{k_2}{2} \int dz$$

so that

$$I(z) = \log_e z + \frac{k_1}{2} - \frac{k_2}{2} z \qquad .....(10)$$

(c) If $\underline{0.2 < D \lesssim 2.0}$ then $F = 1 + \frac{D}{2} + \frac{D^2}{12}$

then

$$I(z) = \int\frac{dz}{z} + \frac{k_1}{2} - \frac{k_2}{2}\int dz + \frac{k_1^2}{12} - \frac{k_1 k_2}{6} z + \frac{k_2^2}{12} z^2 \int\frac{dz}{z}$$

so that

$$I(z) = \log_e z + \frac{k_1}{2} - \frac{k_2}{2} z + \frac{k_1^2}{12} - \frac{k_1 k_2}{6} + \frac{k_2^2}{24} z^2 \qquad .....(11)$$

In all experiments, the calculated values of I(z) when plotted against time gave straight lines providing that the last two or three points were omitted (when approaching the photostationary state). Several plots of I(z) against time (t) are shown in Fig IV. A value for ϕt was obtained from the slope of the graph (A) by using the following equation:

$$\phi t = A \cdot \frac{vy_\infty}{I_o \varepsilon t}$$

The values of ϕt calculated for several azobenzenes at 313, 365, 405 and 436 mμ are shown in TablesVII, VIII, IX, and X respectively. Due to the strong absorption band exhibited by *trans*-azobenzenes in the 310-350 mμ region, all the quantum yields

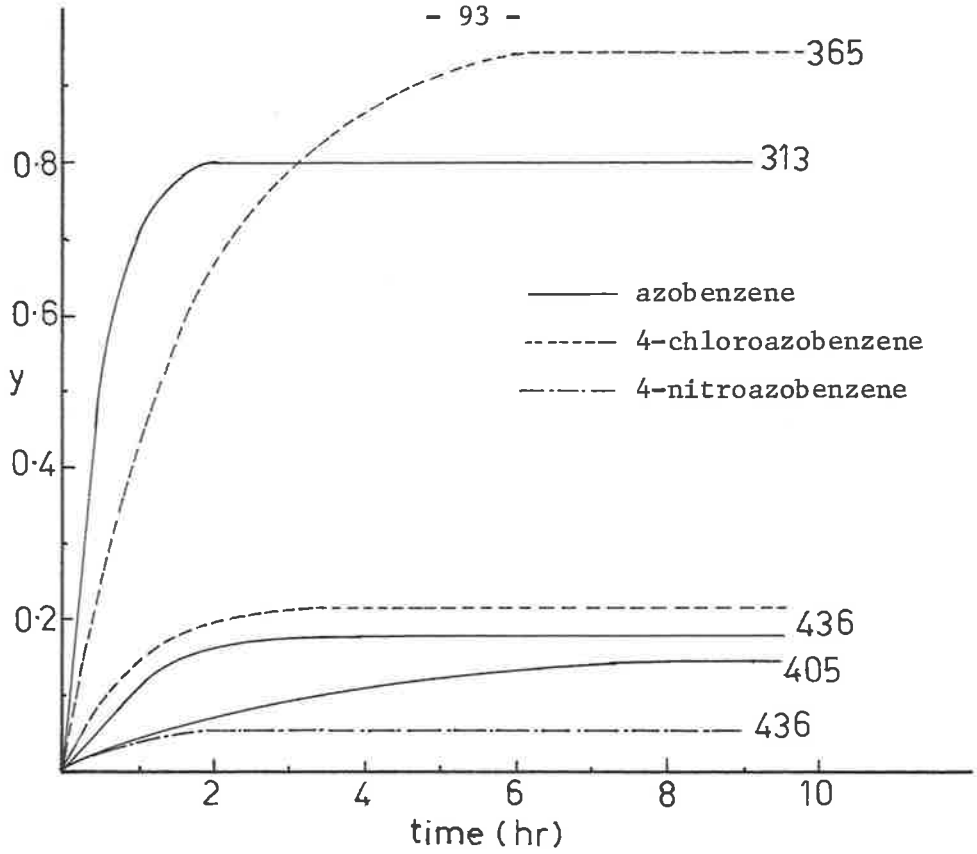


Fig. III - Fraction of *cis* isomer as a function of time at several wavelengths

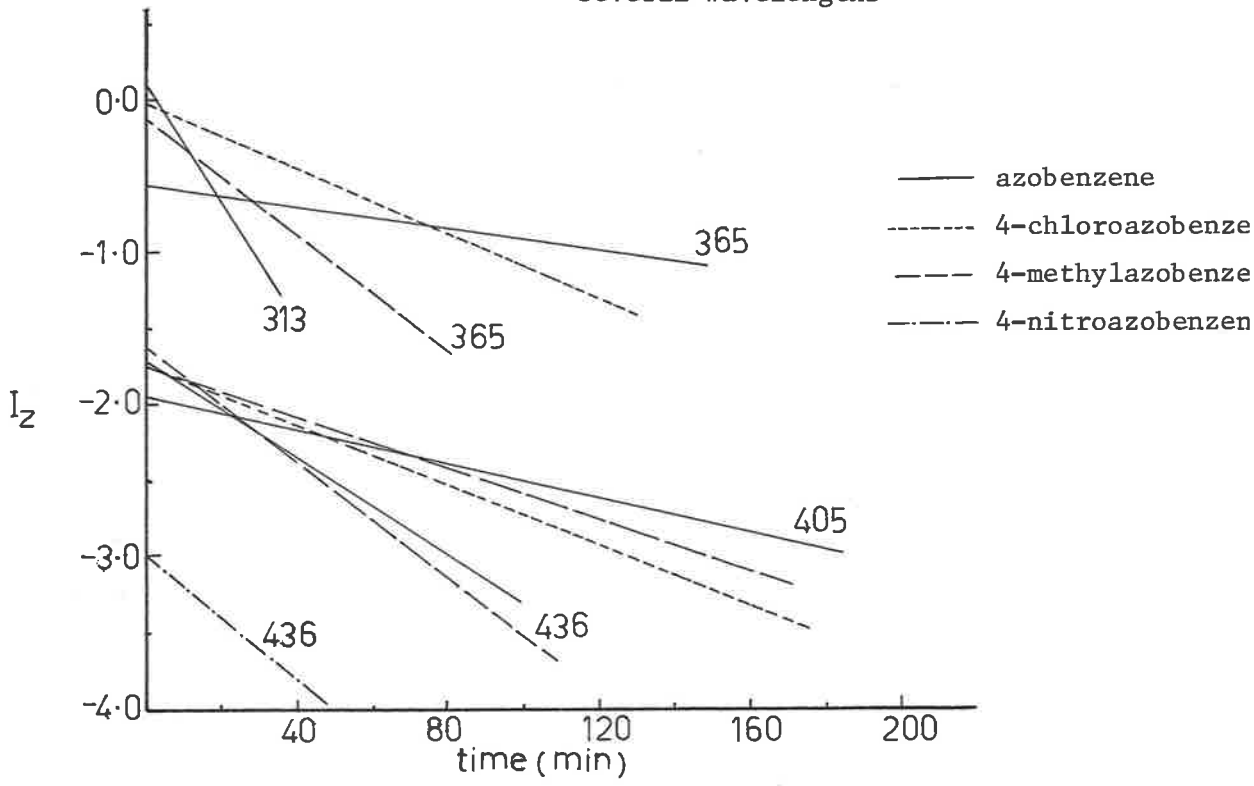


Fig. IV - Plots of I_z vs. time at several wavelengths

determined at 313 mμ (and some at 365 mμ) were deduced from equation (11) (since $0.2 < D < 2.0$). In these cases calculation of ϕt was accomplished with the aid of a computer. For a similar reason ($D > 0.2$) values of ϕt determined from more concentrated solutions at 365, 405 and 436 mμ (asterisks) were also computed using equation (11). All other values of ϕt at 365, 405, and 436 mμ were calculated from the less complicated equation (9) since very dilute solutions were employed to satisfy requirement (a) ($D < 0.02$). In these measurements, the reaction was followed at 320 mμ ($D > 0.2$) and not at the wavelength of the exciting radiation where ($D < 0.02$).

The computed values (asterisks) of ϕt (and the corresponding values of y_∞) shown in Tables IX and X are significantly lower than the other results. This phenomenon is possibly due to the more concentrated solutions employed in the former measurements, since these were observed to darken noticeably during the course of the photoreaction. Such a color change would be expected to result in erroneous optical density readings thus leading to inaccurate values of y_∞ and ϕt. No such color change was observed for the photoreactions of the dilute solutions and the values of ϕt determined for these solutions are considered to be the more accurate values.

TABLE VII. Quantum Yields for *trans* → *cis* Isomerization of Substituted Azobenzenes in Acetic Anhydride at 313 mμ

Substituent	c_o (M)	$I_o \times 10^7$ einsteins min^{-1}	y_∞	$\phi t \rightarrow c$
- (1)	3.450×10^{-5}	0.464	0.796	0.10
-	2.460×10^{-5}	0.477	0.783	0.11
4-methyl- (95)	2.372×10^{-5}	0.489	0.734	0.13
4-methyl-	4.744×10^{-5}	0.498	0.730	0.11
4-chloro- (3)	3.017×10^{-5}	0.468	0.865	0.11
2-methyl- (128)	3.172×10^{-5}	0.468	0.895	0.12
4-methoxy- (69)	1.751×10^{-5}	0.454	0.380	0.26
2,6-dichloro- (130)	5.016×10^{-5}	0.472	0.798	0.16
4-nitro- (100)	2.063×10^{-5}	0.457	0.147	0.03†

† Approximate only since εc was only approximate

TABLE VIII. Quantum Yields for *trans* → *cis* Isomerization of Substituted Azobenzenes in Acetic Anhydride at 365 mμ

Substituent	c_o (M)	$I_o \times 10^7$ einsteins min^{-1}	y_∞	$\phi t \rightarrow c$
- (1)	2.965×10^{-5}	0.764	0.573	0.16
-	1×10^{-3}	0.773	0.426	0.15*
4-methyl- (95)	4.744×10^{-5}	0.748	0.880	0.17*
4-methyl-	2.372×10^{-5}	0.755	0.929	0.16
4-chloro- (3)	3.017×10^{-5}	0.764	0.937	0.13
4-methoxy- (69)	1.751×10^{-5}	0.749	0.801	0.23*

* $\phi t \rightarrow c$ calculated by a computer

TABLE IX. Quantum Yields for *trans* → *cis* Isomerization of Substituted Azobenzenes in Acetic Anhydride at 405 mμ

Substituent	c_o (M)	$I_o \times 10^7$ einsteins min^{-1}	y_∞	$\phi t \rightarrow c$
- (1)	1×10^{-3}	0.319	0.128	0.22*
-	2.965×10^{-5}	0.313	0.145	0.30
4-methyl- (95)	4.744×10^{-5}	0.334	0.184	0.37
4-methyl-	3.083×10^{-5}	0.301	0.187	0.37
4-chloro- (3)	3.017×10^{-5}	0.319	0.149	0.38

* $\phi t \rightarrow c$ calculated by a computer

TABLE X. Quantum Yields for *trans* → *cis* Isomerization of Substituted Azobenzenes in Acetic Anhydride at 436 mμ

Substituent	c_o (M)	$I_o \times 10^7$ einsteins min^{-1}	y_∞	$\phi t \rightarrow c$
- (1)	1×10^{-3}	0.615	0.155	0.18*
-	2.965×10^{-5}	0.594	0.183	0.33
-	2.965×10^{-5}	0.573	0.176	0.31
4-methyl- (95)	2.372×10^{-5}	0.617	0.211	0.34
4-methyl-	4.744×10^{-5}	0.594	0.205	0.32
4-chloro- (3)	3.017×10^{-5}	0.594	0.206	0.36
2-methyl- (128)	3.127×10^{-5}	0.621	0.187	0.34
4-methoxy- (69)	1.751×10^{-5}	0.617	0.125	0.43
4-nitro- (100)	2.063×10^{-5}	0.644	0.049	0.09†
2,6-dichloro- (130)	5.016×10^{-5}	0.618	0.231	0.46
2,6,2',6'-tetramethyl- (131)	3.532×10^{-5}	0.627	0.158	0.36

* $\phi t \rightarrow c$ calculated by a computer

† Approximate value since εc was only approximate

TABLE XI. Absorption Maxima and Extinction Coefficients of *trans*-Azobenzenes in Acetic Anhydride

Substituent	$\pi \rightarrow \pi^*$		$n \rightarrow \pi^*$	
	λ_{max}	ε	λ_{max}	ε
- (1)	318	22,000	444	480
4-methyl- (95)	327	24,000	441	604
4-chloro- (3)	324	24,220	444	578
4-bromo- (141)	-	-	444	593
4-methoxy- (69)	347	26,310	433	958
4-nitro- (100)	331	24,410	456	625
3-methyl- (140)	-	-	443	504
2-methyl- (128)	324	21,700	454	515
2,6-dimethyl- (129)	316	14,700	455	583
2,6-dichloro- (130)	< 300	*c.* 13,000	447	430
2,6,2',6'-tetramethyl- (131)	310	11,680	468	597
2,6,2',6'-tetrachloro- (144)	<< 300	-	459	600

TABLE XII. Absorption Maxima and Extinction Coefficients of *cis*-Azobenzenes in Acetic Anhydride

Substituent	$n \rightarrow \pi^*$		ε at 300 mμ*
	λ_{max}	ε	
- (6)	432	1,240	3,060
4-methyl- (133)	435	1,240	3,620
4-chloro- (134)	434	1,390	4,060
2-methyl- (136)	433	1,170	2,960
2,6-dimethyl- (138)	435	920	1,600
2,6-dichloro- (137)	418	880	1,980
2,6,2',6'-tetramethyl- (139)	452	1,480	3,060
2,6,2',6'-tetrachloro- (132)	438	1,150	3,010

* λ_{max} for $\pi\pi^*$ absorption of *cis*-azobenzenes is <300 mμ

Considering the differences in solvents used, the quantum yields determined for azobenzene in this work compare favourably with other determinations of ϕt which have been made. For example, Zimmerman *et al.*[15] obtained the following values of ϕt using isooctane as solvent: 0.10-0.12 at 313 mμ; 0.12 at 365 mμ; 0.21-0.23 at 405 mμ; and 0.27-0.28 at 436 mμ. Birbaum and Style[13] using ethanol as solvent obtained: 0.36 at 436 mμ; and 0.20 at 365 mμ for azobenzene, and 0.28 at 436 mμ; and 0.21 at 365 mμ for 4-chloroazobenzene.

The values of ϕt determined at 313 and 436 mμ for 4-nitroazobenzene are only approximate since arbitrary values for the extinction coefficients (εc) of the *cis* isomer were used in the calculations. Nevertheless, the smaller values of ϕt for 4-nitroazobenzene at 313 and 436 mμ are considered to be real.

From the quantum yields in Tables VII, VIII, IX and X it appears that the effects of substituents on ϕt are relatively small at all wavelengths, except in the case of 4-nitro- and 4-methoxyazobenzenes. In this respect it may be significant that the 4-nitro and 4-methoxy groups are the only substituents (of those examined) which exert strong mesomeric electronic effects on the molecule.

The absorption spectra of the *cis*- and *trans*-azobenzenes in acetic anhydride are shown in Figs. Va, VIa, VII, VIII, IX, X, and XI (see appendix) and the respective λ_{max} values and extinction coefficients are shown in Tables XI and XII. Solutions of the *cis* isomers in acetic anhydride underwent gradual darkening in color

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on standing, accompanied by the appearance of a new absorption maximum at 550-560 mμ. The increase of optical density with time at 550-560 mμ was more rapid for the *cis* compounds containing electron-donating substituents (the more basic compounds; see Figs. X and XI). This phenomenon probably explains the gradual darkening of the reaction solutions previously observed during rate studies of *trans* → *cis* photoisomerization in acetic anhydride.

From the spectral diagrams it is apparent that the spectra of the *cis*-isomers are not significantly effected by different substituents or their positions of attachment around the molecule. This is in accordance with previous observations.[93] The *trans* isomers containing mesomeric electron-donating groups (*p*-CH_3O- and *p*-CH_3-) show bathochromic shifts of the ππ* absorption, a phenomenon which has been observed by other workers.[92,93] In addition, however, it seems that the positions of substituents around the molecule can also have an effect on the spectra of the *trans* isomers. For example, a considerable hypsochromic shift and corresponding decrease in intensity has occurred on introduction of methyl or chloro groups into the 2 and 6 positions of the molecule. These changes are even more pronounced when methyl or chloro groups are introduced into the four *ortho* positions. In fact it appears that on increasing the number of *ortho* substituents of *trans*-azobenzenes the ππ* absorption begins to resemble the corresponding absorption band of the *cis* isomer. A possible explanation for this phenomenon became apparent on examination of "Catalin" models of the *trans* compounds (129), (130),

(131), and (144). In the disubstituted compounds, a steric interaction occurred between one *ortho* substituent and the non-adjacent nitrogen atom of the azo linkage (Fig. XII). Two such interactions were present in the tetrasubstituted compounds. If these interactions were severe enough to twist the phenyl rings out of the nodal plane of the π electrons of the azo linkage, then overlap between the π orbitals of the phenyl rings and those of the azo linkage would be considerably reduced as is the case in *cis*-azobenzenes. Under these circumstances one would expect the $\pi\pi^*$ absorption of the *trans* isomer to resemble that of the *cis* isomer.

(129) X = CH_3
(130) X = Cl

Fig. XII

(131) X = CH_3
(144) X = Cl

Several workers[6,23-27] have measured the rates of thermal *cis* → *trans* isomerization for monosubstituted azobenzenes. Generally the observed substituent effects have been small, the activation energies being of the order of 21-24 k.cal/mole.[24] Relative rates of thermal *cis* → *trans* isomerization of the *cis* isomers prepared in this work are shown in Fig. XIII. The thermal rates of isomerization of the *ortho* substituted compounds (137), (138), (139) and (132) are noticeably slower than those for the monosubstituted compounds. In

contrast the rates of *trans* → *cis* photoisomerization of compounds (130) and (131) are comparable with those of the monosubstituted azobenzenes. This observation is probably directly related to the above-mentioned steric interactions which occur in the *trans* isomers of the *ortho* di- and tetra-substituted azobenzenes. For example, the reaction co-ordinate for thermal *cis* → *trans* isomerization of the monosubstituted azobenzenes might resemble Fig. XIVA whereas the corresponding co-ordinate for compounds (137), (138), (139), and (132) might resemble Fig. XIVB.

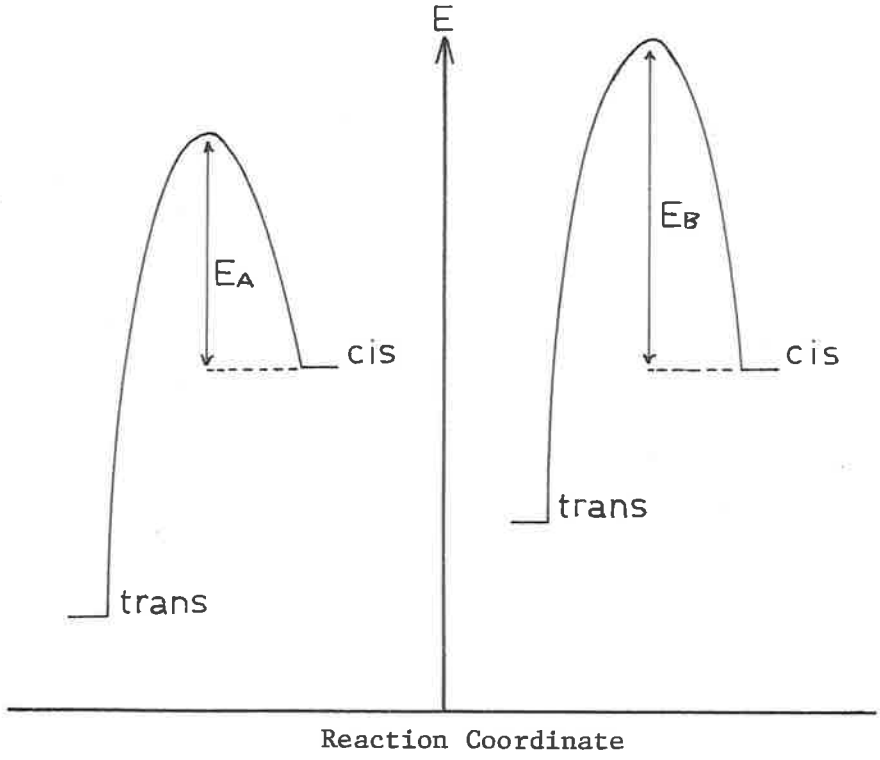
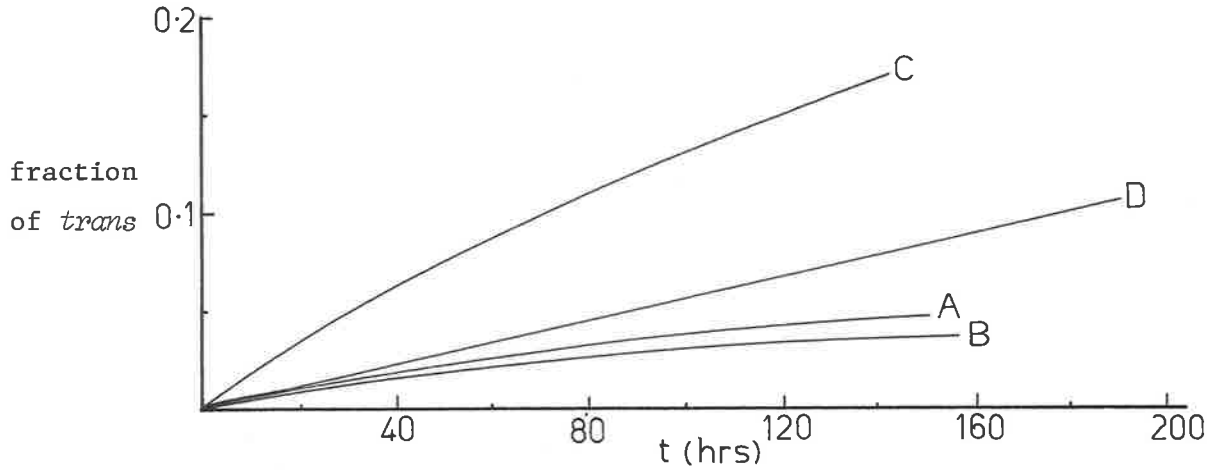


Fig. XIVA Fig. XIVB



Relative rates of thermal *cis* → *trans* isomerization in acetic anhydride; (A) 2,6-dichloroazobenzene, (B) 2,6-dimethylazobenzene, (C) 2,6,2',6'-tetramethylazobenzene, and (D) 2,6,2',6'-tetrachloroazobenzene.

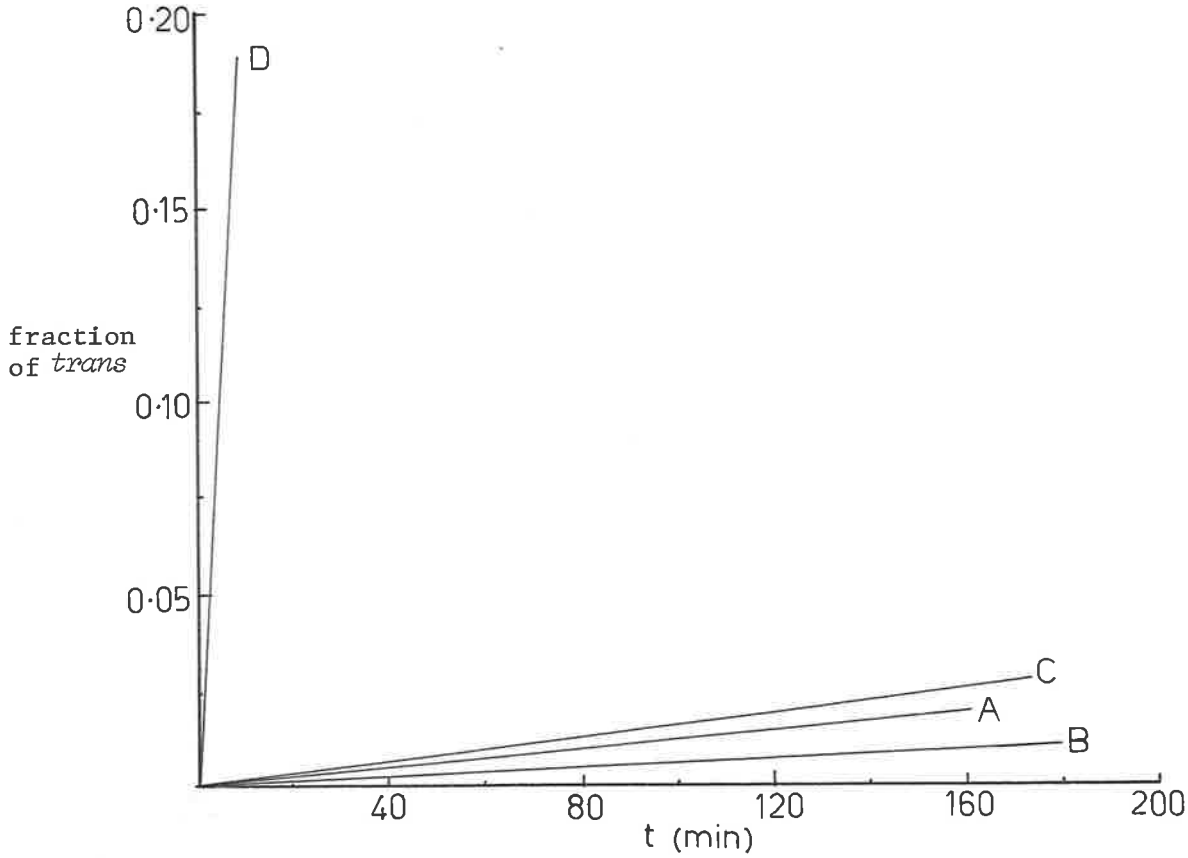


Fig. XIII - Relative rates of thermal *cis* → *trans* isomerization in acetic anhydride; (A) azobenzene, (B) 4-methylazobenzene, (C) 4-chloroazobenzene, and (D) 4-methoxyazobenzene.

2. Determination of Quantum Yields for the Photoreactions of *trans*-Azobenzenes in Acetic Anhydride-Hydrochloric Acid Solution

Photometric rate studies for the photoreactions of *trans*-azobenzenes with acetic anhydride-hydrochloric acid solutions (and acetyl chloride) were carried out under experimental conditions identical to those employed for the determinations of ϕt described in the preceding section. The reaction rate was measured by following the rate of disappearance of the azo compound, and this was accomplished by recording the change in optical density (D) as a function of time (t). Measurements of D were carried out at the wavelength of the exciting radiation (313, 365, 405, and 436 mμ), the absorption due to the photoproducts being zero at these wavelengths.

The following symbols are used in the rate equations:

t = time of irradiation (min);

D = optical density of the reaction solution at any time, t;

v = volume of solution in reaction cell (litres);

εt = extinction coefficient of the *trans*-azobenzene in acetic anhydride-hydrochloric acid solution (or acetyl chloride);

ϕ = quantum yield;

l = path of reaction cell (cm) = 1 cm in all experiments;

K = rate constant (min^{-1});

K^1 = rate constant (mole min^{-1})

c = concentration (M) of azo compound at any time, t;

I_o = amount of light entering the reaction cell (einsteins min^{-}

The rate equation for the photochemical reaction in a cell, which is completely evenly illuminated with monochromatic light, can be written as equation (1), provided that: (a) Beer's Law is obeyed; (b) the reaction involves a unimolecular photochemical change of the azo compound; and (c) the rate of disappearance of the azo compound is proportional to the number of light quanta it absorbs in unit time.[50]

$$-\frac{dc}{dt} = -\frac{dD}{dt} \cdot \frac{v}{\varepsilon t l} \qquad .....(1)$$

and

$$-\frac{dD}{dt} = K(1 - 10^{-D}) \qquad .....(2)$$

If the above assumptions leading to derivation of equation (1) are valid then a plot of $-\log_e(10^D-1)$ against time (t) (from the integrated form of equation 1) should be linear. Accordingly, for all the photoreactions carried out in acetic anhydride-hydrochloric acid solution, the graphs of $-\log_e(10^D-1)$ against t were found to be linear. The quantum yields were calculated by conversion of the rate constant K to the constant K^1 as follows:

$$K^1 = \frac{Kv}{\varepsilon t l} = \frac{Kv}{\varepsilon t} \qquad \text{since } l = 1 \text{ cm}$$

and the quantum yields for the photoreactions were readily obtainable from equation (3),

$$\phi = \frac{K^1}{I_o} \qquad .....(3)$$

The quantum yields and related data for the photochemical reactions of *trans*-azobenzenes with acetic anhydride-hydrochloric acid solution at 313, 365, 405, and 436 mμ are given in Table XIII, XIV, XV, and XVI respectively. Several determinations were carried out in acetyl chloride solution and the values of ϕ obtained in these cases (marked with asterisk) were comparable with the values obtained in acetic anhydride-hydrochloric acid solution.

The absorption spectra of the *trans* azo compounds in acetic anhydride-hydrochloric acid solution are shown in Figs. Vb, VIb and VII (appendix); and the absorption maxima and corresponding extinction coefficients are given in Table XVII. No change in the extinction coefficients was observed when these solutions were allowed to stand in the absence of light for several weeks. The absorption spectra of compounds (1), (95), and (3) were also recorded in acetyl chloride solution. However, the extinction coefficients of compounds (1) and (95) increased considerably with time, and only after the solutions had stood for two weeks in darkness did the absorption spectra resemble those recorded in acetic anhydride-hydrochloric acid solution for these two compounds.

On comparing Tables(XI) and (XVII) it is apparent that the change in solvent from acetic anhydride to acetic anhydride-hydrochloric acid has resulted in hypsochromic shifts (>5 mμ) and corresponding increases in the extinction coefficients ($\Delta\varepsilon$) of the $n\pi^*$ absorptions of some azo compounds. Closer examination reveals a definite relation

TABLE XIII. Quantum Yields and Related Data for the Photoreactions of Azobenzenes in Acetic Anhydride-Hydrochloric Acid Solution at 313 mμ

Substituent	$10^5 c_o$ (M)	$10^7 I_o$ (ein. min^{-1})	$10^2 K$ (min^{-1})	$10^9 K^1$ (mole min^{-1})	ϕ
- (1)	2.330	0.501	4.69	6.65	0.13
-	2.330	0.478	4.64	6.69	0.14
-	2.626	0.450	4.05	5.73	0.13*
4-methyl- (95)	2.959	0.473	5.16	7.41	0.16
4-methyl-	2.959	0.487	5.77	8.41	0.17
4-methyl-	2.147	0.463	5.64	8.39	0.18*
4-chloro- (3)	3.281	0.466	3.91	5.24	0.11
4-chloro-	2.619	0.472	4.44	5.89	0.12*
2-methyl- (128)	2.033	0.459	4.71	8.03	0.17
4-methoxy- (69)	1.690	0.454	0.638	1.81	0.04
4-nitro- (100)	3.049	0.559	0.891	0.139	2.5×10^{-3}
2,6-dimethyl- (129)	2.189	0.461	4.28	8.60	0.19
2,6-dichloro- (130)	4.778	0.484	3.51	9.48	0.20
2,6,2',6'-tetramethyl- (131)	2.272	0.456	2.70	7.00	0.15

* Acetyl chloride used as solvent.

TABLE XIV. Quantum Yields and Related Data for the Photoreactions of Azobenzenes in Acetic Anhydride-Hydrochloric Acid Solution at 365 mμ

Substituent	$10^4 c_o$ (M)	$10^7 I_o$ (ein. min^{-1})	$10^2 K$ (min^{-1})	$10^8 K^1$ (mole min^{-1})	ϕ
- (1)	8.340	0.746	0.207	1.35	0.18
-	8.340	0.761	0.208	1.26	0.17
4-methyl- (95)	3.994	0.790	1.93	1.65	0.21
4-methyl-	2.020	0.769	1.80	1.54	0.20
4-methyl-	2.118	0.790	1.94	1.65	0.21*
4-chloro- (3)	2.188	0.789	0.996	1.16	0.15
4-methoxy- (69)	0.1690	0.757	1.82	0.344	0.05

* Acetyl chloride used as solvent

TABLE XV. Quantum Yields and Related Data for the Photoreactions of Azobenzenes in Acetic Anhydride-Hydrochloric Acid Solution at 405 mμ

Substituent	$10^4 c_o$ (M)	$10^7 I_o$ (ein.min^{-1})	$10^3 K$ (min^{-1})	$10^9 K^1$ (mole min^{-1})	ϕ
- (1)	8.340	0.311	0.993	8.76	0.28
-	8.340	0.314	0.999	8.82	0.28
4-methyl- (95)	9.985	0.300	2.15	9.16	0.31
4-methyl-	3.994	0.313	2.24	9.42	0.30
4-methyl-	2.118	0.307	1.91	8.51	0.28*
4-chloro- (3)	5.469	0.309	1.06	8.62	0.28

* Acetyl chloride used as solvent

TABLE XVI. Quantum Yields and Related Data for the Photoreactions of Azobenzenes in Acetic Anhydride-Hydrochloric Acid Solution at 436 mμ

Substituent	$10^4 c_o$ (M)	$10^7 I_o$ (ein. min^{-1})	$10^3 K$ (min^{-1})	$10^8 K^1$ (mole min^{-1})	ϕ
- (1)	8.340	0.601	3.28	1.89	0.31
-	8.340	0.590	3.21	1.84	0.31
-	5.326	0.584	3.27	1.82	0.31*
4-methyl- (95)	9.985	0.594	5.94	1.82	0.31
4-methyl-	3.994	0.600	5.90	1.86	0.31
4-methyl-	2.118	0.625	6.34	1.94	0.31*
4-chloro- (3)	5.469	0.635	3.74	1.85	0.29
4-chloro-	5.238	0.634	3.52	1.77	0.28*
2-methyl- (128)	5.082	0.623	3.69	1.81	0.29
4-methoxy- (69)	1.690	0.636	4.84	0.258	0.04
4-nitro- (100)	5.141	0.630	1.25	0.688	0.11
2,6-dimethyl- (129)	5.472	0.614	3.33	1.75	0.28
2,6-dichloro- (130)	2.389	0.627	0.571	0.400	0.06
2,6,2',6'-tetramethyl- (131)	5.680	0.646	1.83	1.26	0.20

* Acetyl chloride used as solvent

TABLE XVII. Absorption Maxima and Extinction Coefficients of *trans*-Azobenzenes in Acetic Anhydride-Hydrochloric Acid Solution

Substituent	$\pi \rightarrow \pi^*$		$n \rightarrow \pi^*$	
	λ_{max}	ε	λ_{max}	ε
- (1)	319	21,700	437	535
4-methyl- (95)	327	23,430	436	960
4-chloro- (3)	323	24,700	441	605
4-bromo- (141)	-	-	443	600
4-methoxy- (69)	346	22,200	456	6,500
4-nitro- (100)	333	24,400	457	627
3-methyl- (140)	-	-	437	602
2-methyl- (128)	325	19,000	447	620
2,6-dimethyl- (129)	316	15,020	453	623
2,6-dichloro- (130)	<300	*c.*13,500	448	440
2,6,2',6'-tetramethyl- (131)	311	11,480	468	570

TABLE XVIII. Relationship Between $\Delta\varepsilon$ and the Basicities of the *trans*-Azobenzenes

Substituent	pKa[69]	$\Delta\varepsilon$	log $\Delta\varepsilon$
4-methoxy- (69)	-0.02	5,542	3.74
4-methyl- (95)	-1.11	356	2.55
3-methyl- (140)	-1.47	98	1.99
- (1)	-1.64	55	1.74
4-bromo- (141)	-2.22	7	0.84
4-nitro- (100)	-3.35	2	0.30
2-methyl- (128)	-	105	2.02
4-chloro- (3)	-	27	1.43
2,6-dimethyl- (129)	-	40	1.60
2,6-dichloro- (130)	-	10	1.00
2,6,2',6'-tetramethyl- (131)	-	-27	-

between $\Delta\varepsilon$ and the expected basicity of the azo compound; and it is found that a plot of log $\Delta\varepsilon$ against pKa (known[69] for compounds (1), (95), (140), (141), (100), and (69)) gives an approximately linear relationship (Table XVIII and Fig. XV). In the presence of a strong acetylating reagent such as acetic anhydride-hydrochloric acid

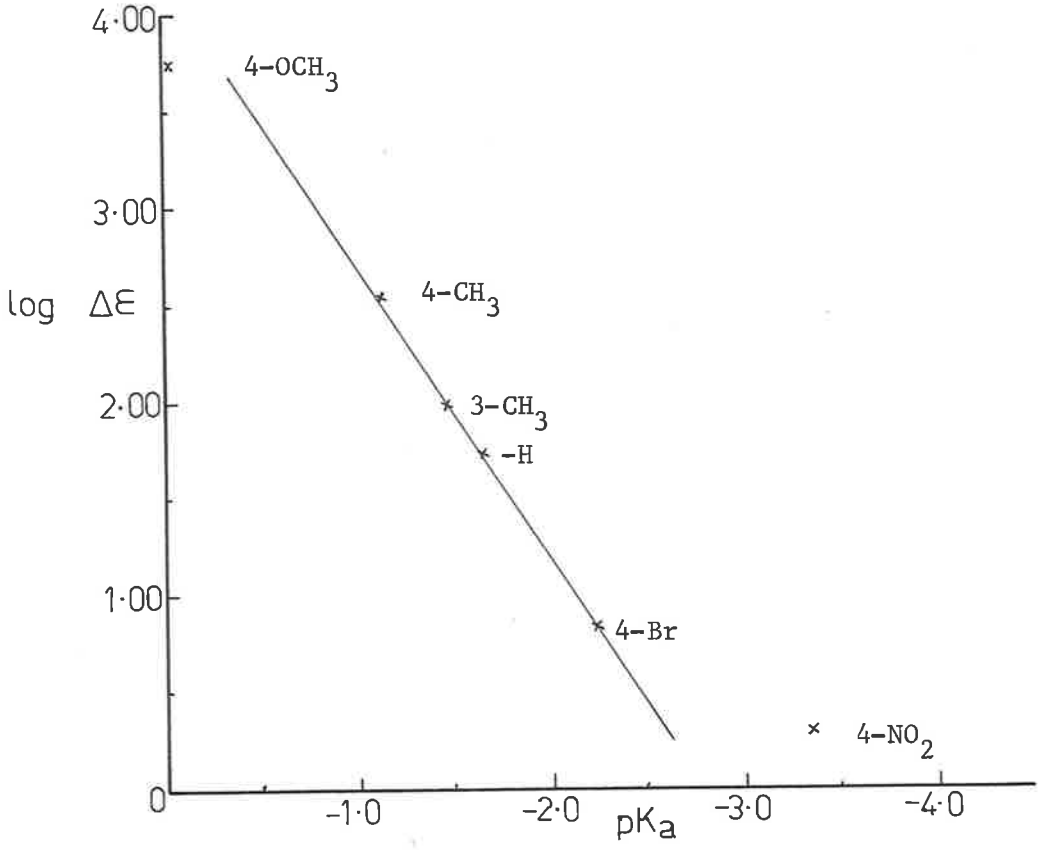
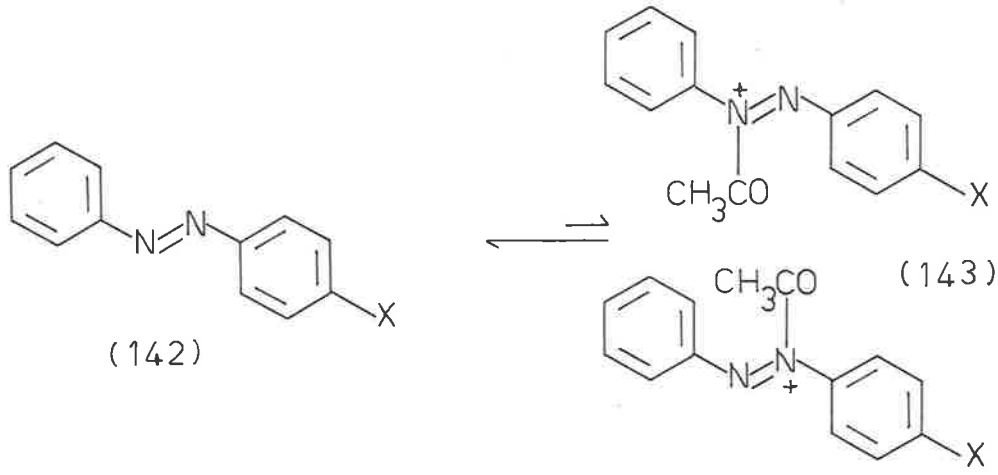


Fig. XV - Approximately linear relationship between log $\Delta\varepsilon$ and pK_a for several azobenzenes (Solvents: acetic anhydride and acetic anhydride-hydrochloric acid).

solution, some interaction between the weakly basic azo compound and the acetylating agent could be expected which, in the case of the more basic compounds, may be great enough to alter the absorption characteristics of the free base. For example, if an equilibrium

mixture (142⇌143) was formed immediately on mixing an azobenzene in acetic anhydride-hydrochloric acid, then one would expect the concentration of (143) to depend on the basicity of the azo compound (and hence on X). The conjugate acids and the related metal halide complexes of azobenzenes show strong absorption ($\pi\pi^*$; ε *c.* 2.0-3.0 x 10^4) at slightly shorter wavelengths (410-440 mμ) than the corresponding $n\pi^*$ absorptions of the free bases. On this basis, it would not be unreasonable to expect the cation (143) to absorb strongly in the 410-440 mμ region, and this may in fact account for the $\Delta\varepsilon$ values (and hypsochromic shifts) observed for the more basic azobenzenes.



In Table XIX, quantum yields (ϕt) for *trans* → *cis* isomerization in acetic anhydride are compared with quantum yields (ϕ) for the photochemical reaction in acetic anhydride-hydrochloric acid solution. Taking into consideration: (a) the different solvents in which ϕ and ϕt were determined (spectral differences discussed above); and (b) the different methods used to calculate ϕ and ϕt, then the values of ϕ and ϕt for monosubstituted azobenzenes (1), (95), (128), (3), and (100) at the wavelengths examined are in reasonable agreement.

These results then support the presumption that the photochemical reaction of *trans*-azobenzene with acetyl chloride involves initial *trans* → *cis* photoisomerization (rate determining step) followed by a fast non-photochemical reaction of the *cis* isomer with acetyl chloride. However, it is apparent from Table XIX that this mechanism is not straightforward for all azobenzenes. For example, the value of ϕ for 4-methoxyazobenzene is constant at the three wavelengths examined and considerably lower than the values obtained for ϕt. Similarly, compounds (130) and (131) have values of ϕ lower than ϕt at 436 mμ. In the latter cases, however, it appears that the *cis* isomers only react slowly with the acetic anhydride-hydrochloric acid solution so that the rate of *trans* → *cis* isomerization is not always the rate determining step. This is certainly the case for *cis*-2,6,2',6'-tetrachloroazobenzene (132), the half-life of this compound in acetic anhydride-hydrochloric acid being *c.* 250 hours. The unreactive nature of (132) is probably caused by the strong electron-attracting effect (-I) of the four *o*-chloro groups, since acetylation at the azo linkage would be retarded under these circumstances. Similar reasoning could be used to explain the slow nature of the photochemical reaction of *trans*-2,4,2',4'-tetrachloroazobenzene with acetyl chloride which was discussed in Part I.2 of this thesis.

TABLE XIX. Comparison of ϕt (Acetic Anhydride) with ϕ (Acetic Anhydride-Hydrochloric Acid) at 313, 365, 405 and 436 mμ

Substituent	313 mμ		365 mμ		405 mμ		436 mμ	
	ϕt	ϕ	ϕt	ϕ	ϕt	ϕ	ϕt	ϕ
- (1)	0.11†	0.14†	0.16†	0.18†	0.30†	0.28†	0.32†	0.31†
4-methyl- (95)	0.12†	0.17†	0.17†	0.21†	0.37†	0.31†	0.32†	0.31†
2-methyl- (128)	0.12	0.17	-	-	-	-	0.34	0.29
4-chloro- (3)	0.11	0.12	0.13	0.15	0.38	0.28	0.36	0.29†
4-methoxy- (69)	0.26	<0.04	0.23	0.05	-	-	0.43	0.04
2,6-dichloro- (130)	0.16	0.20*	-	-	-	-	0.46	0.06*
4-nitro- (100)	0.03	<0.01	-	-	-	-	0.09	0.11
2,6,2',6'-tetramethyl- (131)	-	-	-	-	-	-	0.36	0.20

† averaged from 2 or more determinations

* concentration at 313 mμ = 4.778×10^{-5}M and concentration at 436 mμ = 2.389×10^{-3}M

EXPERIMENTAL

GENERAL

In all photochemical reactions solutions of the reactants were exposed to direct sunlight for the period indicated in sealed Pyrex tubes. When the volume of the solutions exceeded 50 ml a Pyrex "culture flask" (31 x 23 x 6.5 cm) was used as the container.

Column chromatography was carried out using either B.D.H. neutral alumina (which had been activated by heating at 400° for 15 hr prior to use), or Mallinckrodt silicic acid as the column packing.

A Perkin-Elmer 800 gas chromatograph (fitted with the indicated column) was employed for qualitative and quantitative gas chromatography. An Aerograph Autoprep A-700 gas chromatograph was used for preparative gas chromatography.

All solvents employed for chromatography and crystallization purposes were dried and redistilled before use. The light petroleum had b.p. 50-65°.

The acetyl chloride was a commercial preparation and was redistilled before use. The *trans*-azobenzene was also a commercial preparation and this was chromatographically purified before use. The aqueous methanolic potassium hydroxide employed for hydrolyses consisted of a 15% (w:v) solution of potassium hydroxide in 10% (v:v) aqueous methanol.

Melting points (m.p.) were determined with a Gallenkamp melting point apparatus and are uncorrected.

Infrared spectra were determined with a Perkin-Elmer 237 spectrophotometer; ultraviolet visible spectra were determined with an Optica CF_4 recording spectrophotometer.

Nuclear magnetic resonance spectra (n.m.r.) were recorded by Mr. R.L. Paltridge with a Varian DP60 spectrometer operating at 60 Mc/s and with tetramethylsilane as the internal standard.

Mass spectra were carried out by Mr. D.B. Cobb with a Hitachi Perkin-Elmer RMU 6D spectrometer operated at 75 eV.

Microanalyses were carried out by the Australian Microanalytical Service, Melbourne.

I.1. PHOTOCHEMICAL REACTION OF *TRANS*-AZOBENZENE WITH ACETYL CHLORIDE

4-Chloroazobenzene (3)

4-Chloroazobenzene was available from previous work,[1,2] and this sample had m.p. 86-87° (lit.[111] 87.5°).

2-Chloroazobenzene (35)

2-Chloroazobenzene was prepared by condensation of nitrosobenzene (1.0 g) with *o*-chloroaniline (1.2 g) in glacial acetic acid (2 ml);[45] and this when chromatographically purified and recrystallized from methanol formed red prisms (1.1 g; 57%), m.p. 30-31° (lit.[112,113] 33°, 29-31°).

2- and 4-Chloroazobenzene from trans-*Azobenzene*

A solution of *trans*-azobenzene (64 g) in acetyl chloride (640 ml) was exposed to bright sunlight in a sealed "culture flask" for 2 hr. Excess acetyl chloride was removed by distillation, and the residue was heated with a mixture of potassium hydroxide (75 g), methanol (300 ml), and water (100 ml), under reflux for 6 hr. During this time the hydrolysed material underwent extensive oxidation (atmospheric oxygen), as shown by the development of a pronounced orange color. A stream of air was thereafter drawn through the hydrolysis mixture continuously for 3 hr, in order to complete the oxidation. The precipitated orange solid was removed by filtration, washed thoroughly with water, dried, and recrystallized from methanol.

4-Chloroazobenzene (56 g; 73%) was thereby obtained as orange needles, m.p. 86-87°. The methanol was then removed from the mother liquors by distillation; and the residual dark orange oil (16.5 g) was shown by comparisons of infrared spectra to be a mixture of 2- and 4-chloroazobenzene. The isomer ratio in the mixture was shown by gas chromatography (see below) to be 1.2:1.

Gas Chromatography

A Perkin-Elmer 800 gas chromatograph was used with a 12 ft. by $\frac{1}{4}$ in. aluminium/5% QF-1 column (Silicone-Fluoro/FS 1265) at 180-182° with nitrogen as carrier gas (flow rate *c.* 100 ml/min). Samples of pure azobenzene, 4-chloroazobenzene and 2-chloroazobenzene, of standard mixtures of 2- and 4-chloroazobenzenes, and of mixed products (as used for peak identification, calibration, and analysis, respectively), were injected as 5% (w:v) solutions in chloroform (1-3 μl per injection). The following retention times were observed: azobenzene (5 min 30 sec); 4-chloroazobenzene (9 min 8 sec); and 2-chloroazobenzene (10 min 33 sec). A range of standard mixtures containing 2-chloroazobenzene and 4-chloroazobenzene in widely varying proportions was examined for calibration purposes; and the ratios of the recorded peak areas were found to give a smooth-curve graph when plotted against percentage compositions of the mixtures. The calibration graph was thereafter used for estimation of the relative amount of 2- and 4-chloroazobenzene in the final product obtained from the reaction sequence described above.

I.2. REACTIONS LEADING TO DI-, TRI-, TETRA-, AND PENTA-CHLOROAZOBENZENES

Materials and Reference Compounds

4-Chloroazobenzene and 2-chloroazobenzene

These compounds were available from previous work (see Part I.1)

4,4'-Dichloroazobenzene (37)

This compound was available from earlier work.[94]

2,4-Dichloroazobenzene (38)

This compound was prepared through condensation of nitrosobenzene with 2,4-dichloroaniline[114] in glacial acetic acid.[95] The product was purified chromatographically (alumina-light petroleum) and finally recrystallized from ethanol to give orange plates, m.p. 107° (lit.[95] 105°).

2,4'-Dichloroazobenzene (39)

o-Chloroaniline (0.4 g) was dissolved in warm glacial acetic acid (1 ml), and *p*-chloronitrosobenzene[116] (0.5 g) was added. The mixture was heated (100-110°) for 3 hr, and the crude product, which separated as a solid mass when the mixture was cooled, was removed and chromatographed (alumina-light petroleum). The *2,4'-dichloroazobenzene* (main band) was thereby separated from

impurities and was finally recrystallized from light petroleum as orange needles (0.21 g; 30%), m.p. 112-113° (Found: C, 57.6; H, 3.4; N, 10.8. $C_{12}H_8Cl_2N_2$ requires C, 57.4; H, 3.2; N, 11.1%).

2,2'-Dichloroazobenzene (40)

This compound was prepared by reduction of *o*-chloronitrobenzene with zinc and alkali, according to the method used for the preparation of symmetrically substituted azobenzenes.[117] The product had m.p. 134-135° (lit.[115,118] 136, 137°).

2,4,4'-Trichloroazobenzene (42)

2,4-Dichloroaniline[114] (1.15 g) was dissolved in warm glacial acetic acid (2 ml). *p*-Chloronitrosobenzene[116] (1.0 g) was added to the solution, and the mixture was heated to *c*. 120° for several hours. The crude product, which separated when the mixture was cooled, was collected and chromatographically purified (alumina-light petroleum-benzene). The *2,4,4'-trichloroazobenzene* (main band) was thereby separated from impurities and was finally recrystallized from methanol as orange needles (0.35 g; 18%), m.p. 133-134° (Found: C, 50.9; H, 2.8; N, 9.6. $C_{12}H_7Cl_3N_2$ requires C, 50.5; H, 2.5; N, 9.8%).

2,4'-Dichloro-4-methoxyazobenzene (43)

By a similar method to that described[119] for the preparation of 4-hydroxyazobenzene, *p*-chlorophenyldiazonium chloride was coupled

with *m*-chlorophenol. The 2,4'-dichloro-4-hydroxyazobenzene so formed was methylated with dimethyl sulphate (cf. the preparation of anisole[120]), and the resulting *2,4-dichloro-4-methoxyazobenzene* was chromatographically purified (alumina-light petroleum-ether) and recrystallized from light petroleum to give yellow-orange plates, m.p. 87.5-88.0° (Found: C, 55.6; H, 3.8; N, 9.9; O, 6.0. $C_{13}H_{10}Cl_2N_2O$ requires C, 55.5; H, 3.6; N, 10.0; O, 5.7%).

2,2',4-Trichloroazobenzene (44)

A sample of this compound was available from previous work.[96]

2,4,2',4'-Tetrachloroazobenzene (46)

This compound was prepared by reduction of 2,4-dichloronitrobenzene with zinc and alkali, the experimental procedure being essentially similar to that involved in the preparation of 2,2'-dichloroazobenzene. The crude product was chromatographically purified (alumina-light petroleum). The 2,4,2',4'-tetrachloroazobenzene (main band) so obtained formed orange needles when recrystallized from light petroleum, m.p. 165-166° (lit.[121] 161-162°) (Found: C, 44.8; H, 2.2; N, 8.7. Calc. for $C_{12}H_6Cl_4N_2$: C, 45.0; H, 1.9; N, 8.7%).

2,4,2'-Trichloro-4'-hydroxyazobenzene (50)

2,4-Dichlorophenyldiazonium chloride was coupled with *m*-

chlorophenol in a procedure essentially similar to that used for the preparation of 4-hydroxyazobenzene.[119] The crude product was chromatographically purified (silica-ether-light petroleum). The product was then recrystallized several times from light petroleum to form orange needles of *2,4,2'-trichloro-4'-hydroxyazobenzene*, m.p. 147-148° (Found: C, 47.8; H, 2.7; N, 8.9. $C_{12}H_7Cl_3N_2O$ requires C, 47.8; H, 2.3; N, 9.3%).

Attempted Synthesis of 2,4,6,2',4'-Pentachloroazobenzene (52)

2,4,6-Trichloronitrosobenzene[122] (0.20 g) was added to a solution of 2,4-dichloroaniline (0.16 g) in glacial acetic acid (1 ml) and the mixture heated at *c.* 100° for 16 hr. The reaction mixture was neutralized, extracted with ether, and the residue remaining after evaporation of the ether was chromatographed (alumina-light petroleum). Elution of the column yielded none of the required product.

Reaction Sequences

In each of the five experiments described below, a 3-4% (w:v) solution of the stated quantity of azo compound in acetyl chloride was exposed to bright sunlight until the photochemical reaction was complete (indicated period). The excess acetyl chloride was then distilled off (last traces under reduced pressure), and a small portion of the residual product was removed for examination and (where possible) characterization. The bulk of the material was thereafter

hydrolysed in a 20% (w:v) solution in boiling aqueous methanolic potassium hydroxide for 6-8 hr, and air was then drawn through the reaction mixture for 3-4 hr in order to complete the oxidation of the deacetylated hydrazo compound(s) to the corresponding azo compound(s). This treatment caused the azo compound(s) to precipitate virtually completely from the reaction mixture, and the final product in each case was removed by filtration, washed with water until free of alkali, and dried. Further treatment was then effected, as indicated in each case.

Dichloroazobenzenes from 4-Chloroazobenzene

4-Chloroazobenzene (50 g) was irradiated in an acetyl chloride solution for 2 hr. The material remaining after removal of the acetyl chloride was hydrolysed in boiling aqueous methanolic potassium hydroxide (6 hr) and oxidized with air. The precipitated product (55 g) was recrystallized from ethanol to give 4,4'-dichloroazobenzene (24 g; 41%) as orange-yellow needles, m.p. 188°; the compound was shown to be identical (mixed melting point and infrared spectrum) with the authentic material described above. When the ethanolic mother liquors were diluted with water, a considerable amount of material (28 g) was recovered. This was warmed with light petroleum, and the warm solution was filtered. The undissolved material at this stage proved to be a further quantity (2.5 g; 4%) of 4,4'-dichloroazobenzene. When the filtered light petroleum solution was cooled (ice-bath), 2,4-dichloroazobenzene (12 g; 21%) was deposited

as orange plates, m.p. 105° (lit.[115] 105°), and this was shown to be identical (mixed melting point and infrared spectrum) with the described authentic sample. The mother liquors from the latter recrystallization were reduced to dryness, and the residual solid was recrystallized from ethanol. A further quantity (3.5 g; 6%) of 2,4-dichloroazobenzene (m.p. 105°) was thereby obtained. The remaining ethanolic mother liquors were then evaporated to dryness, and the residue was dissolved in light petroleum and chromatographed repeatedly on alumina. An almost complete separation of two fractions were thereby effected, the first fraction yielding still more 2,4-dichloroazobenzene (4 g; 7%) and the second fraction yielding 2,4'-dichloroazobenzene (2.3 g; 4%). A mixture of the two latter compounds (0.85 g) was contained in the "overlap" of the chromatograms. The 2,4'-dichloroazobenzene was shown to be identical (mixed melting point and infrared spectrum) with the authentic sample described above.

Dichloroazobenzenes from 2-Chloroazobenzene

Following irradiation of 2-chloroazobenzene (0.18 g) in acetyl chloride, the acetyl chloride was removed; and, after hydrolysis/oxidation of the residual material, the final product (0.21 g) was examined as follows. The product was dissolved in acetone (1% w:v) and subjected to gas chromatography at 220° in a Perkin-Elmer 800 gas chromatograph, fitted with a 12 ft by $\frac{1}{8}$ in. Carbowax 20M column, nitrogen being used as carrier gas (flow rate *c.* 28 ml/min).

Three peaks were observed, corresponding to the following retention times: 5 min 36 sec, 7 min 2 sec, and 7 min 29 sec. The retention times were identical with those observed with authentic samples of 2,4-dichloroazobenzene, 2,4'-dichloroazobenzene, and 2,2'-dichloroazobenzene respectively, when these were chromatographed under the same conditions. The solution of the product in acetone was also chromatographed at 200° through a 12 ft by $\frac{1}{4}$ in. 5% QF-1 column with nitrogen as carrier gas (flow rate *c.* 100 ml/min), and peaks corresponding to the following retention times were observed: 7 min 0 sec, 7 min 56 sec, and 9 min 0 sec. In this case also, the retention times were found to be identical with those of authentic samples of 2,4-dichloroazobenzene, 2,4'-dichloroazobenzene and 2,2'-dichloroazobenzene respectively. Standard mixtures of 2,4- and 2,4'-dichloroazobenzene and of 2,4'- and 2,2'-dichloroazobenzene were then examined (with the Carbowax column) for calibration purposes. From the relative peak areas it was found that the product obtained from 2-chloroazobenzene was a mixture of 2,4-dichloro, 2,4'-dichloro-, and 2,2'-dichloroazobenzene in the ratio 6.25:9:1.

2,4,4'-Trichloroazobenzene from 4,4'-Dichloroazobenzene

4,4'-Dichloroazobenzene (21.4 g) was irradiated in acetyl chloride for 3 hr. (Due to the relatively low solubility of this azo compound in acetyl chloride, it was necessary to stir the reaction mixture during this period.) Removal of the acetyl chloride left a white crystalline residue, a small portion of which was recrystallized

from methanol to give N,N'-*diacetyl-2,4,4'-trichlorohydrazobenzene* (41), m.p. 164-165° (Found: C, 51.6; H, 3.7; N, 7.2. $C_{16}H_{13}Cl_3N_2O_2$ requires C, 51.7; H, 3.5; N, 7.5%). The infrared spectrum of the compound (Nujol) showed bands at 1705 (C=O), 1675 (C=O), 1330, 1315, 1250, 970, 855, and 810 cm^{-1}. When the compound was boiled with aqueous methanolic potassium hydroxide in the presence of air, 2,4,4'-trichloroazobenzene was formed; this was identified (mixed melting point and infrared spectrum) with the authentically prepared sample (see above).

The bulk of the white crystalline residue was subjected to hydrolysis/oxidation in boiling aqueous methanolic potassium hydroxide, and the final product was chromatographed on alumina (light petroleum). The first fraction from the chromatogram yielded 2,4,4'-trichloroazobenzene (17.4 g; 72%) which, when recrystallized from methanol, had m.p. 133-134° (alone or admixed with the authentic sample). The infrared spectrum of the compound was identical with that of the authentic specimen. The second fraction from the chromatogram afforded 2,4'-dichloro-4-methoxyazobenzene (0.5 g; 2%) which, when recrystallized from methanol, had m.p. 87.5-88.0°, not depressed on admixture with the authentic sample. The infrared spectrum of the compound (Nujol) showed bands at 1595, 1570, 1230, 880, and 840 cm^{-1} and this was identical with the spectrum of the authentic sample. The latter compound was also formed directly from 2,4,4'-trichloroazobenzene when this was treated for several hours with boiling aqueous methanolic potassium hydroxide.

Trichloroazobenzenes from 2,4-Dichloroazobenzene

2,4-Dichloroazobenzene (8.8 g) was irradiated in acetyl chloride for 2 hr. After removal of the acetyl chloride a white solid residue was obtained, and a small portion of this was recrystallize from methanol to give *N*,*N*'-diacetyl-2,4,4'-trichlorohydrazobenzene, m.p. 164-165°, which was shown to be identical (mixed melting point and infrared spectrum) with the material formed from 4,4'-dichloroazobenzene. The remainder of the white solid residue was subjected to hydrolysis/oxidation in aqueous methanolic potassium hydroxide; and the final product was chromatographed on alumina (light petroleum). The first compound eluted from the column was 2,4,4'-trichloroazobenzene (6.9 g; 68%), which had m.p. 133-134° when recrystallized from methanol. The compound was identical (infrared spectrum and mixed melting point) with the authentic sample described above. The second compound eluted was 2,2',4-trichloroazobenzene (0.29 g; 3%) which had m.p. 93.5-94.5° (Found: C, 50.7; H, 2.75; N, 9.7. Calc. for $C_{12}H_7Cl_3N_2$: C, 50.5; H, 2.5; N, 9.8%). The compound was identical (infrared spectrum) with the authentic material referred to above. The final compound eluted from the column was 2,4'-dichloro-4-methoxyazobenzene (0.1 g; 1%); and this had m.p. 85-87° when recrystallized from methanol. The infrared spectrum of the compound was identical with that of the authentic sample; and the melting point was not depressed on admixture with authentic material.

2,4,2',4'-Tetrachloroazobenzene from 2,4,4'-Trichloroazobenzene

A solution of 2,4,4'-trichloroazobenzene (16.7 g) in acetyl chloride was irradiated for 2 hr. After the acetyl chloride was removed a white crystalline solid remained, and a small portion of this was recrystallized from methanol to give N,N'-*diacetyl-2,4,2',4'-tetrachlorohydrazobenzene* (46), m.p. 164-165° (Found: C, 47.6; H, 3.3; N, 6.7. $C_{16}H_{12}Cl_4N_2O_2$ requires C, 47.3; H, 3.0; N, 6.9%). The infrared spectrum of the compound (Nujol) showed bands at 1705 (C=O), 1680 (C=O), 1320, 1310, 1090, 975, 850, 810 and 765 cm^{-1}. The compound yielded 2,4,2',4'-tetrachloroazobenzene when boiled with aqueous methanolic potassium hydroxide in the presence of air. The remainder of the white crystalline solid was subjected to hydrolysis/oxidation in aqueous methanolic potassium hydroxide, and the final product was chromatographed on alumina (light petroleum).

The first fraction afforded 2,4,2',4'-tetrachloroazobenzene (12.2 g; 65%) which after recrystallization from methanol had m.p. 163-164°. The compound was shown to be identical (infrared spectrum and mixed melting point) with the authentic sample described above.

The second fraction was eluted with benzene-light petroleum (8% v:v); and this afforded *2,4,2'-trichloro-4'-methoxyazobenzene* (48) (0.73 g; 4%) as orange crystals, m.p. 135-136° (Found: C, 49.5; H, 3.0; N, 8.7; O, 5.2. $C_{13}H_9Cl_3N_2O$ requires C, 49.5; H, 2.9; N, 8.9; O, 5.1%). The infrared spectrum of the compound (Nujol) showed bands at 1590, 1565, 1270, 1230, 1050, 870, 850, 820 and 805 cm^{-1}.

The third fraction was eluted with benzene-light petroleum

(10% v:v) and this yielded *2,4,4'-trichloro-2'-methoxyazobenzene* (49) (0.15 g; 0.8%) in the form of dark red needles (recrystallization from light petroleum), m.p. 137-138° (Found: C, 49.5; H, 3.1; N, 8.6. $C_{13}H_9Cl_3N_2O$ requires C, 49.5; H, 2.9; N, 8.9%). The infrared spectrum of the compound (Nujol) showed bands at 1585, 1570, 1245, 875, 865, 830, and 810 cm^{-1}.

Both of the trichloromethoxyazobenzenes were shown to be formed in appreciable quantities when 2,4,2',4'-tetrachloroazobenzene was separately treated with boiling aqueous methanolic potassium hydroxide for several hours.

Demethylation of 2,4,2'-Trichloro-4'-methoxyazobenzene (48)

Freshly sublimed anhydrous aluminium trichloride (0.3 g) was added to a boiling solution of 2,4,2'-trichloro-4'-methoxyazobenzene (0.08 g) in benzene (40 ml). The mixture was boiled for 8 min and thereafter shaken with excess water. The benzene layer was removed, the aqueous layer was extracted with chloroform, and the benzene and chloroform layers were combined and reduced to dryness. The residual orange solid was then chromatographed (silica-ether-light petroleum), and the main fraction from the column afforded 2,4,2'-trichloro-4'-hydroxyazobenzene (0.05 g; 65%) as orange crystals m.p. 146-147° (from light petroleum). The melting point was not depressed on admixture with the authentic sample described above. The infrared spectrum of the compound (CCl_4) showed a sharp band at 3590 (OH) and bands at 1590, 1575, 1230, and 1160 cm^{-1}, and this was identical with the spectrum of the authentic sample.

Demethylation of 2,4,4'-Trichloro-2'-methoxyazobenzene (49)

By a similar procedure to the foregoing, 2,4,4'-trichloro-2'-methoxyazobenzene (0.05 g) was demethylated in benzene (20 ml) with aluminium trichloride (0.15 g). After the decomposition with water, the extracted material was similarly chromatographed on a column of silica. The first fraction yielded unchanged starting material and the second fraction gave the demethylated product. The recovered starting material was subjected again to the demethylation procedure and the two quantities of demethylated product were combined and recrystallized from light petroleum. In this manner, *2,4,4'-trichloro-2'-hydroxyazobenzene* (0.03 g; 63%) was obtained as yellow-orange crystals, m.p. 167-168° (Found: C, 48.1; H, 2.8; N, 9.0. $C_{12}H_7Cl_3N_2O$ requires C, 47.8; H, 2.3; N, 9.3%).

Photoreaction of 2,4,2',4'-Tetrachloroazobenzene with Acetyl Chloride

2,4,2',4'-Tetrachloroazobenzene (4.0 g) was irradiated in acetyl chloride solution for 90 hr. The residue remaining after evaporation of the excess acetyl chloride (last traces under reduced pressure) was chromatographed on a column of alumina (light petroleum).

The first fraction yielded an orange crystalline solid (mixture) which, after several recrystallizations from light petroleum, gave *2,4,6,2',4',-pentachloroazobenzene* (52) (0.3 g), m.p. 133-134° (Found: C, 40.6; H, 1.75; N, 7.8. $C_{12}H_5Cl_5N_2$ requires C, 40.7; H, 1.42; N, 7.9%). The infrared spectrum of the compound (Nujol)

showed bands at 1570, 1555, 1540, 1120, 1095, 855, 820, 785 and 715 cm^{-1}. Evaporation of the mother liquors left a mixture of compounds and further separation was not effected.

The second fraction was eluted with ether-light petroleum (80% v:v) and afforded a colorless glass which was subjected directly to hydrolysis/oxidation in aqueous methanolic potassium hydroxide. The final product was chromatographed on alumina (light petroleum).

Removal of the eluate from the first fraction left a mixture which, after recrystallization (light petroleum), afforded 2,4,2',4'-tetrachloroazobenzene (1.03 g), m.p. 162-164° (alone or admixed with an authentic sample). Evaporation of the mother liquors to dryness gave a mixture of compounds (0.21 g) which were not further separated.

The second fraction was eluted with ether-light petroleum (5% v:v) and yielded 2,4,4'-trichloro-2'-methoxyazobenzene (0.04 g) which was identified by direct comparison (mixed m.p. and the infrared spectrum) with the authentic compound.

Further elution with ether-light petroleum (5% v:v) resulted in a third fraction and this afforded 2,4,2'-trichloro-4'-methoxyazobenzene (0.2 g) which was identified by direct comparison (mixed m.p. and the infrared spectrum) with the authentic sample.

The final compound eluted from the column (ether-light petroleum 5% v:v) was *2,4,2',6'-tetrachloro-4'-methoxyazobenzene* (56) (0.034 g; 1%) in the form of dark-red crystals, m.p. 152-153° (Found: C, 44.7; H, 2.54; N, 8.0. $C_{13}H_8Cl_4N_2O$ requires C, 44.6; H, 2.30; N, 8.0%).

The infrared spectrum of the compound (Nujol) showed bands at 1582, 1560, 1545, 1290, 1250, 1095, 1065, 1030, and 795 cm^{-1}.

Examination of the Products from the Photoreaction of 2,4,2',4'-Tetrachloroazobenzene with Acetyl Chloride

A solution of 2,4,2',4'-tetrachloroazobenzene (0.70 g) in acetyl chloride (20 ml) was irradiated for 80 hr. The residue remaining after removal of the acetyl chloride was dissolved in ether, the ethereal solution neutralized (Na_2CO_3 solution), dried, and evaporated to dryness. The residue was chromatographed on a column of silica (ether-light petroleum mixtures).

The first fraction (light petroleum) afforded a mixture of 2,4,2',4'-tetrachloroazobenzene and 2,4,6,2',4'-pentachloroazobenzene in the ratio of 3:7. These compounds were identified by comparative gas chromatography (see below).

The second fraction was eluted with ether-light petroleum (15% v:v) and yielded a white crystalline compound (0.45 g), m.p. 110-125°, the infrared spectrum (Nujol) of which, showed bands of 3250 (N-H), 1650-1660 (C=O), 1555, 1330, 1240, 1130, 877, 845, 813, 776, 748, and 720 cm^{-1}. After several recrystallizations (ether-light petroleum) the compound had m.p. 119-129°. The mass spectrum was determined (see appendix), and this in conjunction with the above data indicated that the mixture consisted of *N*-acetyl-2,4,2',4'-tetrachlorohydrazobenzene (53) and *N*'-acetyl-2,4,6,2',4'-pentachlorohydrazobenzene (54).

The third fraction was eluted with ether-light petroleum (25% v:v) and this gave N,N'-*diacetyl-2,4,6,2',4'-pentachlorohydrazobenzene* (55) (0.16 g; 17%) as white crystals, m.p. 193-194° (Found: C, 43.4; H, 2.65; N, 6.2. $C_{16}H_{11}Cl_5N_2O_2$ requires C, 43.6; H, 2.52; N, 6.4%). The infrared spectrum of the compound (Nujol) showed bands at 1723 (C=O), 1688 (C=O), 1548, 1360, 1298, 1095, 853, 830, and 660 cm^{-1}. (See appendix for the mass spectrum.)

Hydrolysis of N,N'-*Diacetyl-2,4,6,2',4'-pentachlorohydrazobenzene* (55)

A solution of *N,N'*-diacetyl-2,4,6,2',4'-pentachlorohydrazobenzene (0.06 g) in aqueous methanolic potassium hydroxide (17 ml) was boiled under reflux for 75 min. After extraction with ether and subsequent removal of the ether, the final product was chromatographed on alumina (light petroleum).

The first fraction yielded a mixture (0.019 g) of 2,4,2',4'-tetrachloroazobenzene and 2,4,6,2',4'-pentachloroazobenzene in the ratio of 37:73. The product ratio was determined by analytical gas chromatography (see below).

Elution with ether-light petroleum (5% v:v) gave a mixture (0.009 g) of methoxy compounds on removal of the eluate. This mixture was dissolved in acetone (1% w:v) and subjected to gas chromatography at 270° using a 12 ft by $\frac{1}{4}$ in. 10% SE52 column with nitrogen as the carrier gas (flow rate *c.* 120 ml/min). Several peaks were observed, but the three main peaks had the following retention times: 4 min 54 sec,

5 min 43 sec, and 7 min 10 sec and these were identical to the retention times observed for authentic samples of (48), (49), and (56) respectively.

Hydrolysis of the Mixture of Monoacetyl Compounds (53) and (54)

A solution of the mixed compounds (53) and (54) (0.052 g) in aqueous methanolic potassium hydroxide (15 ml) was boiled under reflux for 30 min. The final mixture was diluted with water and extracted with ether. The separated ethereal solution was dried, evaporated to dryness, and the remaining residue chromatographed on a column of alumina (light petroleum).

The first fraction afforded a mixture (0.02 g) of 2,4,2',4'-tetrachloroazobenzene and 2,4,6,2',4'-pentachloroazobenzene and these were shown to be in the ratio of 20:80 by gas chromatography (see below).

The second fraction was eluted with ether-light petroleum (15% v:v) and yielded a mixture of methoxy compounds. The mixture was dissolved in acetone (1% w:v) and subjected to gas chromatography at 270° using a 12 ft by $\frac{1}{4}$ in. 10% SE52 column, with nitrogen as carrier gas (120 ml/min flow rate). Only one large peak and several small peaks were observed. The retention time of the large peak was 7 min 10 sec and this was identical to the retention time of an authentic sample of 2,4,2',6'-tetrachloro-4'-methoxyazobenzene.

Irradiation of N,N'*-Diacetyl-2,4,6,2',4'-pentachlorohydrazobenzene in Acetyl Chloride*

A solution of *N*,*N*'-diacetyl-2,4,6,2',4'-pentachlorohydrazobenzene (0.02 g) was irradiated in acetyl chloride (1 ml) solution for a period of 50 hr. No coloration developed in the solution during this period and removal of the excess acetyl chlorided afforded unchanged *N*,*N*'-diacetyl compound.

Irradiation of the Mixture of Monoacetyl Compounds in Acetyl Chloride

A solution of the mixed monoacetyl compounds (0.02 g) in acetyl chloride (1 ml) was irradiated for 25 hr. Evaporation of the excess acetyl chloride left an orange residue which was chromatographed on alumina (light petroleum).

The first fraction gave a mixture (0.002 g) of 2,4,2',4'-tetrachloroazobenzene and 2,4,6,2',4'-pentachloroazobenzene and the product ratio was shown to be 5:95 by gas chromatography (see below).

No other colored compounds were eluted from the column.

Gas Chromatography

Product ratios of 2,4,2',4'-tetrachloroazobenzene and 2,4,6,2',4'-pentachloroazobenzene were determined with a 12 ft by $\frac{1}{4}$ in. 10% SE52 column at 270° and with nitrogen as carrier gas (flow rate *c*. 120 ml/min). Samples of the individual pure azo compounds

(52 and 47), of standard mixtures (of 52 and 47), and of the mixed products (as used for peak identification, calibration, and analysis respectively), were injected as 1% (w:v) solutions in acetone. The following retention times were observed: 2,4,2',4'-tetrachloroazobenzene (4 min 20 sec) and 2,4,6,2',4'-pentachloroazobenzene (5 min 20 sec). The analytical procedure was carried out in a manner essentially similar to that described for the analysis of 2- and 4-chloroazobenzene (Experimental Part I.1).

I.3. SUBSTITUTED *TRANS*-AZOBENZENES

Starting Materials and Reference Compounds

4,4'-Dimethoxyazobenzene (60)

This compound was prepared by reduction of *p*-nitroanisole with zinc and alkali according to the method used for the preparation of symmetrically substituted azobenzenes.[117] The product had m.p. 163-164° (lit.[123] 164°).

2-Chloro-4,4'-dimethoxyazobenzene (65)

p-Methoxyphenyldiazonium chloride was coupled with *m*-chlorophenol in a procedure essentially similar to that used for the preparation of 4-hydroxyazobenzene.[119] The 2-chloro-4-hydroxy-4'-methoxyazobenzene so formed was methylated with dimethyl sulphate (cf. the preparation of anisole[120]), and the resulting *2-chloro-4,4'-dimethoxyazobenzene* was chromatographically purified (alumina-light petroleum-ether). Recrystallization from light petroleum gave orange plates, m.p. 114.5-115.5° (Found: C, 60.9; H, 4.77; N, 9.7; O, 11.8. $C_{14}H_{13}ClN_2O_2$ requires C, 60.8; H, 4.73; N, 10.1; O, 11.6%).

4-Methoxyazobenzene (69)

A sample of this compound was available from earlier work.[94]

2-Chloro-4-methoxyazobenzene (71)

By a similar method to that described for the preparation of 4-hydroxyazobenzene,[119] phenyldiazonium chloride was coupled with *m*-chlorophenol. The 2-chloro-4-hydroxyazobenzene so formed was methylated with dimethyl sulphate (cf. the preparation of anisole[120]), and the resulting *2-chloro-4-methoxyazobenzene* was chromatographically purified (alumina-light petroleum-ether) and recrystallized from light petroleum to give yellow-orange crystals, m.p. 57-58° (Found: C, 63.1; H, 4.51; N, 11.6; O, 6.7. $C_{13}H_{11}ClN_2O$ requires C, 63.3; H, 4.46; N, 11.4; O, 6.5%).

2,2'-Dimethoxyazobenzene (74)

This compound was prepared by reduction of *o*-nitroanisole with zinc and alkali in a reaction similar to that used for the preparation of 4,4'-dimethoxyazobenzene. The product had m.p. 150-152° (lit. 153°[118]).

Attempted Synthesis of 4-Chloro-2,2'-dimethoxyazobenzene (77)

The method of Martynoff[127,128] was used in an attempt to prepare 4-chloro-2,2'-dimethoxyazobenzene. A mixture of 3-chloro-6-nitroanisole (0.3 g) (see below) and *o*-anisidine (0.24 g) was heated to *c*. 200° with an oil bath. Sodium hydroxide (0.5 g) was added to the well stirred mixture over a 15 min period, and after this, heating was continued for a further 10 min. On cooling, the black mass was stirred with several portions of hot light petroleum until

no further colored material was extracted. The residue obtained after evaporation of the light petroleum was chromatographed on alumina (light petroleum). No 4-chloro-2,2'-dimethoxyazobenzene was eluted from the column.

3-Chloro-6-nitroanisole (78)

This compound was synthesised from *m*-chlorophenol by a method described in the literature.[129] The 3-chloro-6-nitroanisole was recrystallized from light petroleum and obtained as buff needles, m.p. 72-73° (lit.[129] 70.5-71.5°).

2-Methoxyazobenzene (79)

This compound was prepared by condensation of *o*-anisidine with nitrobenzene in the presence of excess sodium hydroxide.[127] The crude product was chromatographically purified (alumina-light petroleum). 2-Methoxyazobenzene was obtained as a red crystalline solid, m.p. 40-41° (lit.[127] 41°).

4-Chloro-2'-methoxyazobenzene (80)

p-Chloroaniline (1.0 g) and *o*-nitroanisole (1.0 g) were condensed in the presence of sodium hydroxide (0.5 g), the experimental procedure being essentially similar to that involved in the preparation of 2-methoxyazobenzene. The dark colored reaction mixture was stirred with several portions of hot light petroleum until no further

colored material was extracted. The combined extracts were dried, evaporated to dryness, and the remaining residue chromatographed (alumina-light petroleum). The first red-orange band was eluted with ether-light petroleum (10% v:v) and evaporation of the solvent left a red oil which slowly crystallized. Recrystallization from light petroleum afforded red needles of *4-chloro-2'-methoxyazobenzene* (0.34 g; 18%), m.p. 75.5-76.0° (Found: C, 62.9; H, 4.46; N, 11.2; O, 6.9. $C_{13}H_{11}ClN_2O$ requires C, 63.3; H, 4.49; N, 11.4; O, 6.5%). (See appendix for the mass spectrum)

4-Chloro-2-methoxyazobenzene (81)

This compound was prepared by condensation of aniline (0.2 g) with 3-chloro-6-nitroanisole[129] (0.3 g) in the presence of sodium hydroxide (0.2 g), the experimental details being similar to those in the above-mentioned synthesis of 4-chloro-2'-methoxyazobenzene. The crude product was chromatographically purified (alumina-ether-light petroleum) and the *4-chloro-2-methoxyazobenzene* (0.12 g; 30%) so obtained, formed red-orange needles when recrystallized from light petroleum, m.p. 80-81°. The infrared spectrum of the compound (Nujol) showed bands at 1587, 1580, 1480, 1250, 1017, 870, 827, 798, 755 and 680 cm^{-1}. (See appendix for the mass spectrum.)

3,3-Dimethoxyazobenzene (82)

m-Nitroanisole was reduced with zinc and alkali, the experimental procedure being essentially similar to that involved

in the preparation of 4,4'-dimethoxyazobenzene. After recrystallization from light petroleum, 3,3-dimethoxyazobenzene was obtained as yellow-orange plates, m.p. 77-78° (lit.[130,132] 73-74°, 78°).

4-Chloro-3,3'-dimethoxyazobenzene (83)

By a similar method to that described[127] for the preparation of 2-methoxyazobenzene, 2-chloro-5-nitroanisole (1.9 g) (see below) and *m*-anisidine (1.5 g) were condensed at 200° in the presence of dry powdered sodium hydroxide (1.2 g). The crude reaction product was extracted with ether, the ethereal solution then being dried and evaporated to dryness. The remaining residue was chromatographed on a column of alumina.

Elution with ether-light petroelum (15% v:v) resulted in an orange band being collected as the first fraction. Removal of the solvent left *4-chloro-3,3'-dimethoxyazobenzene* (0.72 g; 32%) which, after recrystallization from light petroleum, was obtained as orange plates, m.p. 96-97° (Found: C, 61.1; H, 4.71; N, 10.2; O, 11.4. $C_{14}H_{13}ClN_2O_2$ requires C, 60.8; H, 4.73; N, 10.1; O, 11.6%). (See appendix for the mass spectrum.)

6-Chloro-3,3'-dimethoxyazobenzene (84)

This compound was prepared by a process essentially similar to that employed in the foregoing synthesis of 4-chloro-3,3'-dimethoxyazobenzene. 4-Chloro-3-nitroanisole (1.9 g) (see below) was condensed with *m*-anisidine. The resulting *6-chloro-3,3'-*

dimethoxyazobenzene was chromatographically purified (alumina-light petroleum-ether) and recrystallized from light petroleum to give orange crystals (0.41 g; 15%), m.p. 73-74° (Found: C, 60.8; H, 4.76; N, 10.3. $C_{14}H_{13}ClN_2O_2$ requires C, 60.8; H, 4.73; N, 10.1%). (See appendix for the mass spectrum.)

2-Chloro-5-nitroanisole (85)

This compound was synthesised in several steps from *o*-anisidine according the the method of van Erp.[133] 2-Chloro-5-nitroanisole was obtained as pale yellow crystals, m.p. 81-82° (lit.[133] 82.5°).

4-Chloro-3-nitroanisole (86)

2-Nitro-4-methoxyaniline was prepared from *p*-anisidine according to the method described by Fanta and Tarbell.[134] A solution of 2-nitro-4-methoxyphenyldiazonium chloride was then prepared and slowly added to a warm solution of cuprous chloride in concentrated hydrochloric acid[131] and the final reaction mixture was steam distilled. After cooling and filtering the distillate, 4-chloro-3-nitroanisole was obtained as pale yellow crystals, m.p. 44-45° (lit.[133,135] 43°, 45°).

3-Methoxyazobenzene (87)

This compound was prepared from nitrobenzene and *m*-anisidine by the method of Martynoff.[127] The crude reaction mixture was

distilled and the fraction, b.p. 160-160.5°/2.0 mm, was collected as a red oil which slowly crystallized. Recrystallization from light petroleum gave orange crystals of 3-methoxyazobenzene, m.p. 32-33° (lit.[127] 33°).

4-Chloro-3'-methoxyazobenzene (88)

Using an experimental procedure similar to that involved in the above preparation of 3-methoxyazobenzene, *p*-chloroaniline (0.75 g) and *m*-nitroanisole (0.75 g) were condensed in the presence of sodium hydroxide (0.5 g). The crude product was chromatographically purified (alumina-light petroleum). The *4-chloro-3'-methoxyazobenzene* so obtained (first fraction) was recrystallized from light petroleum to give yellow-orange crystals (0.41 g; 27%), m.p. 89-90° (Found: C, 63.6; H, 4.64; N, 11.5. $C_{13}H_{11}ClN_2O$ requires C, 63.3; H, 4.49; N, 11.4%). (See appendix for the mass spectrum.)

4-Chloro-3-methoxyazobenzene (89)

This compound was prepared from 2-chloro-5-nitroanisole[133] (1.9 g) and aniline (1.1 g), the experimental procedure for the synthesis and purification being essentially similar to that involved in the preparation of 4-chloro-3,3'-dimethoxyazobenzene. The *4-chloro-3-methoxyazobenzene* (0.51 g; 20%) was recrystallized from light petroleum to give orange plates, m.p. 78-79° (Found: C, 63.1; H, 4.57; N, 11.6. $C_{13}H_{11}ClN_2O$ requires C, 63.3; H, 4.49; N, 11.35%). (See appendix for the mass spectrum.)

3-Chloroazobenzene (90)

This compound was available from previous work.[94]

3,4'-Dichloroazobenzene (91)

p-Chloroaniline and *m*-chloronitrobenzene were condensed in the presence of dry powdered sodium hydroxide, the procedure being essentially similar to that used in the preparation of 2-methoxyazobenzene. The dark colored reaction mixture was stirred with several portions of hot light petroleum until no further colored material was extracted by the solvent. Evaporation of the light petroleum left a dark residue, which was chromatographed (alumina-light petroleum). The first fraction afforded *3,4'-dichloroazobenzene*, which after recrystallization from methanol, was obtained as yellow-orange needles, m.p. 113-114° (Found: C, 57.5; H, 3.25. $C_{12}H_8Cl_2N_2$ requires C, 57.4; H, 3.21%). (See appendix for the mass spectrum.)

2,3'-Dichloroazobenzene (92)

This compound was prepared from *o*-chloroaniline and *m*-chloronitrobenzene, the experimental details being similar to those employed in the foregoing synthesis of 3,4'-dichloroazobenzene. The crude product was chromatographically purified (alumina-light petroleum) and after recrystallization from methanol, *2,3'-dichloroazobenzene* was obtained as orange needles, m.p. 51-52° (Found: C, 57.2; H, 3.35. $C_{12}H_8Cl_2N_2$ requires C, 57.4; H, 3.21%). (See appendix for the mass spectrum.)

3,4-Dichloroazobenzene (93)

3,4-Dichloroaniline (1.6 g) (see below) was dissolved in warm glacial acetic acid (5 ml) and nitrosobenzene (1.07 g) was added. The mixture was heated (95-100°) for 8 hr and then poured into water. The aqueous solution was extracted with light petroleum and the separated extract was then shaken with sodium carbonate solution. After drying, the light petroleum was evaporated and the remaining residue chromatographed on alumina (light petroleum). The first fraction yielded *3,4-dichloroazobenzene* (1.5 g; 60%) which, after recrystallization from methanol, was obtained as yellow-orange needles m.p. 85-86° (Found: C, 57.0; H, 3.13. $C_{12}H_8Cl_2N_2$ requires C, 57.4; H, 3.21%). (See appendix for the mass spectrum.)

3,4-Dichloroaniline

This compound was prepared by reduction of 3,4-dichloronitrobenzene with iron powder and concentrated hydrochloric acid.[136] The product was purified by recrystallization (aqueous ethanol) and obtained as colorless plates, m.p. 70-71° (lit.[137] 71.5°).

3- and 4-Methylazobenzenes (94 and 95)

These compounds were prepared by condensation of the appropriate toluidine (2.5 g) with nitrosobenzene (2.5 g) in glacial acetic acid (10 ml).[44] 3-Methylazobenzene was purified by distillation and obtained as a bright red oil, b.p. 120-122°/0.7 mm (lit.[44]

180-185°/14 mm). The 4-methylazobenzene was chromatographically purified (alumina-light petroleum) and finally recrystallized from methanol, m.p. 70-71° (lit.[138] 71-72°).

4-Chloro-4'-methylazobenzene (96)

p-Chloroaniline and *p*-nitrotoluene were condensed in the presence of dry powdered sodium hydroxide, the procedure being essentially similar to that used in the preparation of 2-methoxyazobenzene. The reaction mixture was stirred with several portions of hot light petroleum until no more colored material was extracted by the solvent. Evaporation of the light petroleum left a dark residue and this was subjected to chromatography (alumina-light petroleum). The first fraction afforded 4-chloro-4'-methylazobenzene, which after recrystallization from light petroleum was obtained as orange prisms, m.p. 155-156° (lit.[139] 149-150°). (See appendix for the mass spectrum.)

2-Chloro-4-methylazobenzene (97)

This compound was prepared by condensation of 3-chloro-*p*-toluidine (see below) with nitrosobenzene in glacial acetic acid. The reaction mixture was heated at 95-100° for 16 hr. Extraction of the product and subsequent purification was effected according to the method already described for the preparation of 3,4-dichloroazobenzene. After recrystallization from methanol, *2-chloro-4-methylazobenzene* was obtained as orange crystals, m.p. 44-45° (Found: C, 67.5; H, 4.92. $C_{13}H_{11}ClN_2$ requires C, 67.7; H, 4.81%). (See appendix for the mass spectrum.)

*3-Chloro-*p*-toluidine*

This compound was prepared by chlorination of acetyl—*p*-toluidine.[140] After distillation, 3-chloro-*p*-toluidine was obtained as a colorless liquid, b.p. 108-112°/20 mm (lit.[141] 223-224°/760 mm).

3- and 4-Nitroazobenzenes (99 and 100)

These compounds were prepared by condensation of the appropriate nitroaniline with nitrosobenzene in glacial acetic acid.[46] In each case the products were chromatographically purified (alumina-light petroleum). After recrystallization from ethanol, 3-nitroazobenzene was obtained as red-orange crystals, m.p. 94-95° (lit.[142] 95.5-96°). The 4-nitroazobenzene was recrystallized twice from methanol to give red-pink plates, m.p. 134-135° (lit.[143] 134-135°).

4-Chloro-4'-nitroazobenzene (101)

p-Nitroaniline (1.4 g) and *p*-chloronitrobenzene (1.6 g) were heated together (170-180°) and dry powdered sodium hydroxide (0.3 g) was added to the mixture over a 10 min period. (Strict temperature control was necessary as a violent reaction occurred when the temperature of the reaction mixture was allowed to exceed 190°.) The cooled reaction mixture was stirred with portions of hot light petroleum until no more colored material was extracted. After drying the extract, the light petroleum was evaporated, and the remaining dark colored residue chromatographed (alumina-light petroleum)

The first fraction afforded unchanged *p*-chloronitrobenzene. Elution with ether-light petroleum (5% v:v) gave a second fraction which yielded *4-chloro-4'-nitroazobenzene* (0.04 g; 1.5%). Recrystallization (light petroleum) gave orange crystals, m.p. 173-174° (Found: C, 55.5; H, 3.32. $C_{12}H_8ClN_3O_2$ requires C, 55.1; H, 3.08%). (See appendix for the mass spectrum.)

2-Chloro-4'-nitroazobenzene (102)

This compound was prepared and purified in a similar manner to that described for the preparation of 4-chloro-4'-nitroazobenzene. *o*-Chloronitrobenzene (1.6 g) was used instead of *p*-chloronitrobenzene. After recrystallization from light petroleum, *2-chloro-4'-nitroazobenzene* (0.06 g; 2.3%) was obtained as orange crystals, m.p. 130-131° (Found: C, 54.9; H, 3.33. $C_{12}H_8ClN_3O_2$ requires C, 55.1; H, 3.08%). (See appendix for the mass spectrum.)

Reaction Sequences

Photoreaction of 4,4'-Dimethoxyazobenzene (60)

4,4'-Dimethoxyazobenzene (1.0 g) was irradiated in acetyl chloride solution (100 ml) for 2 hr. The material remaining after evaporation of the acetyl chloride was dissolved in ether, and a considerable amount of ether-insoluble polymeric material was removed by filtration. The ethereal solution was washed with sodium carbonate solution, dried, evaporated to dryness, and the resulting residue chromatographed on silica (light petroleum).

The first fraction was eluted with ether-light petroleum (15% v:v) and afforded white needles of *N*,*N*'-diacetyl-2,6-dichloro-4-methoxyaniline (61) (0.021 g; 0.9%), m.p. 105-106°. The infrared spectrum of the compound (Nujol) showed bands at 1705-1725 (C=O), 1587, 1270, 1240, 1205,1083, 1040, 1005, 833, and 800 cm^{-1} (See appendix for the mass spectrum.)

The second fraction was eluted with ether-light petroleum (30% v:v) and yielded *N*,*N*'-diacetyl-2-chloro-4-methoxyaniline (62) (0.13 g; 6.5%) as a colorless oil, b.p. 105-108°/0.1 mm. The infrared spectrum of the compound (film) showed bands at 1700-1720 (C=O), 1600, 1495, 1365, 1285, 1240, 1065, 1030, 1005, and 855 cm^{-1}. (See appendix for the mass spectrum.)

From the third fraction, which was eluted with ether-light petroleum (40% v:v), white crystals of *N*-acetyl-2-chloro-4-methoxyaniline (63) (0.28 g; 17%) were obtained. Recrystallization from ether gave white needles, m.p. 113.5-114.5° (lit.[124] 114°). The infrared spectrum (Nujol) showed bands at 3,300 (N-H), 1655 (C=O), 1530, 1360, 1275, 1210, 1050, 1035, 870, and 815 cm^{-1}. (See appendix for the mass spectrum.)

The fourth fraction was eluted with ether-light petroleum (70% v:v) and afforded a colorless glass (0.09 g) which was not identified. It was subjected to alkaline hydrolysis and oxidation (see below).

The final fraction was eluted with ether-light petroleum (90% v:v) and yielded *p*-acetanisidide (64) (0.22 g; 16%) which after two recrystallizations from ether was obtained as white plates, m.p. 125-127° (lit.[125] 130-132°). The infrared spectrum of the compound was identical with that of an authentic sample; and the melting point was not depressed on admixture with authentic material.

Alkaline Hydrolysis of the Unidentified Colorless Glass

The unidentified colorless glass (0.07 g) (fourth fraction of the foregoing experiment) was boiled under reflux for 6 hr in aqueous methanolic potassium hydroxide solution. The final mixture was diluted with water and extracted with ether; the ethereal extract was then dried and evaporated to dryness. The remaining residue was chromatographed on alumina (light petroleum).

Elution with ether-light petroleum (30% v:v) afforded 2-chloro-4,4'-dimethoxyazobenzene (0.006 g), which after recrystallization from light petroleum, gave yellow-orange crystals, m.p. 114-115° (alone or admixed with the authentic sample). The infrared spectrum was identical with that of the authentic sample.

The second fraction was eluted with ether and yielded a brown oil (0.03 g), the infrared spectrum of which, was identical with that of an authentic sample of *p*-anisidine (66).

Photoreaction of 4-Methoxyazobenzene (69)

A solution of 4-methoxyazobenzene (1.0 g) in acetyl chloride (100 ml) was irradiated for 2 hr. After removal of the excess acetyl chloride, a colorless glass remained, and this was dissolved in ether. The ethereal solution was washed with sodium carbonate solution, dried, and finally evaporated to dryness. The remaining residue was subjected to chromatography on a column of silica (light petroleum).

The first fraction was eluted with ether-light petroleum (15% v:v) and afforded *N*,*N*-diacetyl-2,6-dichloro-4-methoxyaniline (61) (0.04 g; 1.5%) as white needles, m.p. 105-107°. This compound was identified (mixed melting point and the infrared spectrum) by comparison with a previously characterized sample (from the photoreaction of 4,4'-dimethoxyazobenzene).

Elution with ether-light petroleum (25% v:v) gave the second fraction and this yielded *N*,*N*-diacetyl-2-chloro-4-methoxyaniline (62) (0.055 g; 2.4%) as a viscous oil, b.p. 105-108° at 0.1 mm. Again it was shown to be identical (infrared spectrum) with the previously chracterized sample obtained from the photoreaction of 4,4'-dimethoxyazobenzene.

The third fraction was eluted with ether-light petroleum (40% v:v) and gave a colorless glass (1.36 g), b.p. 160-165°/0.05 mm. During distillation of the glass, white crystals of acetanilide (0.05 g; 4%), m.p. 110-112° (lit. 114°) sublimed and were collected separately. The melting point was not depressed on admixture with an authentic sample; and the infrared spectrum was identical with that of an authentic specimen.

Alkaline Hydrolysis of the Photoproduct

A portion of the colorless glass (0.93 g) obtained from the above experiment was dissolved in aqueous methanolic potassium hydroxide, and the solution boiled under reflux for 6 hr. At the end of this period air was bubbled through the solution for 2 hr,

the mixture then diluted with water and finally extracted with ether. Evaporation of the ether gave an orange oil, which was chromatographed on alumina (light petroleum).

The only product eluted from the column (ether-light petroleum, 5% v:v) was obtained as an orange oil which slowly crystallized. Gas chromatography of the product using a 12 ft x $\frac{1}{8}$ in. Carbowax 20M column with nitrogen as carrier gas (flow rate *c*. 28 ml/min), gave two peaks, the area ratios of which were *c*. 25:1.

Recrystallization of the product from light petroleum gave 2-chloro-4-methoxyazobenzene (0.61 g; 88%), m.p. 54-56° (alone or admixed with the authentic specimen). The infrared spectrum was identical with that of the authentic sample. (See appendix for the mass spectrum.)

The minor product remaining in the mother liquors was not identified.

Photoreaction of 2,2'-Dimethoxyazobenzene (74)

2,2'-Dimethoxyazobenzene (0.84 g) was irradiated in acetyl chloride solution (84 ml) for $3\frac{1}{2}$ hr. The residue remaining after evaporation of the excess acetyl chloride was dissolved in ether, and the ethereal solution washed with sodium carbonate solution. Removal of the ether left a thick oil which slowly crystallized, and this was chromatographed on silica (light petroleum).

Elution with ether-light petroleum (0-35% v:v) gave small quantities of several unidentified oils.

Further elution (ether-light petroleum, 50% v:v) afforded *N*-acetyl-4-chloro-2-methoxyaniline (75) (0.03 g; 2.2%), which, after two recrystallizations from light petroleum was obtained as white crystals, m.p. 145-147°. (See appendix for the mass spectrum.)

The second main fraction was eluted with ether-light petroleum (80% v:v) and yielded a colorless glass, which after crystallization from ether gave white needles of N,N'-*diacetyl-4-chloro-2,2'-dimethoxyhydrazobenzene* (76) (1.0 g; 79%), m.p. 130-131° (Found: C, 59.5; H, 5.12; N, 7.5; O, 17.6. $C_{18}H_{20}ClN_2O_4$ requires C, 59.6; H, 5.28; N, 7.7; O, 17.6%). The infrared spectrum of the compound (Nujol) showed bands at 1695 (C=O), 1675 (C=O), 1495, 1327, 1272, 1232, 1020, 865, 835, and 760 cm^{-1}. (See appendix for the mass spectrum.)

Alkaline Hydrolysis of N,N'-*Diacetyl-4-chloro-2,2'-dimethoxyhydrazobenzene*

N,N'-Diacetyl-4-chloro-2,2'-dimethoxyhydrazobenzene (0.58 g) in aqueous methanolic potassium hydroxide was boiled under reflux for 5 hr. The mixture was diluted with water, extracted with ether, and the ethereal solution shaken with sodium hypobromite solution[126] to oxidize any remaining hydrazo compound. (Darkening of the ethereal solution occurred at this stage and it appeared that the sodium hypobromite was oxidizing the azo compound) The ethereal solution was dried, evaporated to dryness, and the remaining dark colored product was chromatographed on alumina (light petroleum).

Elution with ether-light petroleum (5% v:v) afforded *4-chloro-2,2'-dimethoxyazobenzene* (0.22 g; 50%) as red orange needles, m.p.

121-122° (Found: C, 60.5; H, 4.73; N, 10.1; O, 11.8. $C_{14}H_{13}ClN_2O_2$ requires C, 60.7; H, 4.73; N, 10.1; O, 11.6%). The infrared spectrum (Nujol) showed bands at 1592, 1480, 1250, 1235, 1150, 1015, 870, 828, 795 and 740 cm^{-1}. (See appendix for the mass spectrum.)

A considerable quantity of dark material remained at the top of the column.

Photoreaction of 2-Methoxyazobenzene (79)

A solution of 2-methoxyazobenzene (0.5 g) in acetyl chloride (50 ml) was irradiated for 2 hr. The excess acetyl chloride was distilled off and the remaining residue dissolved in ether. After shaking the ethereal solution with sodium carbonate solution, the ether layer was separated, dried, and evaporated to dryness. The residue was chromatographed on a column of silica (ether-light petroleum

Elution with ether-light petroleum (30-70% v:v) yielded a colorless glass (0.74 g), b.p. 165-168°/0.05 mm which failed to crystallize. The colorless glass was subjected to alkaline hydrolysis and oxidation (see below).

Alkaline Hydrolysis of the Photoproduct

A portion of the colorless glass (0.42 g) obtained in the foregoing experiment was boiled under reflux for 5 hr in an aqueous methanolic potassium hydroxide solution. Air was passed through the

solution for an additional $1\frac{1}{2}$ hr and then water was added to precipitate the products. The mixture was extracted with ether, the ethereal solution then dried, and evaporated to dryness. The remaining residue was passed through a column of alumina and eluted with light petroleum.

Only a single orange band was eluted and after reducing the volumn of this fraction to *c*. 2 ml, a portion (1 ml) was removed and evaporated to dryness. The residue was dissolved in chloroform (50% w:v) and subjected to preparative gas chromatography at 230° using a 12 ft by $\frac{1}{4}$ in. 20% Carbowax 20 M column with nitrogen as carrier gas (flow rate *c*. 160 ml/min). Two very broad and only partially separated peaks were obtained, their retention times being *c*. 3 hr. The fraction corresponding to the peak having the longest retention time was recrystallized several times from light petroleum, and yielded 4-chloro-2'-methoxyazobenzene as red-orange needles, m.p. 75-76° (alone or admixed with the authentic sample). The infrared spectrum was identical with that of the authentic sample. The fraction corresponding to the peak with the shorter retention time could not be purified by recrystallization, and was shown by comparisons of infrared spectra to be a mixture of 4-chloro-2'-methoxyazobenzene and 4-chloro-2-methoxyazobenzene. Gas chromatography (see below) of the portion of solution set aside (see above) showed that the ratio of 4-chloro-2'-methoxyazobenzene to 4-chloro-2-methoxyazobenzene was 68:32.

Gas Chromatography

Analytical gas chromatography was carried out with a 12 ft by $\frac{1}{8}$ in. 3% Carbowax 20M column at 220° and with nitrogen as carrier gas (flow rate *c.* 28 ml/min). 4-Chloro-2'-methoxyazobenzene and 4-chloro-2-methoxyazobenzene as individual pure samples or standard mixtures, and samples of the mixed products (as used for peak identification, calibration, and analysis respectively) were injected as 1% (w:v) solution in acetone. The following retention times were observed: 4-chloro-2-methoxyazobenzene (9 min 53 sec); and 4-chloro-2'-methoxyazobenzene (10 min 36 sec). A calibration graph for estimation of the isomer ratio was prepared by the method described in Part I.1.

Photoreaction of 3,3'-Dimethoxyazobenzene (82)

3,3'-Dimethoxyazobenzene (1.0 g) was irradiated in acetyl chloride solution (100 ml) for $\frac{3}{4}$ hr. The residue remaining after evaporation of the excess acetyl chloride was dissolved in ether, and the ethereal solution washed with sodium carbonate solution. Removal of the ether left a thick oil which was chromatographed on silica (light petroleum).

Only one broad band was eluted from the column and this was collected in two fractions: fraction A (0.7 g) (ether-light petroleum 40-50% v:v); and fraction B (0.7 g) (ether-light petroleum 50-100% v:v). Both fractions were separately subjected to alkaline hydrolysis and oxidation (see below).

Alkaline Hydrolysis of Photoproducts

Fractions (A) and (B) from the above photoreaction were dissolved in aqueous methanolic potassium hydroxide solution and boiled under reflux for 6 hr. Air was bubbled through the solutions for a further 2 hr and then the products were precipitated by dilution with water. The mixtures were extracted with ether, the ethereal solution dried, and then evaporated to dryness. After chromatography (alumina-light petroleum-ether), the product from fraction (A) was obtained as orange crystals (0.32 g), m.p. 58-80°, and the product from fraction (B) was also obtained as orange crystals (0.33 g), m.p. 84-88°. The product, m.p. 58-80°, could not be purified by recrystallization, but the product, m.p. 84-88°, was obtained pure after two recrystallizations from light petroleum. The latter compound was identified as 4-chloro-3,3'-dimethoxyazobenzene, m.p. 96-97°, by comparison (mixed melting point and the infrared spectrum) with the authentic sample.

The product from fraction (A) and the remaining product from fraction (B) were combined and subjected to preparative gas chromatography using a 5 ft by $\frac{1}{4}$ in. 20% SE52 column at 270°, and nitrogen as carrier gas (flow rate *c.* 200 ml/min). The mixture was resolved into two separate peaks and the corresponding fractions were collected. The first fraction afforded 3,3'-dimethoxyazobenzene (0.06 g; 6%), m.p. 73-75° (alone or admixed with an authentic sample) and the second fraction (longer retention time) yielded a mixture of isomeric chloro-3,3'-dimethoxyazobenzenes. Attempts to resolve the latter mixture with a 5% QF-1 column, a 3% Carbowax 20M column, and a 5% SE52 column were unsuccessful.

Photoreaction of 3-Methoxyazobenzene (87)

3-Methoxyazobenzene (0.8 g) was irradiated in acetyl chloride solution (80 ml) for 3 hr. After evaporation of the excess acetyl chloride, the remaining residue was dissolved in ether and the ethereal solution washed with sodium carbonate solution. Evaporation of the ether left a viscous oil (1.2 g) which was chromatographed on silica (light petroleum). The only band eluted from the column was divided into the following fractions: fraction A (0.67 g; eluted with ether-light petroleum 30-40% v:v); and fraction B (0.53 g; eluted with light petroleum 40-75% v:v). Fractions (A) and (B) were separately subjected to alkaline hydrolysis and oxidation (see below).

Alkaline Hydrolysis of Photoproducts

Fractions (A) and (B) were boiled under reflux for 6 hr in an aqueous methanolic potassium hydroxide solution, and air was bubbled through the solutions for a further 2 hr. After dilution with water, the mixture from the hydrolysis of fraction (A) was filtered and afforded 4-chloro-3'-methoxyazobenzene (0.19 g) which after recrystallization from light petroleum gave orange plates, m.p. 86-88° (alone or admixed with the authentic sample). The infrared spectrum was identical with that of the authentic compound. The filtrate was combined with the reaction products from fraction (B) and the mixture extracted with ether. After drying the ethereal

solution, the ether was evaporated and the remaining residue (0.52 g) was chromatographed (alumina-light petroleum). Only one broad orange band was eluted and after reducing the volume of this fraction to *c*. 2 ml, a portion (1 ml) was subjected to preparative gas chromatography using a 5 ft by $\frac{1}{4}$ in. 20% SE52 column at 250° with nitrogen as carrier gas (flow rate *c*. 200 ml/min). Two peaks were observed and the corresponding fractions collected. 3-Methoxyazobenzene (0.02 g; 2.5%) was obtained from the first fraction (shorter retention time) and the infrared spectrum of this compound was identical with that of an authentic sample. The second fraction afforded a mixture of isomeric chloro-3-methoxyazobenzene. Gas chromatography (see below) showed this fraction consisted of 4-chloro-3'-methoxyazobenzene and 4-chloro-3-methoxyazobenzene in the ratio of 36.5:63.5.

Gas chromatography (see below) of the portion of solution set aside after chromatography of the hydrolysis products showed the ratio of 3-methoxyazobenzene to chloromethoxyazobenzenes in the mixture was 9:91.

Several recrystallizations (light petroleum) of the remainder of the fraction from which 3-methoxyazobenzene had been separated by preparative gas chromatography, afforded orange plates of 4-chloro-3-methoxyazobenzene, m.p. 77-79° (alone or admixed with the authentic sample). The infrared spectrum was identical with that of the authentic compound.

The total overall yields (calculated from product ratios) were as follows: 3-methoxyazobenzene (0.05 g; 6%); 4-chloro-3'-methoxy-

azobenzene (0.30 g; 32%); and 4-chloro-3-methoxyazobenzene (0.36 g; 39%). The isomer ratio of the latter two products was 45:55.

Gas Chromatography

A 12 ft by $\frac{1}{8}$ in. 3% Carbowax 20M column at 200° and with nitrogen as carrier gas (flow rate *c.* 28 ml/min) was used for analysis of the mixture of 4-chloro-3'-methoxyazobenzene and 4-chloro-3-methoxyazobenzene. Using authentic samples of these compounds, the procedure for the analysis was essentially similar to that employed for the analysis of a mixture of 2- and 4-chloroazobenzenes (see Experimental Part I.1).

The yield of 3-methoxyazobenzene was determined by gas chromatography using a 12 ft by $\frac{1}{4}$ in. 5% SE52 column at 250° with nitrogen as carrier gas (flow rate *c.* 100 ml/min). A calibration graph was prepared from standard mixtures of 3-methoxyazobenzene and 4-chloro-3'-methoxyazobenzene and the analysis carried out by a procedure similar to that used for the estimation of the isomer ratio of 2- and 4-chloroazobenzenes (see Experimental Part I.1).

Photoreaction of 3-Chloroazobenzene (90)

3-Chloroazobenzene (0.2 g) was irradiated in acetyl chloride solution (20 ml) for 2 hr. The material remaining after removal of the acetyl chloride was dissolved in an aqueous methanolic potassium hydroxide solution and boiled under reflux for 5 hr. After diluting

with water, the reaction mixture was extracted with ether, the ethereal solution dried, and then evaporated to dryness. The remaining residue was chromatographed on alumina (light petroleum). Only a single orange band was eluted and removal of the solvent left an orange oil (0.20 g) which slowly crystallized. The product was dissolved in acetone (1% w:v) and subjected to gas chromatography at 190° using a 12 ft by $\frac{1}{4}$ in. 5% QF-1 column with nitrogen as the carrier gas (flow rate *c*. 100 ml/min). Only a large and small peak were observed. A similar result was obtained when the above process was repeated using a 12 ft by $\frac{1}{8}$ in. 3% Carbowax 20M column at 210° (flow rate *c*. 28 ml/min). In both cases the small peak had an identical retention time to an authentic sample of 2,3'-dichloroazobenzene. Only a single symmetrical peak was obtained when a mixture of authentic 3,4- and 3,4'-dichloroazobenzene was subjected to gas chromatography using the above columns.

Several recrystallizations (light petroleum) of the chromatographed hydrolysis products, afforded orange needles (0.02 g) of 3,4'-dichloroazobenzene, m.p. 112-114° (alone or admixed with the authentic specimen). The infrared spectrum was identical with that of the authentic compound.

Photoreaction of 3-Methylazobenzene (94)

A solution of 3-methylazobenzene (0.3 g) in acetyl chloride (30 ml) was irradiated for 1 hr. The residue which remained after

removal of the acetyl chloride was subjected to alkaline hydrolysis and the resulting products were chromatographed, the experimental details being similar to those described in the foregoing reaction of 3-chloroazobenzene. Only a single orange band was eluted and removal of the solvent afforded an orange oil (0.34 g) which slowly crystallized. This product was subjected to gas chromatography using the same columns under similar conditions as employed for the attempted separation of products from the above-mentioned reaction of 3-chloroazobenzene. Once again, however, the products could not be resolved.

Photoreaction of 4-Methylazobenzene (95)

4-Methylazobenzene (0.30 g) was irradiated in acetyl chloride solution (30 ml) for $1\frac{1}{2}$ hr. The material remaining after removal of the acetyl chloride was dissolved in aqueous methanolic potassium hydroxide and boiled under reflux for 6 hr. The reaction mixture was diluted with water, extracted with ether, and after drying, the ethereal solution was evaporated to dryness. The remaining residue was chromatographed on alumina (light petroleum). One broad orange band was eluted and removal of the solvent left an orange oil (0.3 g) which slowly crystallized. Gas chromatography (see below) showed that the mixture consisted of 4-chloro-4'-methylazobenzene and 2-chloro-4-methylazobenzene in the ratio of 26.5:73.5.

Recrystallization (light petroleum) of the chromatographed material afforded yellow crystals of the less soluble 4-chloro-4'-

methylazobenzene, m.p. 70-71° (alone or admixed with the authentic specimen). The infrared spectrum was identical with that of the authentic compound. Evaporation of the mother liquors left an oil, the infrared spectrum of which was identical with that of authentic 2-chloro-4-methylazobenzene.

Gas Chromatography

The product was dissolved in acetone (1% w:v) and subjected to gas chromatography at 190° using a 12 ft by $\frac{1}{8}$ in. 3% Carbowax 20M column, nitrogen being using as carrier gas (flow rate *c*. 28 ml/min). Two peaks were observed with the following retention times: 5 min 53 sec, and 6 min 52 sec. These retention times were identical to those observed with authentic samples of 4-chloro-4'-methylazobenzene and 2-chloro-4-methylazobenzene respectively, when these were chromatographed under the same conditions. The above process was repeated using a 12 ft by $\frac{1}{4}$ in. 5% QF-1 column at 198° with nitrogen as carrier gas (flow rate *c*. 100 ml/min). The retention times in this case were, 8 min 10 sec, and 9 min 40 sec, which were found to be identical with those of authentic 4-chloro-4'-methylazobenzene and the 2-chloro-4-methyl isomer respectively. Analysis of the mixture was then carried out (using the QF-1 column) in the same manner as described for 2- and 4-chloroazobenzenes (see Experimental Part I.1).

Photoreactions of 3- and 4-Nitroazobenzenes

A solution of 4-nitroazobenzene (0.2 g) in acetyl chloride (20 ml) was irradiated for $1\frac{1}{2}$ hr. Removal of the acetyl chloride left a yellow residue which was dissolved in ether. The ethereal solution was washed with sodium carbonate solution, dried, and evaporated to dryness. The remaining residue was chromatographed on silica (ether-light petroleum). Only a single broad band was eluted (ether-light petroleum 80% v:v); and removal of the solvent left a pale yellow glass (0.22 g). The infrared spectrum (film) showed bands *inter alia* at 1675-1710 (C=O), 1365 and 1340-1260 cm^{-1}.

3-Nitroazobenzene (0.2 g) was irradiated in acetyl chloride solution (20 ml) for 6 hr. The product was then isolated and purified, the experimental details being essentially similar to those described for the photoreaction of 4-nitroazobenzene. The photoproducts from both of the above reactions were subjected to alkaline hydrolysis.

Alkaline Hydrolysis of the Photoproducts

The photoproducts were dissolved in aqueous methanolic potassium hydroxide solution and boiled under reflux for 3 hr. The final reaction mixtures contained a considerable quantity of precipitated material and this could not be dissolved in ether. The ether-insoluble material was filtered, washed with water, and finally dried to give an orange solid in each case. After extraction

of the filtrates with ether, the ethereal solution was dried and evaporated to dryness. Only very small amounts of residue remained.

A process similar to that described above was repeated on another sample of photoproduct obtained by irradiation of 4-nitroazobenzene (0.19 g) in acetyl chloride (19 ml). In this case however, the hydrolysis was carried out under an atmosphere of nitrogen, and the mixture was warmed only for a 10 min period. The orange precipitate formed 3 min after dissolving the photoproduct in the aqueous methanolic potassium hydroxide solution. Filtration of the reaction mixture and extraction of the filtrate with ether yielded an ether-insoluble compound (0.1 g) and an ether-soluble compound (0.073 g). The ether-soluble material was chromatographed (alumina-light petroleum).

Elution with ether-light petroleum (5% v:v) gave the first fraction, and removal of the solvent left orange crystals (0.053 g). Recrystallization (acetone) afforded orange needles of 4-chloro-4'-nitroazobenzene (0.04 g), m.p. 170-172° (alone or admixed with the authentic sample). The infrared spectrum was identical with that of the authentic compound. Evaporation of the mother liquors afforded 2-chloro-4'-nitroazobenzene (0.008 g), the infrared spectrum being identical with that of the authentic sample.

The second fraction (ether-light petroleum 25% v:v) yielded yellow crystals (0.005 g) which were recrystallized from acetone, m.p. 200-208°. The mass spectrum showed a molecular ion of *m/e* 458. (See appendix).

The ether-insoluble material had m.p. >230° and the mass spectrum (see appendix) showed a molecular ion of *m/e* 474. (No attempt was made to characterize this material further since it probably consisted of an inseparable mixture of isomers).

II. DARK REACTION OF *CIS*-AZOBENZENE WITH ACETYL CHLORIDE

Materials and Reference Compounds

cis-Azobenzene was prepared by the method described by Badger, Drewer, and Lewis.[50] Recrystallization from cold light petroleum gave orange crystals, m.p. 71-72° (lit.[4] 71.4°).

4-Phenylaminoazobenzene was available from previous work.[48]

Reaction of cis-*Azobenzene with Acetyl Chloride*

Acetyl chloride (12 ml) was added to *cis*-azobenzene (1.0 g) at room temperature in the virtual absence of light. The mixture which immediately acquired a deep blue-purple color, was stirred continuously from the moment of mixing for a period of 1 min, after which it was poured into vigorously stirred ice-water (80 ml). When the resulting aqueous solution had been partly neutralized (to pH 5-6) by addition of sodium carbonate it was extracted several times with ether. The ethereal extracts (A) were combined and treated as described below. The remaining purple aqueous solution (B) was treated separately for isolation of the blue compound.

Evaporation of the combined ethereal extracts (A) yielded a dark viscous oil. This was dissolved in light petroleum, and the solution was chromatographed on a column of silica. The first (orange colored) band was eluted with light petroleum, and this yielded *trans*-azobenzene (0.12 g; 12%) when the eluate was evaporated to dryness. The second (dark-yellow) band was then eluted (ether-

light petroleum 10% v:v). Evaporation of the solvent left a yellow oil which, following addition of a small amount of light petroleum and stirring, crystallized to give 4-phenylaminoazobenzene (108) (0.054 g). Further elution of the column was effected with ether-light petroleum (40% v:v), and the eluate afforded a viscous oil when it was evaporated to dryness. After a time partial crystallization of the oil occurred, and the crystalline product was removed from the non-crystalline material by addition of ether-light petroleum to the mixture, followed by immediate filtration. The filtrate, when evaporated to dryness, yielded *N*,*N*'-diacetyl-4-chlorohydrazobenzene (2) (0.66 g; 40%). The crystalline product, after its removal by filtration, was recrystallized from ether-light petroleum and shown to be *N*'-acetyl-4-chlorohydrazobenzene (107) (0.49 g; 34%). A small amount of blue material was finally eluted from the column (ether-light petroleum 80% v:v), but after evaporation of the eluate only a trace of red-brown resinous material was obtained.

When aqueous solution (B) was rendered alkaline with sodium hydroxide, the color changed from purple to blue. The highly colored material was readily extracted with ether; and, after the extract had been separated, dried, and evaporated, the product (0.121 g) was obtained in a blue-black resinous form.

A similar reaction mixture of *cis*-azobenzene and acetyl chloride was allowed to stand for 170 hr before the excess acetyl chloride was decomposed with water. The purple color had completely disappeared well before the expiration of this period. The working-up

procedure was essentially the same as that described above and the ethereal extract, corresponding to (A), yielded *trans*-azobenzene, 4-phenylaminoazobenzene, *N*,*N*'-diacetyl-4-chlorohydrazobenzene, and *N*'-acetyl-4-chlorohydrazobenzene in practically the same respective yields as before. In this case, however, a small amount (0.03 g) of acetanilide was also obtained from a fraction eluted from the silica column immediately after the 4-phenylaminoazobenzene. No blue product was obtained when the aqueous fraction, corresponding to B, was basified and extracted with ether.

Characterization of Reaction Products

N,*N*'-Diacetyl-4-chlorohydrazobenzene was obtained in a colorless glass-like form. The product showed identical infrared, n.m.r. (integrated), and ultraviolet spectra to those previously recorded[1] for a fully characterized sample.

N'-Acetyl-4-chlorohydrazobenzene was obtained as white needles, m.p. 120-121° (lit.[107] 123-124°). (Ritter and Ritter[107] have used the reversed labelling for the two hydrazo nitrogen atoms.) Its infrared spectrum (Nujol) showed bands *inter alia* at 3300, 3270 (N-H), and 1655 cm^{-1} (C=O). On treatment with phenylhydrazine[107] the compound yielded *p*-chloroaniline and acetanilide. The reduction products were separated by chromatography on silica (ether-light petroleum), and each was identified by direct comparison (mixed m.p. and infrared spectrum) with an authentic sample.

4-Phenylaminoazobenzene had m.p. 80-82° (lit.[144] 82°). The melting point was not depressed on admixture with the authentic sample, and the two samples were identical according to their infrared ($CHCl_3$) and ultraviolet-visible (EtOH) spectra.

The *trans*-azobenzene isolated in the above experiments was identified by direct comparison (mixed m.p. and infrared spectrum) with an authentic sample (Part I.1).

Acetanilide was identified by direct comparison (mixed m.p. and infrared spectrum) with a commercial preparation.

The blue compound (0.04 g) was dissolved in 10% methanolic potassium hydroxide (30 ml), and the solution was boiled under reflux for 4 hr. The cooled reaction was diluted with water and extracted with ether. After separation of the ethereal extract and evaporation of the solvent, a yellow-brown oil was obtained. This was dissolved in light petroleum and chromatographed on a column of silica. The main band, which was eluted with ether-light petroleum (10% v:v), yielded a yellow oil when the solvent was removed; and the oil crystallized when treated with cold light petroleum, yielding 4-phenylaminoazobenzene (0.019 g). Traces of other material were subsequently eluted from the column, but none of these could be identified. A small amount of the blue compound was also dissolved in acetyl chloride, and the solution was allowed to stand in the dark for 15 min. During this time the original absorption band (λ_{max} 560 mμ) was replaced by another at shorter wavelength (λ_{max} 530 mμ). The solution was then stirred with an excess of ice-water

to destroy the acetyl chloride, and sodium carbonate was added until the mixture was neutral. Extraction with ether afforded 4-phenylaminoazobenzene (yield not determined), which was identified spectroscopically.

III. PHOTOINDUCED REACTIONS OF *TRANS*-AZOBENZENE WITH ACYL AND AROYL CHLORIDES

1. *ortho/para* Product Ratios

Materials

The *trans*-azobenzene, 2-chloroazobenzene, and 4-chloroazobenzene were available from earlier work (see Experimental I.1). Trimethylacetyl chloride and 4-methoxybenzoyl chloride were prepared from the appropriate carboxylic acids and thionyl chloride. The former (colorless liquid) had b.p. 105-106° (lit.[145] 105-106°), and the latter (colorless liquid) had b.p. 94-95°/0.6 mm (lit.[146] 140-141°/14 mm). All other acid chlorides used were commerical preparations which were appropriately purified before use. The benzene and cyclohexane employed were of analytical reagent grade and were redistilled and dried before use.

Comparative Reaction Sequences

In general, a solution of *trans*-azobenzene (0.36 g; 0.002 mole) in either the pure acid chloride (15 ml) or benzene (15 ml) containing the dissolved acid chloride (quantity shown in Table VI) was exposed to direct sunlight in a sealed Pyrex tube for the period indicated (Tables V and VI). The excess acid chloride (and benzene when used) was then removed by distillation (reduced pressure for the aroyl chlorides).

The residue was thereafter subjected to hydrolysis and aerial oxidation with a boiling mixture of methanol (35 ml) and 50% (w:v) potassium hydroxide (7 ml). The reaction mixture was cooled, diluted with water (200 ml), and extracted firstly with light petroleum and secondly with ether. The combined extract was dried ($MgSO_4$) and chromatographed on a column of alumina; and the mixture of azo compounds (2- and 4-chloroazobenzene, and in some cases unchanged azobenzene) was eluted as a single broad band. After removal of the solvent, the combined yield (2- and 4-chloroazobenzene) was determined and the mixture was redissolved in chloroform (5% solution) in preparation for gas chromatographic analysis.

Gas Chromatography

The procedure used for gas chromatographic analysis was identical to the procedure previously described in Part I.1 of the Experimental.

2. Photoproducts

Photoreaction of trans-*Azobenzene with Benzoyl Chloride*

A solution of *trans*-azobenzene (0.5 g) in benzoyl chloride (15 ml) was irradiated in sunlight for 20 hr. After removal of the excess benzoyl chloride by distillation (under reduced pressure) the remaining residue was dissolved in ether. The ethereal solution was washed with sodium carbonate solution, separated, dried, and evaporated to dryness. The remaining viscous oil was chromatographed on a column of silica (ether-light petroleum).

The first fraction was eluted with ether-light petroleum (50% v:v). This afforded a colorless glass (1.1 g) which was crystallized from ether to give N,N'-*dibenzoyl-4-chlorohydrazobenzene* (118) (0.34 g; 29%) as white prisms, m.p. 149-150° (Found: C, 72.9; H, 4.56; N, 6.5; O, 8.0. $C_{26}H_{19}ClN_2O_2$ requires C, 73.1; H, 4.49; N, 6.6; O, 7.5%). The infrared spectrum (Nujol) showed bands at 1690 (C=O), 1670 (C=O), 1590, 1488, 1315, 1282, 1100, 1009, 940, 837, 818, 792, 782, 768, 750, 725, 700 and 690 cm^{-1}. (See appendix for the mass spectrum.) Alkaline hydrolysis with methanolic potassium hydroxide and subsequent oxidation yielded 4-chloroazobenzene as the only product. Evaporation of the mother liquors to dryness gave a colorless glass, the infrared spectrum (Nujol) of which showed bands *inter alia* at 3,300 (N-H) and 1660-1670 cm^{-1} (C=O).

Continued elution afforded a second fraction which after removal of the eluate yielded a white solid, m.p. 229-232°; and this was identified as *N*,*N*'-dibenzoyl-5-chloro-2,4'-diaminodiphenyl (117) (0.03 g; 2.7%) by direct comparison (mixed m.p. and infrared spectrum) with an authentic specimen. The authentic compound was prepared by rearrangement of 4-chlorohydrazobenzene (0.1 g) in hydrochloric acid (3*N*; 10 ml) and benzoylation of the resulting 5-chloro-2,4'-diaminodiphenyl. The final product (after recrystallization from ether) was obtained as white crystals m.p. 229-232°; the infrared spectrum (Nujol) of which showed bands at 3,260 (N-H), 1642 (C=O), 1595, 1570, 1500-1520, 1320, and 800 cm^{-1}.

Photoreaction of trans-*Azobenzene with Benzoyl Chloride (Benzene as Solvent)*

trans-Azobenzene (0.72 g; 0.004 mole) in a solution of benzene (30 ml) containing benzoyl chloride (1.4 g; 0.01 mole) was irradiated for 20 hr. The working-up procedure was essentially similar to that described in the foregoing photoreaction. The photoproducts were subjected to chromatography on a silica column (ether-light petroleum).

The first fractions gave unchanged azobenzene (0.2 g; 28%).

The second fraction afforded a mixture (0.43 g) which after recrystallization from ether yielded N'-*benzoyl-2-chlorohydrazobenzene* (119) (0.13 g; 10%) as white prisms, m.p. 144-145° (Found: C, 71.2;

H, 4.83; N, 8.8. $C_{19}H_{15}ClN_2O$ requires C, 70.7; H, 4.7; N, 8.7%). (See appendix for the mass spectrum.) The infrared spectrum (Nujol) showed bands at 3,300 (N-H), 1640 (C=O), 1600, 1040, 740 and 690 cm^{-1}. When this compound was subjected to hydrolysis/oxidation in aqueous methanolic potassium hydroxide, the only product formed was 2-chloroazobenzene.

Further elution with ether-light petroleum gave a third fraction which, after removal of the eluate, was obtained as a colorless glass. The mixture could not be resolved by fractional crystallization.

The fourth fraction was eluted with ether-light petroleum (80% v:v) and afforded *N'*-benzoyl-4-chlorohydrazobenzene (160) (0.13 g; 10%) as pinkish prisms, m.p. 155-156°. The infrared spectrum of this compound (Nujol) showed bands at 3240 (N-H), 1660 (C=O), 1598, 1482, 1332, 1300, 1288, 820, 740, and 685 cm^{-1}. Hydrolysis and subsequent oxidation of this compound in aqueous methanolic potassium hydroxide gave 4-chloroazobenzene as the only product.

IV. REACTIONS OF *CIS*- AND *TRANS*-AZOBENZENES WITH OTHER ACYL COMPOUNDS

Materials

Propionyl Fluoride

A mixture of benzoyl chloride (28 g; 0.2 mole), anhydrous propionic acid (15.2 g; 0.2 mole) and potassium hydrogen fluoride (11.7 g; 0.15 mole) was heated on an oil bath at 100-110° for 1 hr.[147] The reaction mixture was distilled and the following fractions collected: fraction (A) b.p. 40-44°, and fraction (B) b.p. 45-46° (lit.[147] b.p. 42-44°). It was subsequently shown that both fractions (A) and (B) contained some propionyl chloride.

Acetic Anhydride-Hydrofluoric Acid Solution

Hydrofluoric acid (3 ml; 40% w:v) was added dropwise to a cooled (*c.* 5°) and well stirred solution of acetic anhydride in a polythene container. The final mixture was slowly brought to room temperature and used immediately.

Acetic Anhydride-Hydrobromic Acid Solution

Prepared in the manner described above from hydrobromic acid (48% w:v; 30 ml) and acetic anhydride (200 ml).

Aluminium Tri-iodide

Aluminium powder (0.5 g) was shaken with a solution of mercuric chloride in ether (1% w:v; 5 ml) for 2 min. The resulting grey powder

was washed (by decantation) with several portions of anhydrous ether, and a solution of iodine (6.3 g) in anhydrous ether (60 ml) was slowly added.[148] The reaction was completed by boiling the mixture under reflux for 30 min.

Acetyl Cyanide

This compound was prepared from cuprous cyanide and acetyl bromide.[109] After two distillations the acetyl cyanide was obtained as a colorless liquid, b.p. 92-95° (lit.[109] 92-93°).

Acetic Anhydride-Hydrogen Cyanide Solution

Liquefied hydrogen cyanide (3 ml) was slowly added to a cold and well stirred solution of acetic anhydride. The mixture was allowed to warm slowly to room temperature and was used without further delay.

Reaction Sequences

Photoreaction of trans-*Azobenzene with Propionyl Fluoride*

trans-Azobenzene (0.2 g) in propionyl fluoride (fraction A; 5 ml) was irradiated in a sealed Pyrex tube for 50 hr. The purple solution was poured into cold water and the resulting solution neutralized (Na_2CO_3). The mixture was extracted with ether, the ethereal extract separated, dried, and evaporated to dryness. The remaining residue was subjected to hydrolysis/oxidation in boiling

aqueous methanolic potassium hydroxide for 5 hr. The mixture was extracted with ether and the residue remaining after removal of the ether was chromatographed (alumina-light petroleum).

The first fraction afforded 4-chloroazobenzene which was identified by direct comparison (mixed m.p. and the infrared spectrum) with an authentic sample.

Elution with ether-light petroleum (25% v:v) afforded a small quantity of a yellow oil which was identified as 4-phenylamino-azobenzene by comparative thin-layer chromatography.

The same result was obtained on repeating the experiment with the propionyl fluoride obtained as fraction (B).

Reaction of cis-*Azobenzene with Acetic Anhydride-Hydrofluoric Acid Solution*

A solution of *cis*-azobenzene (0.2 g) in acetic anhydride-hydrofluoric acid solution (23 ml) was stirred in the absence of light for $1\frac{1}{4}$ hr. The mixture was poured into cold water and the resulting solution was neutralized (Na_2CO_3). The products were extracted with ether, subjected to hydrolysis/oxidation, and chromatographed on alumina, the procedure being essentially similar to that described in the foregoing experiment.

The first fraction yielded *trans*-azobenzene (0.13 g) which was identified (mixed m.p.) by comparison with an authentic sample.

Elution with ether-light petroleum (25% v:v) afforded 4-phenyl-aminoazobenzene (0.027 g) which was identified by direct comparison (mixed m.p. and the infrared spectrum) with an authentic specimen.

Photoreaction of trans-*Azobenzene with Acetic Anhydride-Hydrobromic Acid Solution*

trans-Azobenzene (15 g) in acetic anhydride-hydrobromic acid solution (230 ml) was irradiated for 3 hr. The volume of the solution was reduced to *c.* 50 ml by distillation (under reduced pressure) and the remaining acetic anhydride was destroyed by the addition of excess methanol. After the methanol and methyl acetate had been distilled off, the remaining solution was diluted with water and neutralized by the addition of sodium carbonate. The aqueous solution was extracted with ether, and after separation, the ethereal solution was evaporated to dryness. The remaining residue was obtained as a colorless glass, a small portion of which was crystallized from ether-light petroleum to give N,N'-*diacetyl-4-bromohydrazobenzene*, m.p. 89-90° (Found: C, 55.3; H, 4.51; N, 8.1; O, 9.6. $C_{16}H_{15}BrN_2O_2$ requires C, 55.4; H, 4.35; N, 8.1; O, 9.2%). The infrared spectrum of the compound (Nujol) showed bands at 1700 (C=O), 1675 (C=O), 1590, 1485, 1315, 1245, 1065, 1010, 998, 965, 840, 760, and 690 cm^{-1}.

The bulk of the photoproduct was dissolved in methanol (200 ml) and an aqueous solution of potassium hydroxide (70% w:v; 25 ml) was added. The mixture was boiled under reflux for 8 hr and air bubbled through the solution for a further 2 hr. After dilution with water (100 ml), the precipitated orange solid was removed by filtration, washed thoroughly with water, dried, and recrystallized from methanol.

4-Bromoazobenzene (16.9 g; 80%) was thereby obtained as orange plates, m.p. 88-89° (lit.[111] 89°). The mother liquors were evaporated to dryness, and subjected to chromatography on a column of alumina (light petroleum). The first fraction afforded a red oil which was shown by gas chromatography to consist mainly of 4-bromoazobenzene. Elution with ether-light petroleum (20% v:v) yielded 4-bromohydrazobenzene (1.1 g; 5%) which was identified by subjecting it to oxidation (with sodium hypobromite) and identifying (mixed m.p.) the 4-bromoazobenzene so formed.

Reaction of cis-*Azobenzene with Aluminium Tri-iodide in Acetic Anhydride*

The ether solution of aluminium tri-iodide (see above) was evaporated to dryness and acetic anhydride (25 ml) poured onto the residue. After cooling, *cis*-azobenzene (0.15 g) was added to the mixture and stirring was continued for a $\frac{1}{2}$ hr in the absence of light. The mixture was poured into cold water, the resulting acidic solution neutralized (Na_2CO_3), and extracted with ether. After drying, the ethereal solution was evaporated to dryness leaving a viscous oil, the infrared spectrum of which showed bands *inter alia* at 3,300 (N-H) and 1650-1670 (C=O) cm^{-1}. The viscous oil was subjected to hydrolysis/oxidation in aqueous methanolic potassium hydroxide for 3 hr and the final product was chromatographed on alumina (light petroleum). Only one fraction was eluted and this afforded *trans*-

azobenzene (0.06 g; 40%) which was identified by direct comparison (mixed m.p. and the infrared spectrum) with an authentic sample.

Photoreaction of trans-*Azobenzene with Acetyl Cyanide*

A solution of *trans*-azobenzene (0.05 g) in acetyl cyanide (5 ml) was irradiated for 30 hr. No noticeable color change occurred during this period and the reaction mixture was poured into water, rendered alkaline (Na_2CO_3), and extracted with ether. Removal of the ether left a dark oil which was chromatographed on alumina (light petroleum).

The first fraction afforded unchanged azobenzene (0.011 g).

Elution with ether-light petroleum (50% v:v) yielded a second fraction which gave colorless plates of α,α-dicyanoethyl acetate (124) (0.39 g), m.p. 68-70° (lit.[109] 69.4-70.2°).

A similar experiment was repeated using *trans*-azobenzene (0.2 g) in acetyl cyanide (5 ml). However in this case the photoproducts were directly subjected to hydrolysis/oxidation in aqueous methanolic potassium hydroxide and the final product chromatographed on alumina (light petroleum). The only fraction eluted afforded unchanged azobenzene (0.16 g; 80%).

Photoreaction of trans-*Azobenzene in Acetic Anhydride-Hydrogen Cyanide Solution*

Azobenzene (0.22 g) in acetic anhydride-hydrogen cyanide solution was irradiated for 24 hr. The working-up procedure was

essentially similar to that described in the foregoing reaction. The photoproducts were chromatographed on a column of silica (light petroleum).

The first fraction contained unchanged azobenzene (0.065 g).

Elution with ether-light petroleum (10-20% v:v) gave a second fraction which afforded 4-phenylaminoazobenzene (0.052 g) which, after recrystallization from light petroleum, was obtained as yellow-orange crystals, m.p. 86-87° (alone or admixed with an authentic specimen). The infrared spectrum was identical to that of an authentic sample.

The third fraction (ether-light petroleum 30% v:v) yielded α,α-dicyanoethyl acetate (0.114 g), the infrared spectrum of which was identical to that of the previously characterized sample (foregoing experiment).

Several oils were eluted in the following fractions but the quantities were too small for identification purposes.

Photoreaction of trans-*Azobenzene with Acetic Anhydride*

trans-Azobenzene (0.2 g) in acetic anhydride solution was irradiated for 60 hr. The dark reaction mixture was poured into water, the resulting solution neutralized (Na_2CO_3) and extracted with ether. The ethereal solution was dried, evaporated to dryness and the remaining residue chromatographed on a column of silica (light petroleum). The first fraction afforded unchanged azobenzene

(0.146 g; 73%). Several small colored bands were eluted from the column but the quantities of compound (<3 mg) were too small for identification purposes.

Reaction of cis-*Azobenzene with Acetic Anhydride*

A solution of *cis*-azobenzene (0.1 g) in acetic anhydride (10 ml) was stirred in the absence of light for 5 hr. The working-up procedure was essentially similar to that described in the foregoing experiment. The final product was chromatographed on alumina (light petroleum). The first fraction afforded *trans*-azobenzene (0.089 g; 89%), m.p. 68-69° (alone or admixed with an authentic sample). Several small colored bands were eluted from the column but the quantities of compound (<2 mg) were too small for identification purposes.

V. QUANTUM YIELD DETERMINATIONS

Materials

trans-*Azobenzenes*

Pure samples of azobenzene, 4-methylazobenzene, 4-chloroazobenzene, 4-methoxyazobenzene and 4-nitroazobenzene were available from earlier work (see Parts I.1, I.2, and I.3).

2-Methylazobenzene (128)

o-Toluidine and nitrosobenzene were condensed in glacial acetic acid, the experimental procedure being essentially similar to that described for the preparation of 3- and 4-methylazobenzenes (see Part I.3). The crude product was chromatographically purified (alumina-light petroleum) and finally distilled to give 2-methylazobenzene as a red liquid, b.p. 116-118°/0.7 mm (lit.[149] b.p. 180-181°/20 mm).

2,6-Dimethylazobenzene (129)

2,6-Dimethylaniline (1.2 g) and nitrosobenzene (1.1 g) in glacial acetic acid (4 ml) were warmed at 50-60° for 72 hr. The mixture was poured into water, extracted with light petroleum, the extract separated, concentrated and passed through a column of alumina (light petroleum). The first fraction afforded 2,6-dimethylazobenzene (0.4 g; 19%) which after distillation was obtained

as a red oil, b.p. 180-181°/20 mm (lit.[150] b.p. 175-176°/16 mm). (See appendix for the mass spectrum.)

2,6-Dichloroazobenzene (130)

2,6-Dichloronitrosobenzene was prepared by oxidation of 2,6-dichloroaniline[151] with hydrogen peroxide in glacial acetic acid.[122] The crude product was isolated as long straw-colored needles, m.p. 170-172° (lit.[122] 175.5-176°).

A mixture of aniline (0.5 g) and 2,6-dichloronitrosobenzene (1.0 g) in glacial acetic acid (2 ml) was heated at 80° for 24 hr. The 2,6-dichloroazobenzene was extracted by a procedure similar to that described above for the preparation of 2,6-dimethylazobenzene. Chromatography (alumina-light petroleum) afforded *2,6-dichloroazobenzene* (0.9 g; 63%) as an orange oil (b.p. 127-128°/0.08 mm) which crystallized on cooling and had m.p. 26.5-27.0° (Found: C, 57.8; H, 3.39; N, 11.6. $C_{12}H_8Cl_2N_2$ requires C, 57.4;; H, 3.21; N, 11.2%).

2,6,2',6'-Tetramethylazobenzene (131)

Lead tetra-acetate (14.2 g; 32 mm) was added over a period of 1 hr to a stirred solution of 2,6-dimethylaniline (3.6 g; 30 mm) in anhydrous benzene (120 ml).[152,110] The solution was stirred for a further 30 min, filtered, and the filtrate evaporated to dryness. The residue was dissolved in light petroleum and chromatographed (alumina-light petroleum). Evaporation of the eluate from the first

fraction afforded red-pink needles of *2,6,2',6'-tetramethylazobenzene* (0.07 g; 2%), which after crystallization from methanol had m.p. 49-50°. (See appendix for the mass spectrum.)

2,6,2',6'-Tetrachloroazobenzene (132)

This compound was prepared from 2,6-dichloroaniline[151] and lead tetra-acetate, the experimental details being essentially similar to those described in the above preparation of 2,6,2',6'-tetramethylazobenzene. The crude product was chromatographically purified (alumina-light petroleum) and after several recrystallizations from methanol, 2,6,2',6'-tetrachloroazobenzene was obtained as dark-red prisms, m.p. 135-136°. (See appendix for the mass spectrum.) This compound was deduced to be the *cis* isomer from the absorption spectrum in acetic anhydride (Fig. X). On irradiation in acetic anhydride (at 313 and 436 mμ) equilibrium *cis*⇌*trans* mixtures were obtained. The absorption spectrum of the *trans* isomer (144) (Fig. VIa) was obtained by heating a solution of the *cis* isomer in acetic anhydride for 2 hr.

cis-*Azobenzenes*

Pure *cis*-azobenzene (m.p. 71-72°) was available from earlier work (see Part II).

The following *cis*-azobenzenes were prepared and purified according to the method described by Badger, Drewer and Lewis.[50]

cis-Azobenzene	m.p.	lit. m.p.
4-methyl- (133)	dark-red needles (MeOH) 36.5-37.5°	36.5-37.5°,[50] 42-45°[5]
4-chloro- (134)	orange plates (MeOH) 45-46°	32°,[7] 38°,[93] 36-37°[50]
4-methoxy- (135)	orange oil	*c.* 25°,[6] oil[90]
2-methyl- (136)	red-orange oil	-
2,6-dichloro- (137)	yellow-orange needles (ether) 112-113°	-
2,6-dimethyl- (138)	yellow-orange oil	-
2,6,2',6'-tetramethyl- (139)	yellow orange needles (ether) 69-71°	-

Compounds Used for Actinometry

The potassium trisoxalatoferrate and 1,10-phenanthroline used for actinometry were available from previous work.[50]

Solvents

The acetic anhydride was a commercial preparation of analytical purity and was distilled before use.

The acetyl chloride was a commercial preparation and was distilled before use.

The acetic anhydride-hydrochloric acid solution employed as solvent in the photochemical reactions was prepared as follows: Concentrated hydrochloric acid (35.5% w:v) (40 ml; 0.46 mole) was

added dropwise to a well stirred and cold solution of acetic anhydride (294 ml; 3.1 mole). Stirring was continued for 15 min after the addition, the solution being gradually allowed to warm to room temperature. This solution was preferred to acetyl chloride because of its much lower volatility.

Apparatus

Photochemical Reactor

The design of the reactor is shown in Fig XVII. The light source (A) was a Philips HPK 125-W high pressure mercury-quartz lamp operated at a stabilized voltage and this was housed in a compartment (B) which was ventilated by a fan positioned underneath the lamp. Light from the lamp (and adjustable reflector (C)) was passed through a heat filter (D) which consisted of a 1-cm quartz cell filled with distilled water. The light was then allowed to pass through a slit (E) (2.0 mm) into a Jarrell-Ash 82-410 monochromator (F). The monochromatic light beam was passed through another slit (E) (2.0 mm) before entering the 1-cm quartz reaction cell which was supported in the compartment (G). Stirring of the solutions was accomplished by placing a small magnetic stirrer underneath the compartment (G) and a small glass-coated iron nail in the quartz cell.

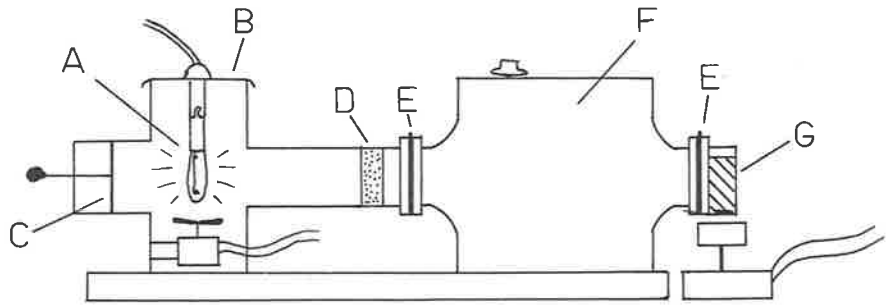


Fig. XVII

Spectrophotometer

A Hitachi Perkin-Elmer 139 spectrophotometer was used for all optical density determinations.

Laboratory Illumination

Quantum yield determinations and the handling of photosensitive materials was carried out only in light which had been passed through Kodak 2 safelight filters.

Quantum Yield Determinations

Actinometry

Potassium trisferrioxalate actinometry according to the method of Hatchard and Parker[153] was used for each quantum yield determination. The actinometer solution consisted of a potassium trisoxalatoferrate solution (0.600 M) in 0.1*N* sulphuric acid. An accurately determined volume of the actinometer solution (calibrated pipette) was placed in a 1-cm quartz cell and irradiated in the

photochemical reactor for a given time. A 2-ml aliquot of the solution was then transferred to a 10-ml volumetric flask, and after adding a 0.1% aqueous solution of 1,10-phenanthroline (1 ml) and acetate buffer solution[153] (1 ml), the solution was diluted to 10 ml. A control solution of ferrioxalate which had not been irradiated was similarly treated. The solutions were allowed to stand in darkness for a $\frac{1}{2}$ hr and then the optical densities at λ 510 mμ (D^{510}) were determined. A net value of D^{510} for the ferrous phenanthroline formed in the irradiated actinometer solution was obtained by subtraction of the control reading from the value obtained for the irradiated solution. A calibration graph (Beer's Law plot) was prepared by measuring D^{510} of standard solutions of ferrous phenanthroline.[153] In this manner, the concentrations $c(Fe^{2+})$ of ferrous ions (mole ml^{-1}) in the irradiated actinometer solutions could be determined and thus used for calculation of the number of quanta (I_o) of light entering the actinometer cell in unit time according to the following equation.

$$I_o = \frac{c(Fe^{2+})\ v}{\phi a(1-T)t}$$

In the above equation, ϕa is the known quantum yield[153] of the actinometer system, (1-T) is the average fraction of incident light absorbed by the actinometer solution at the wavelength of irradiation, and v is the volume (ml) of the actinometer solution.

Measurement of Absorption Spectra

trans-*Azobenzenes*

Two or three solutions of the azo compound were prepared, the concentrations being chosen so that the optical densities (D) were mainly in the range (0.8-0.1) at wavelengths between 300 and 500 mμ. The optical densities were then determined at 10 mμ intervals between 300 and 500 mμ and plotted against the wavelength to give the absorption spectrum. Optical densities were also measured at 313, 365, 405, and 436 mμ since these values were required for the quantum yield calculations

cis-*Azobenzenes*

Absorption spectra of the *cis* azo compounds were determined by a procedure similar to that described above for the *trans* azo compounds. However, in this case the time interval between preparation of the solutions and the measurement of D was made as short as possible due to the rapid thermal *cis* → *trans* isomerization of *cis*-azobenzenes. Accurate values of D at 313, 365, 405, and 436 mμ were determined by calculating the change in optical density with time at these wavelengths and then extrapolating to zero time.

Determination of ϕt in Acetic Anhydride

The concentration (c_o) of the azo compound in acetic anhydride was chosen so that the optical density (D) was in the range (0.2-0.8)

at the wavelength at which the reaction was being followed. An accurately measured volume (v) (calibrated pipette) of this solution was added to the reaction cell, and on commencing irradiation, the optical density was measured as a function of irradiation time. Measurements of D were taken at regular intervals (2-5 min) during the initial stages of the experiment, but the intervals were extended as the photostationary state was approached. The photostationary state was assumed to have been reached when D did not alter after a substantial period of irradiation (*c.* 20 min) and the final optical density (D_∞) was then determined. Only very dilute solutions (*c.* 5×10^{-5}M) could be employed in these quantum yield determinations, since more concentrated solutions developed a dark coloration during irradiation, and results were not reproducible. Thus reactions carried out with 436 or 405 mμ light had to be followed at 320 mμ due to the small extinction coefficients of azo compounds at the longer wavelengths. Immediately the photostationary state had been attained, the actinometer solution was placed in the reactor and irradiated for a period estimated as sufficient to result in a final reading of D^{510} (*c.* 0.4-0.6) when treatment with 1,10-phenanthroline was complete. Calculation of I_o could then be made in the manner described above. Values of I(z) (see Results and Discussion) were calculated from the optical density readings and plotted against time as shown in Fig. IV. In all cases straight lines were obtained (omitting the last 2 or 3 points close to D_∞) and the slope was then used for evaluation of the quantum yield.

Determination of ϕ in Acetic Anhydride-Hydrochloric Acid (and Acetyl Chloride

The experimental procedure used in these determinations was essentially similar to that described in the preceding determinations of ϕt in acetic anhydride. However in this case, the reactions were followed by observing the changes in D at the wavelength of the exciting radiation. Since a photostationary state was not being approached in these experiments, about 10 optical-density readings were taken at 2-5 min intervals and irradiation was then discontinued. The actinometer solution was immediately placed in the reactor and a value for I_o obtained. From the optical-density readings values for log e $(10^D - 1)$ were calculated (see Results and Discussion); and these when plotted against time gave a straight-line graph. The slope of the graph was then used to evaluate the quantum yield.

APPENDIX

(a) NUCLEOPHILIC SUBSTITUTION IN CHLOROAZOBENZENES

Although comprehensive studies by Stepanov *et al.*[155-161] have revealed that *ortho* chloro groups of chloroazo compounds can be replaced by alkoxy or phenoxy groups, the replacement only occurs under very specific conditions. For example, substitution of the chloro group in 1-(2'-chlorophenylazo)-2-naphthol only proceeds in the presence of a copper, nickel or cobalt salt,[160] and only if a 2-hydroxy (or 2-amino) group is attached to the naphthyl group.[158] In 1-(2',3',4',5',6'-pentachlorophenylazo)-2-naphthol only the 2'- and 6'-chloro groups were replaced by alkoxy groups.[161] It appears from these results that the intermediate formation of a copper complex may be more important in bringing about the substitution than the electronic effect of the phenylazo group.

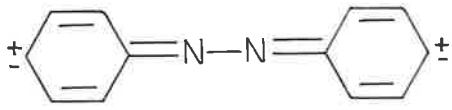
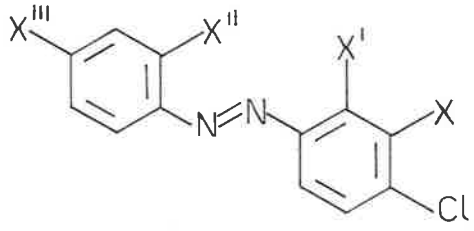


Fig. XVI

The electronic effects of the phenylazo group in azobenzene are generally illustrated as shown in Fig. (XVI) suggesting that activation towards both electrophilic and nucleophilic substitution may occur. Although electrophilic substitutions in azobenzene have been well studied, similar studies with respect to nucleophilic substitutions have not been carried out. The following results, although by no means a comprehensive study, indicate that the phenylazo group does in fact activate aryl chlorides towards nucleophilic substitution.

Experiments in Part I showed that alkaline hydrolysis of *N*,*N*'-diacetyl-2,4,4'-trichlorohydrazobenzene (41) with aqueous methanolic potassium hydroxide resulted in a small yield of 2,4'-dichloro-4-methoxyazobenzene (43) besides the expected trichloroazo compound (42). In a similar manner, *N*,*N*'-diacetyl-2,2',4,4'-tetrachlorohydrazobenzene (46) afforded 2,2',4,4'-tetrachloroazobenzene (47) (major product), 2,2',4-trichloro-4'-methoxyazobenzene (48) and 2,4,4'-trichloro-2'-methoxyazobenzene (49). The following work was carried out to confirm that the methoxy compounds were in fact being produced by nucleophilic displacement of a chloro group by methoxide ion in the chloroazobenzenes.



	X	X'	X''	X'''
(37)	H	H	H	Cl
(38)	H	Cl	H	H
(42)	H	Cl	H	Cl
(47)	H	Cl	Cl	Cl
(125)	Cl	H	H	H

In separate experiments, the series of compounds shown in Table XX were boiled under reflux for the indicated periods in a 10% (w:v) solution of potassium hydroxide in 10% (v:v) aqueous methanol. Considerable quantities of unchanged starting material were recovered in each experiment and this was in each case separated from the methoxy compounds by column chromatography. The combined yields as well as the individual yields of *ortho* and *para* methoxy compounds are

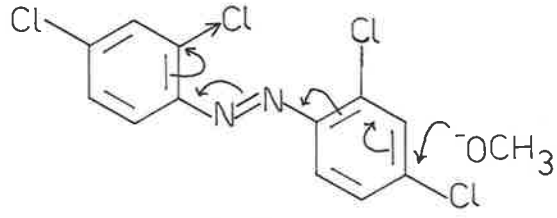
shown in Table XX. Separation of the methoxy isomers obtained from the reactions of 2,4-dichloroazobenzene and 2,4,4'-trichloroazobenzene could only be accomplished by gas chromatography, and the product ratios were assumed to be in the same proportions as the peak areas so that in both cases the product yields were only approximate. The 4-methoxy compounds from all experiments and the 2-methoxy compound from the reaction of (47) were isolated pure and identified by comparison with authentic samples. However, the 2-methoxy products from the reactions of compounds (38) and (42) were not positively identified, since their separation could only be accomplished by gas chromatography.

TABLE XX. Reactions in Aqueous Methanolic Potassium Hydroxide

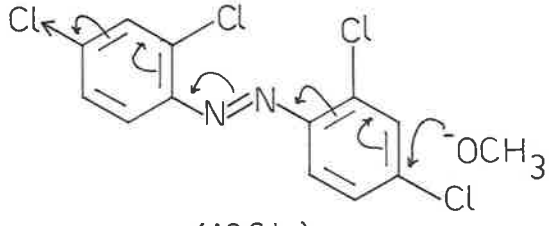
Azobenzene	Reaction Time (hrs.)	% Yield 2-CH_3O-	% Yield 4-CH_3O-	Combined % Yield	% Recovered Starting Material
4,4-dichloro- (37)	10	-	0	0	95
3,4-dichloro- (93)	10	-	5	5	87
2,4-dichloro- (38)	10	*c.* 2	*c.* 15	17	75
2,4,4'-trichloro- (42)	10	*c.* 3	*c.* 21	24	73
2,2',4,4'-tetrachloro- (47)	5	9	35	44	41

Since all the preceding reactions were carried out in aqueous solution, the reaction products were examined for the presence of hydroxyazo compounds. However, in all cases the quantity of material extracted from the acidified reaction mixtures was too small for identification purposes.

Under the reaction conditions used in the above experiments, it is apparent that a phenylazo group alone cannot promote nucleophilic displacement in an aryl chloride. At least one other chloro group *ortho* or *meta* to the one being displaced seems to be a necessity, and even under these conditions the rate of reaction is slow. Results in Table XX show that a 2,4-dichlorophenylazo group is far more effective in promoting nucleophilic substitution in an aryl chloride than the 4-chlorophenylazo group. This result is expected, since the electron-attracting 2-chloro group (-I effect) in the 2,4-dichlorophenylazo residue would tend still further to lower the activation energy required to form the transition state, (viz., the electronic effects illustrated in structure (126a) would reinforce those illustrated in structure (126b)).



(126a)



(126b)

The reactivity of the methoxide ion would be expected to be greatly reduced by the hydroxylic solvent used in the foregoing reactions due to hydrogen-bonding and solvation effects. In contrast, dimethyl sulphoxide as solvent greatly enhances the activity of anions, and accordingly, the reactions of several chloroazobenzenes with sodium methoxide in dimethyl sulphoxide were investigated.

The chloroazobenzenes shown in Table XXI were dissolved in dimethyl sulphoxide, a slight excess of sodium methoxide in methanol added, and the solutions stirred for the indicated period. The 65 hour reaction-period in the case of compound (38) was unwarranted, and secondary reactions of the methoxy compounds may have lowered their yield since a substantial amount of an unidentified red oil was isolated from this reaction. Separation of the 2- and 4-methoxy isomers from the reaction of compound (38) was accomplished only by gas chromatography; and the ratio of the peak areas was assumed to be the product ratio. All methoxy compounds except for the 2-methoxy product from the reaction of 2,4-dichloroazobenzene were identified by comparison with authentic samples.

TABLE XXI. Reactions in Dimethyl Sulphoxide

Azobenzene	Reaction Time & Temp.	% Yield $2\text{-}CH_3O\text{-}$	% Yield $4\text{-}CH_3O\text{-}$	Combined % Yield	% Recovered Starting Compound
2,4-dichloro- (38)	65 hrs at 45°C	*c.* 3	*c.*64	67	0
3,4-dichloro- (93)	5 hrs at 17°C	-	90	90	0
3,4'-dichloro- (91)	5 hrs at 17°C	-	20	20	70

Results in Table XXI show the reactivity of methoxide ions is considerably enhanced when dimethyl sulphoxide is used as solvent. Not only can very mild reaction conditions be used to effect

nucleophilic substitution, but in compound (91), activation by a 3-chlorophenylazo group alone is enough to promote displacement of the 4'-chloro group.

A comprehensive study of reactions of various nucleophiles with chloro- and bromo-azobenzenes is clearly needed to determine the scope of nucleophilic substitutions in azobenzenes. Coupled with the photochemical reaction of azobenzenes with acetyl chloride or bromide, the above nucleophilic displacement reactions may constitute a very convenient route to various *ortho* and *para* substituted azobenzenes.

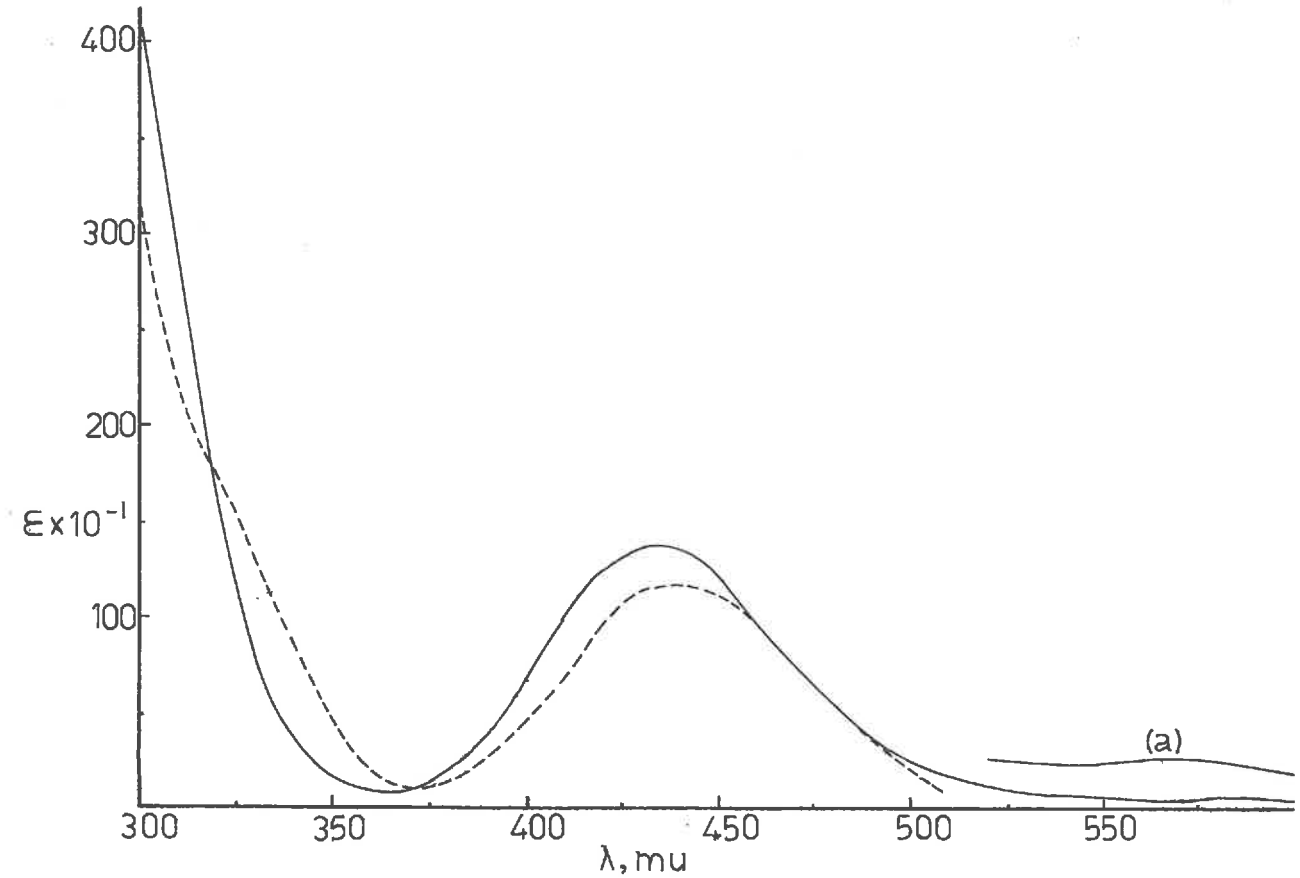


Fig. X - Absorption spectraof *cis*-2,6,2',6'-tetrachloroazobenzene (-----) and *cis*-4-chloroazobenzene (——) in acetic anhydride. (a) After standing in darkness for 21 hr.

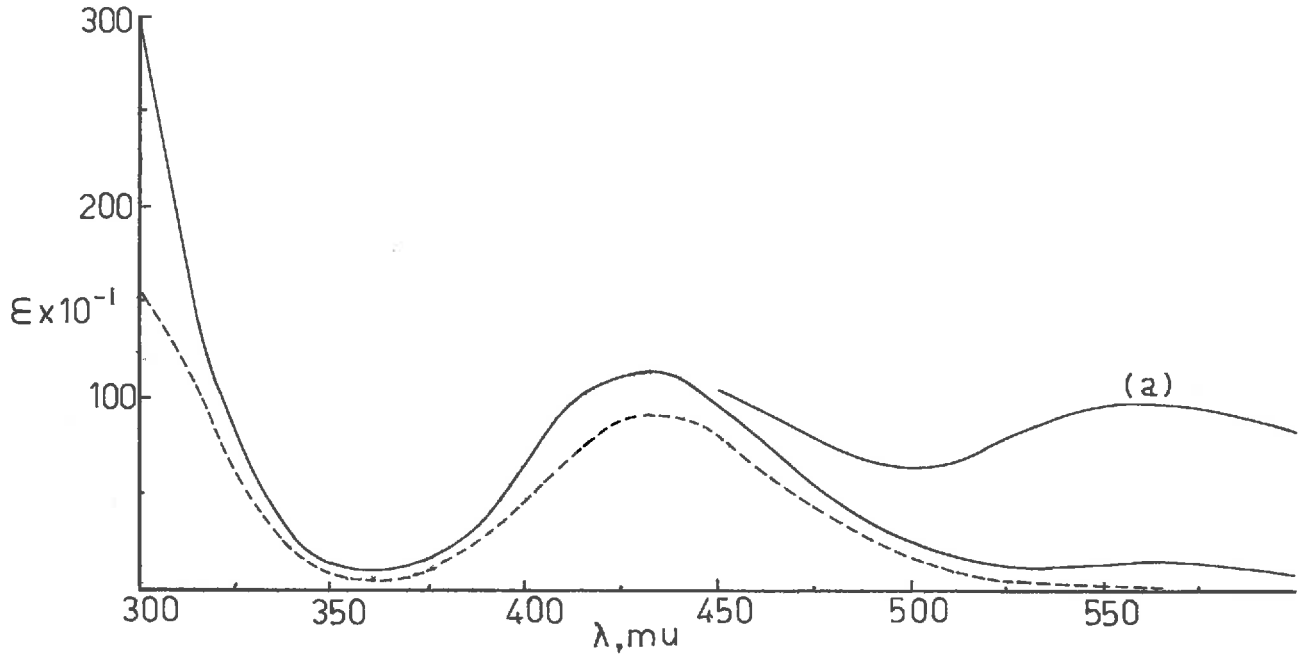


Fig. XI - Absorption spectra of *cis*-2,6-dimethylazobenzene (----) and *cis*-2-methylazobenzene (——) in acetic anhydride. (a) After standing in darkness for 18 hr.

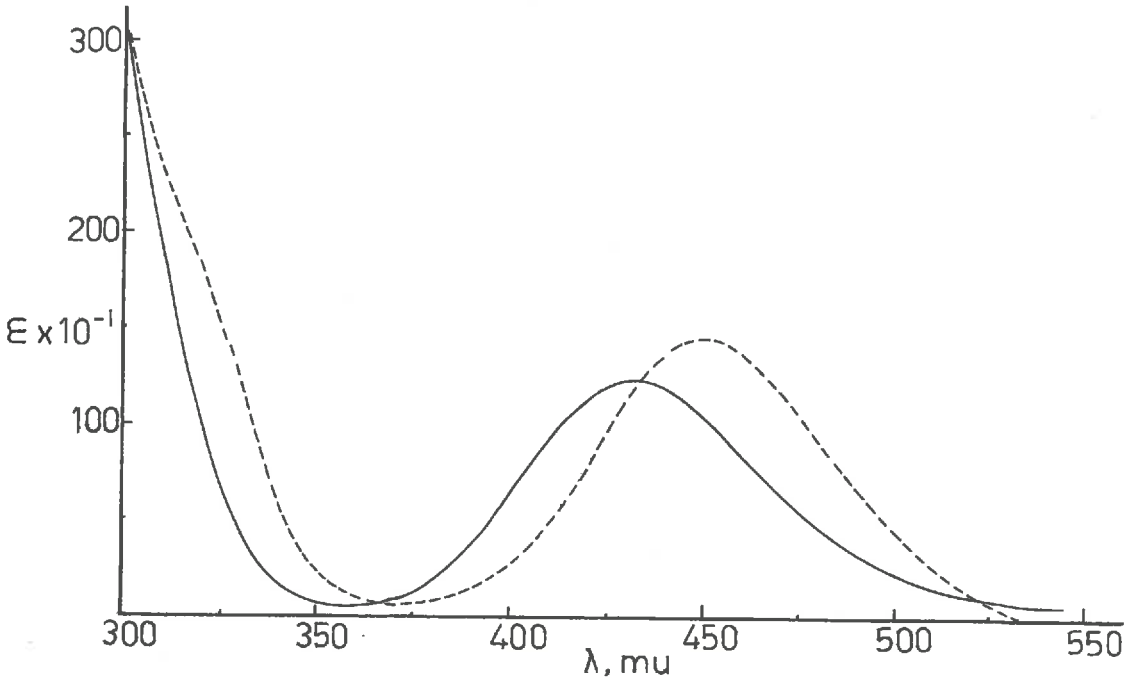


Fig. VIII - Absorption spectra of *cis*-azobenzene (——) and *cis*-2,6,2',6'-tetramethylazobenzene (-----) in acetic anhydride.

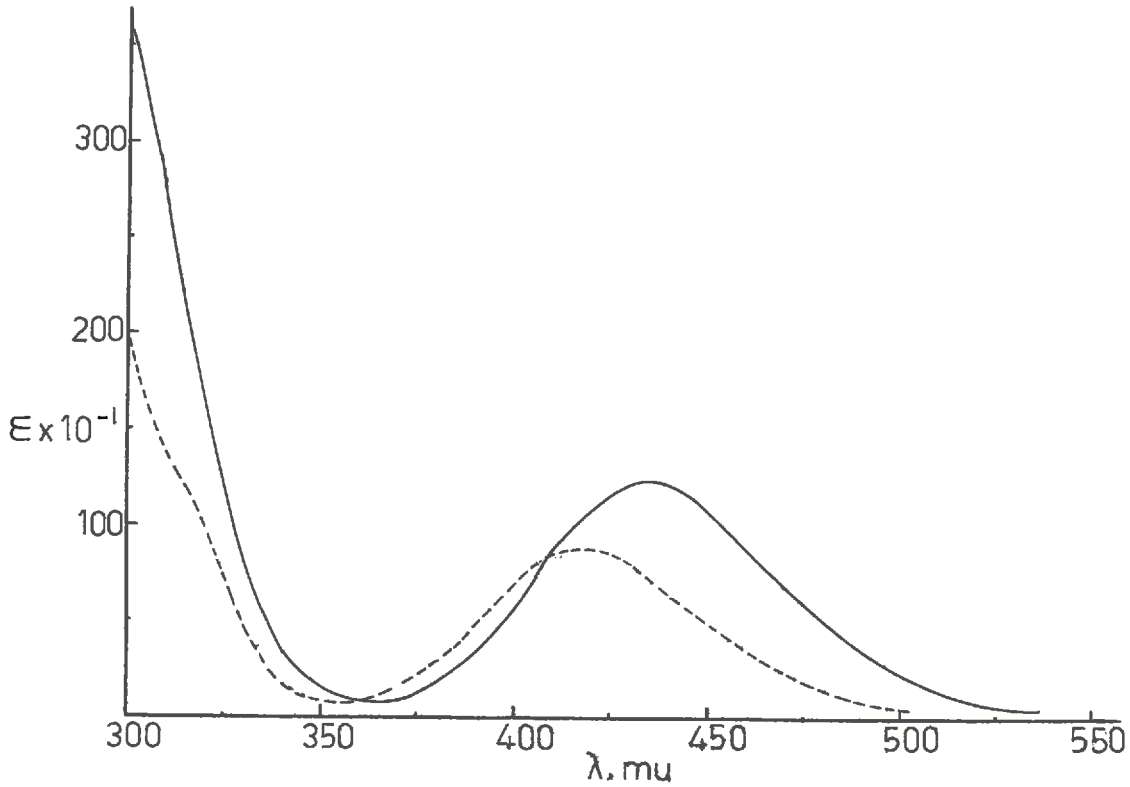


Fig. IX - Absorption spectra of *cis*-4-methylazobenzene (——) and *cis*-2,6-dichloroazobenzene (----) in acetic anhydride.

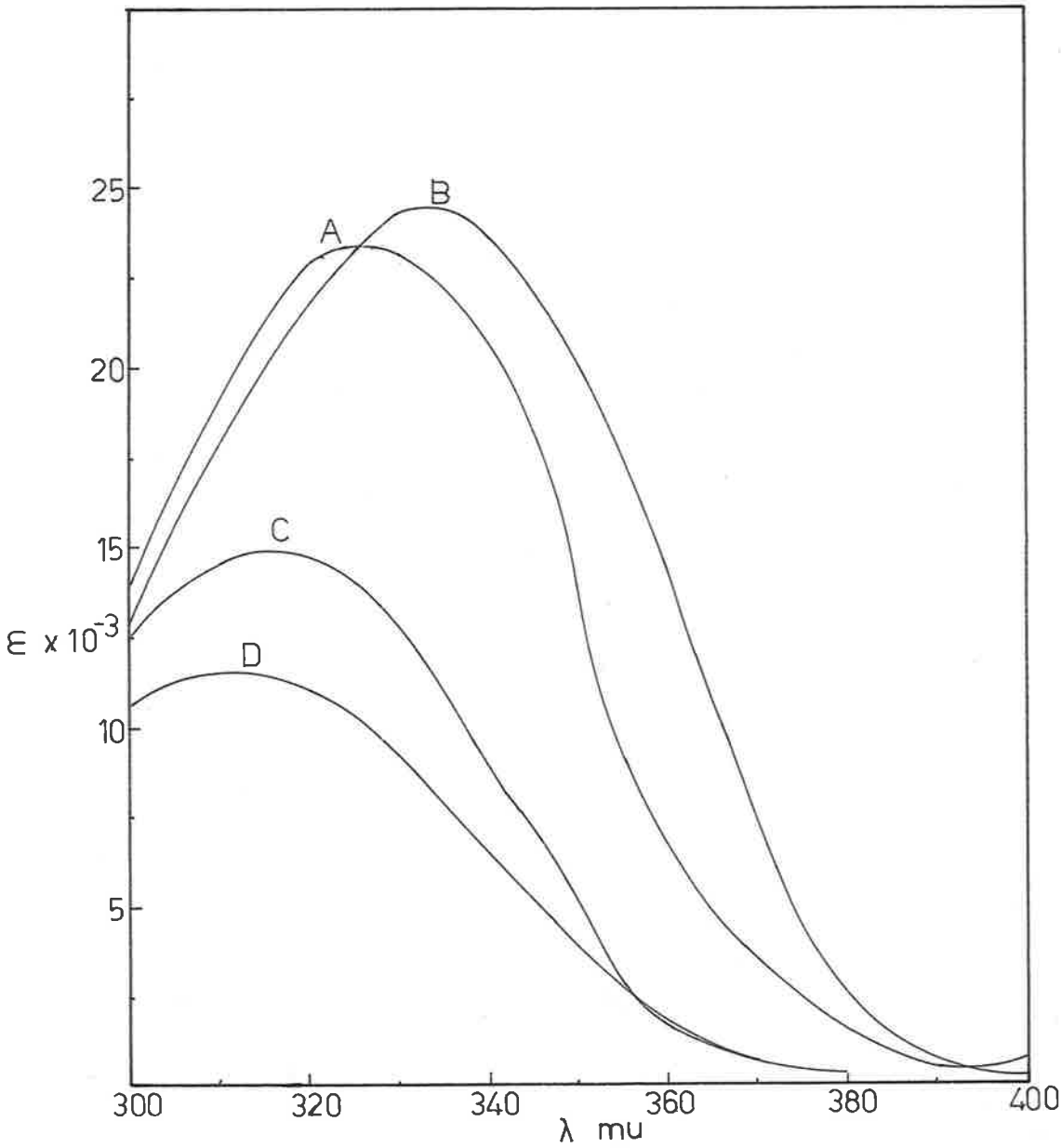


Fig. Vb - Absorption spectra (ππ* band) in acetic anhydride-hydrochloric acid solution; (A) 4-methylazobenzene, (B) 4-nitroazobenzene, (C) 2,6-dimethylazobenzene, and (D) 2,6,2',6'-tetramethylazobenzene.

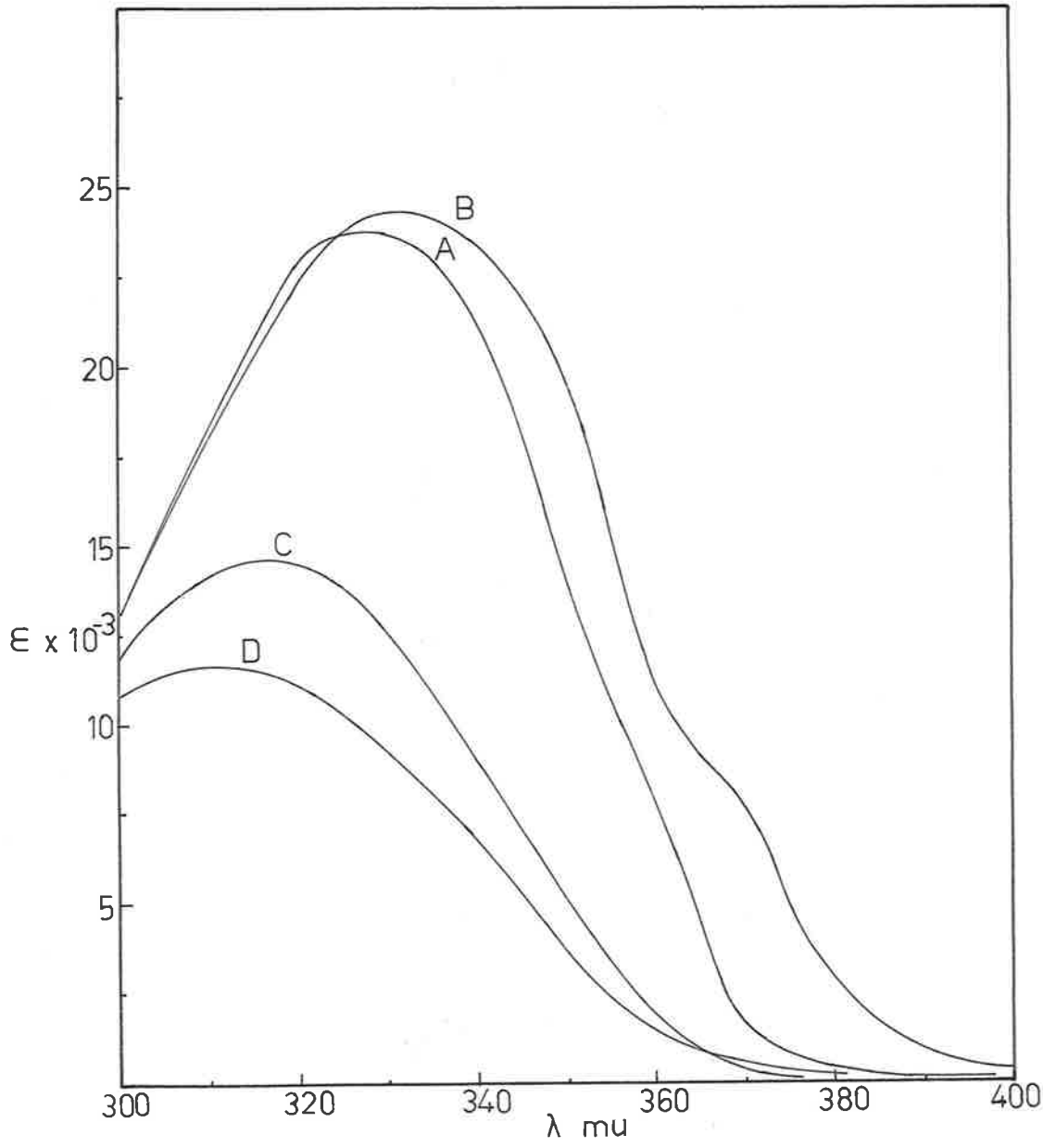


Fig. Va - Absorption spectra (ππ* band) in acetic anhydride; (A) 4-methylazobenzene, (B) 4-nitroazobenzene, (C) 2,6-dimethylazobenzene, and (D) 2,6,2',6'-tetramethylazobenzene.

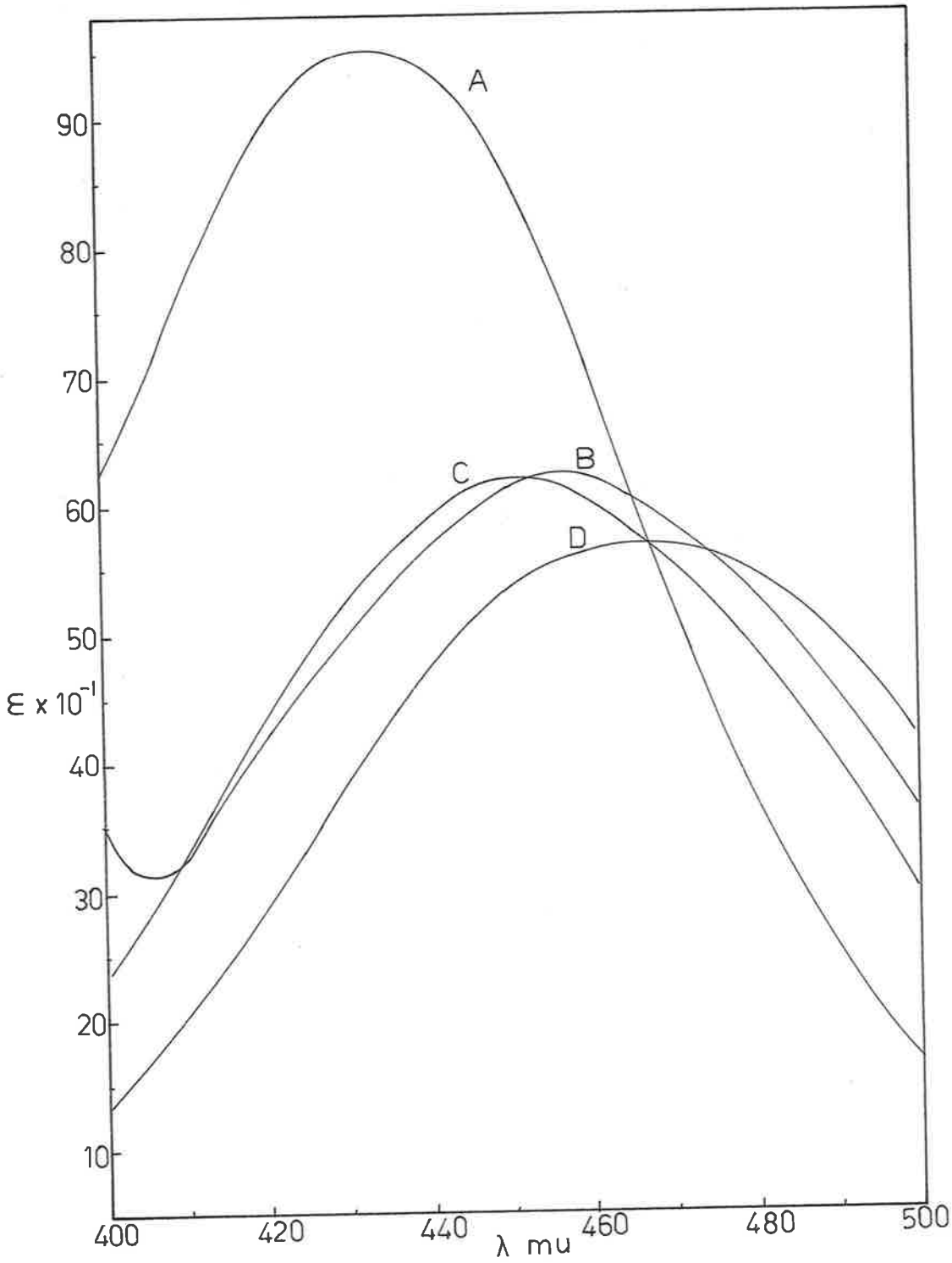


Fig. Vb - Absorption spectra (nπ* band) in acetic anhydride-hydrochloric acid solution; (A) 4-methylazobenzene, (B) 4-nitroazobenzene, (C) 2,6-dimethylazobenzene, and (D) 2,6,2',6'-tetramethylazobenzene.

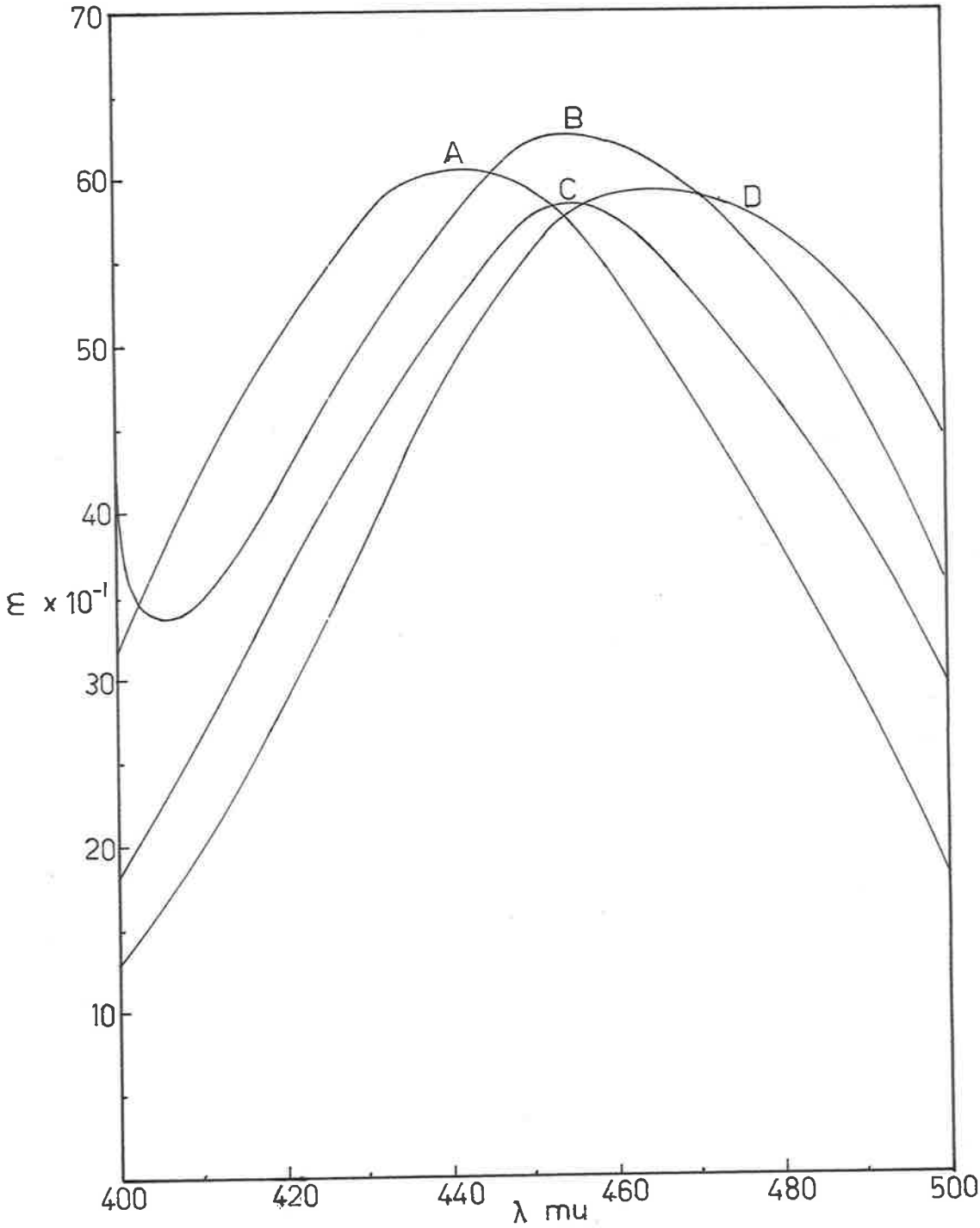


Fig Va - Absorption spectra (nπ* band) in acetic anhydride; (A) 4-methylazobenzene, (B) 4-nitroazobenzene, (C) 2,6-dimethylazobenzene, and (D) 2,6,2',6'-tetramethylazobenzene.

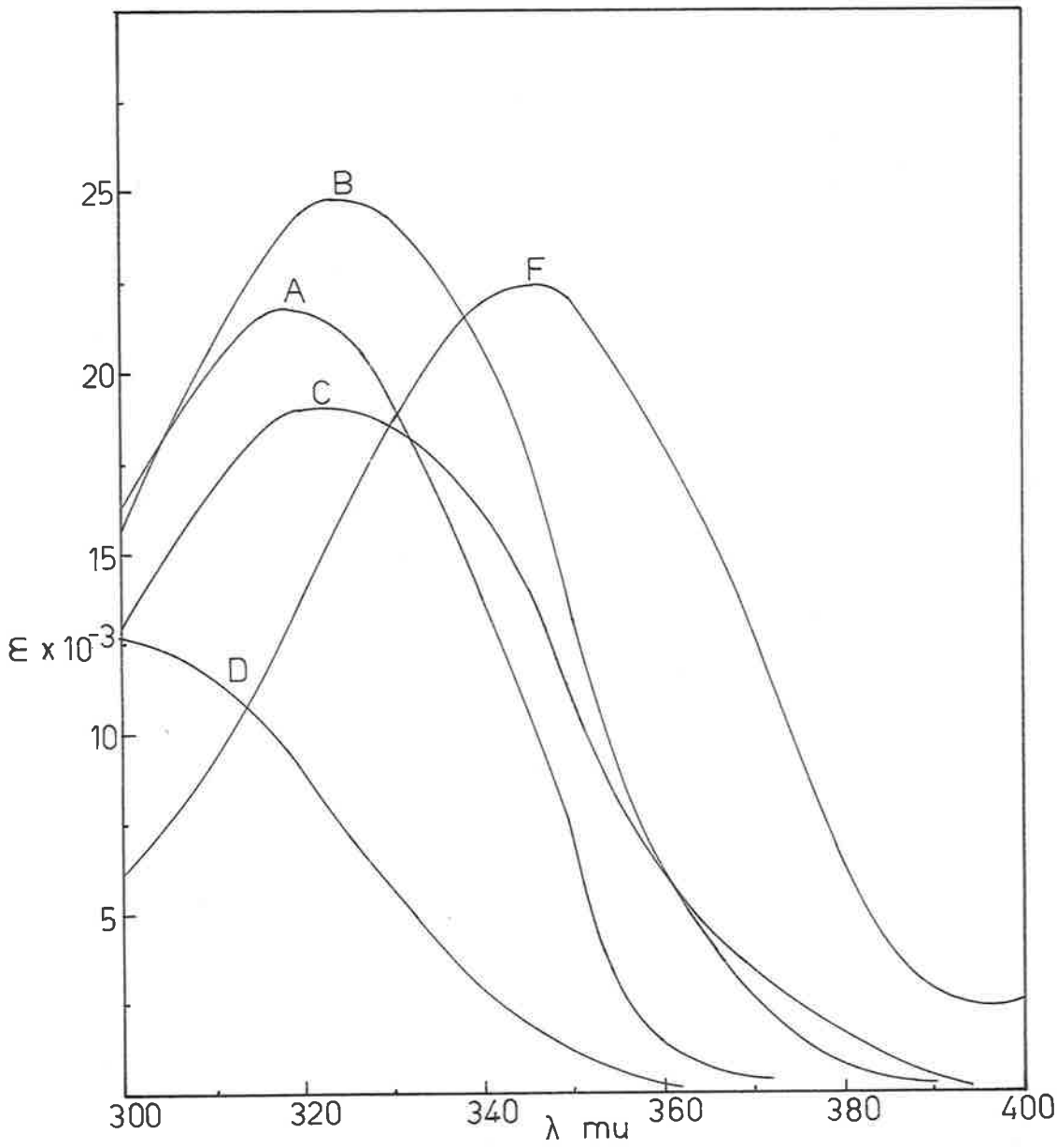


Fig. VIb - Absorption spectra (ππ* band) in acetic anhydride-hydrochloric acid solution; (A) azobenzene, (B) 4-chloroazobenzene, (C) 2-methylazobenzene, (D) 2,6-dichloroazobenzene and (F) 4-methoxyazobenzene.

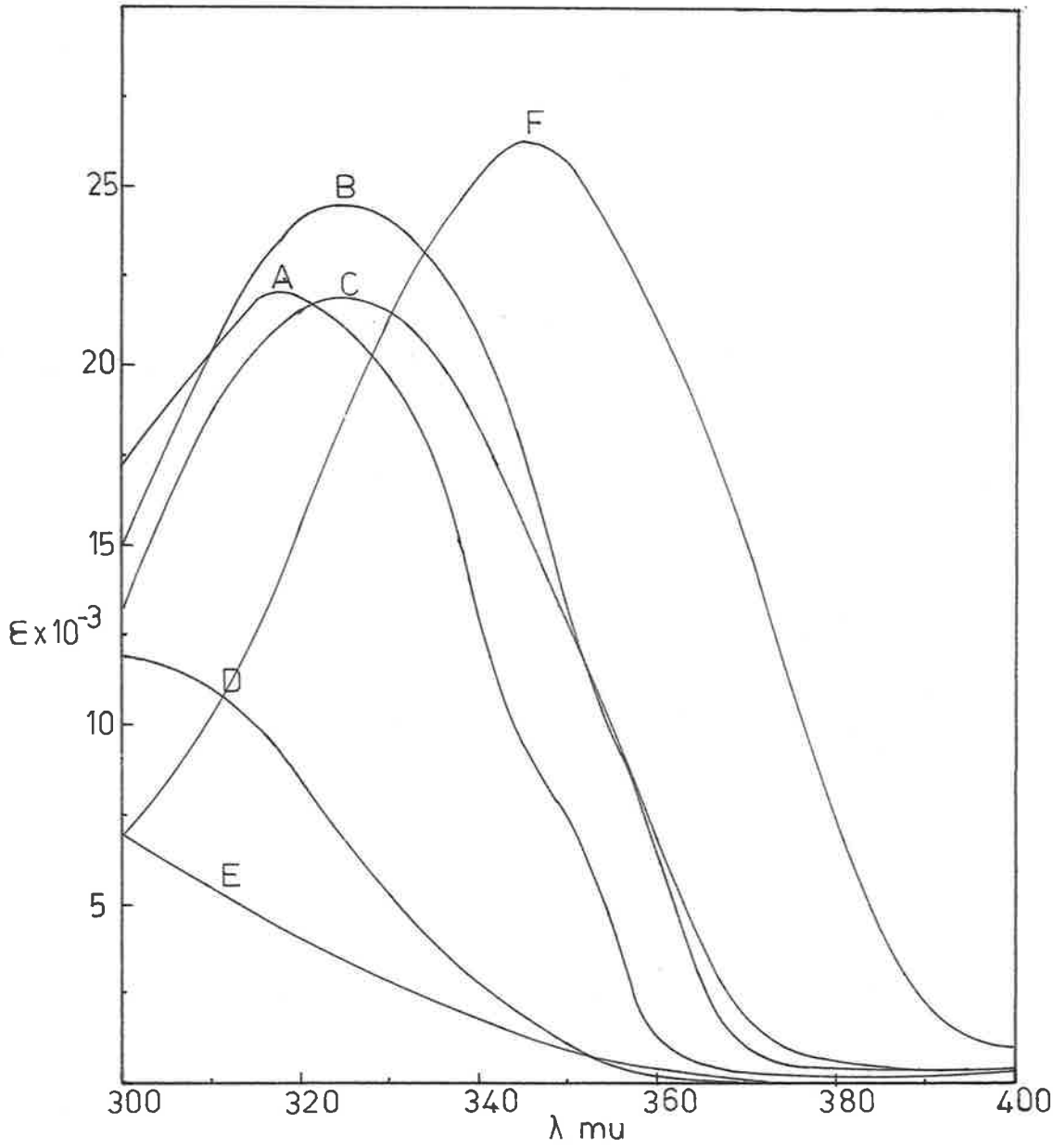


Fig. VIa - Absorption spectra (ππ* band) in acetic anhydride; (A) azobenzene, (B) 4-chloroazobenzene, (C) 2-methylazobenzene, (D) 2,6-dichloroazobenzene, (E) 2,6,2',6'-tetrachloroazobenzene, and (F) 4-methoxyazobenzene.

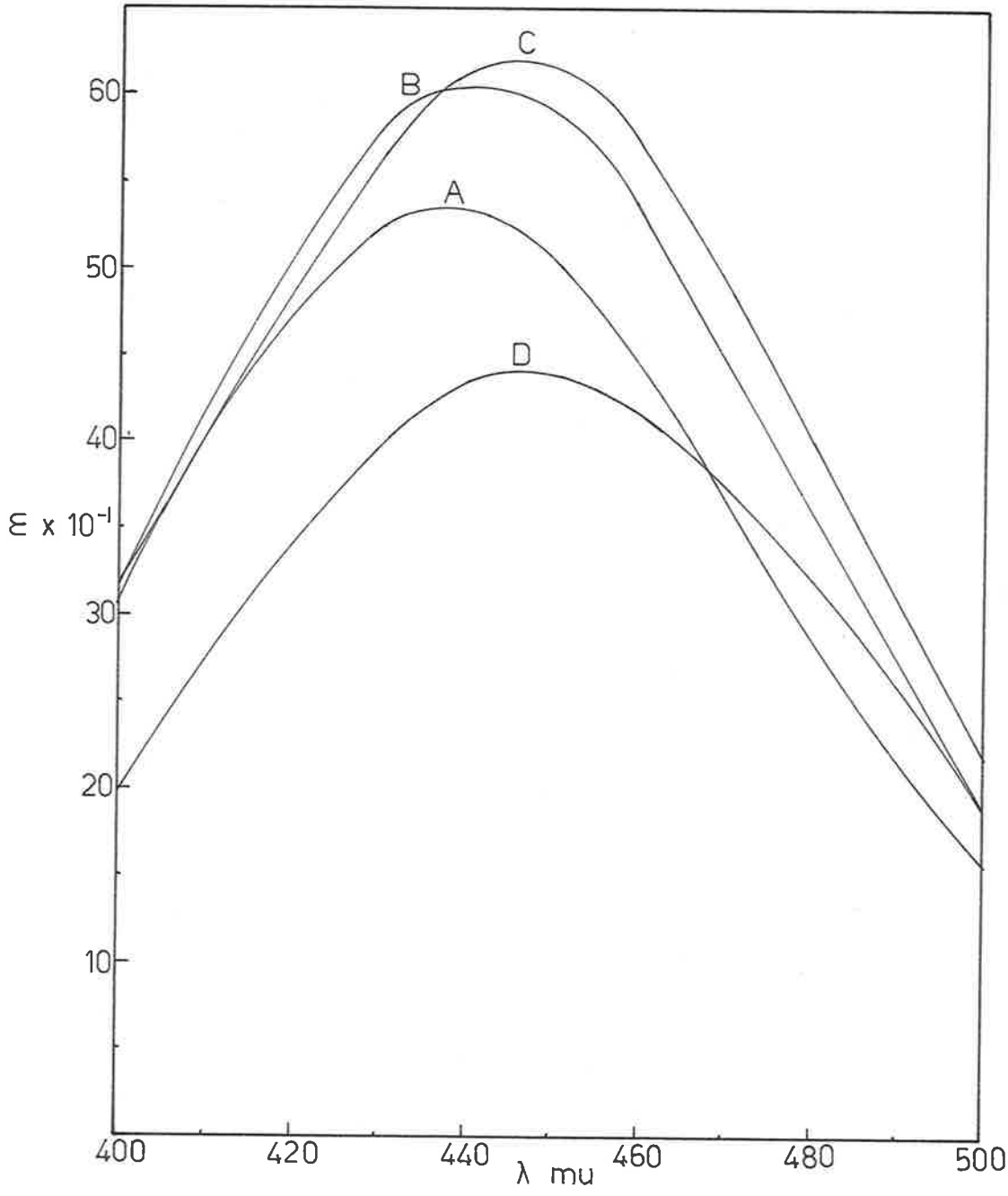


Fig. VIb - Absorption spectra (nπ* band) in acetic anhydride-hydrochloric acid solution; (A) azobenzene, (B) 4-chloroazobenzene, (C) 2-methylazobenzene, and (D) 2,6-dichloroazobenzene.

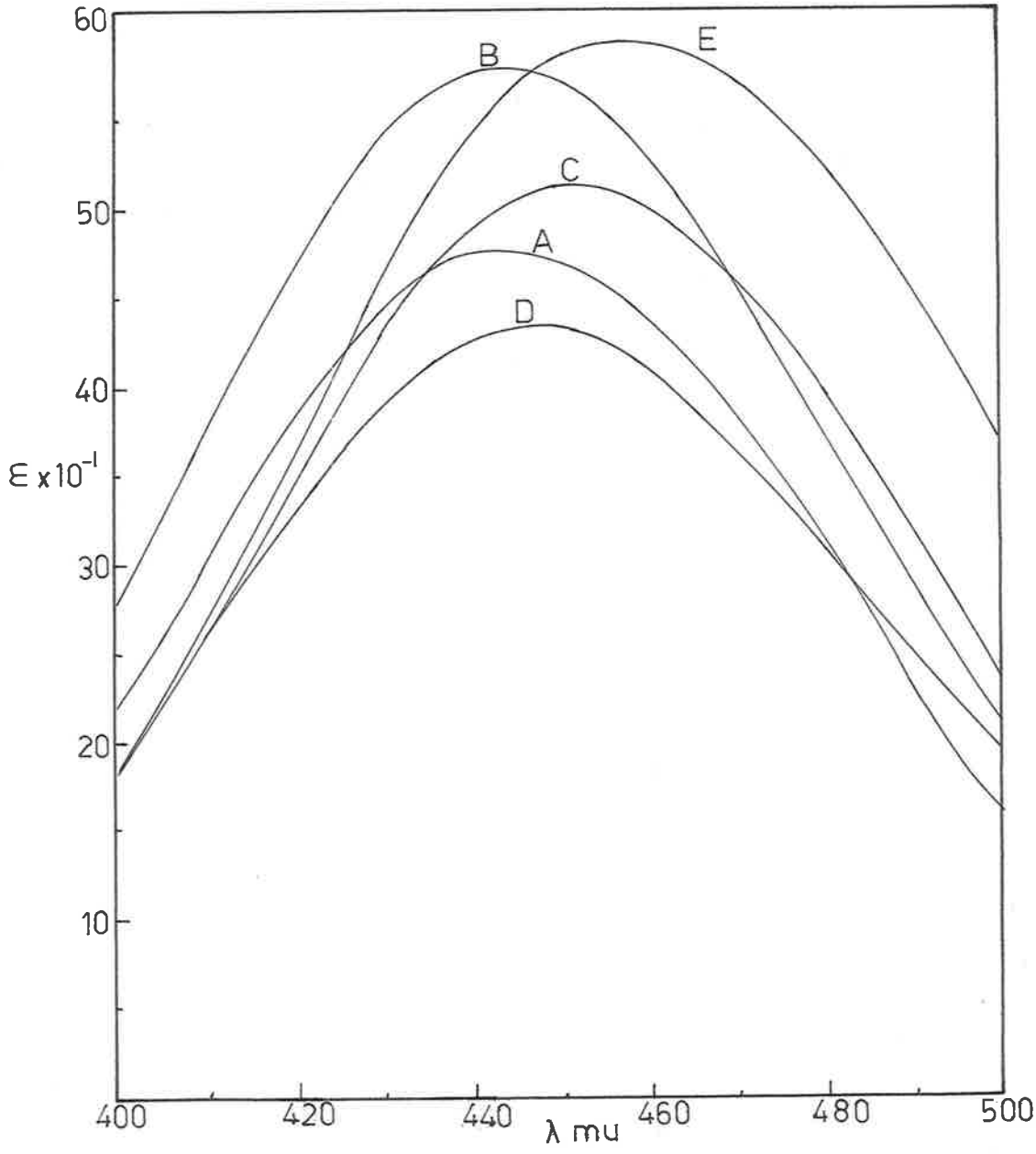
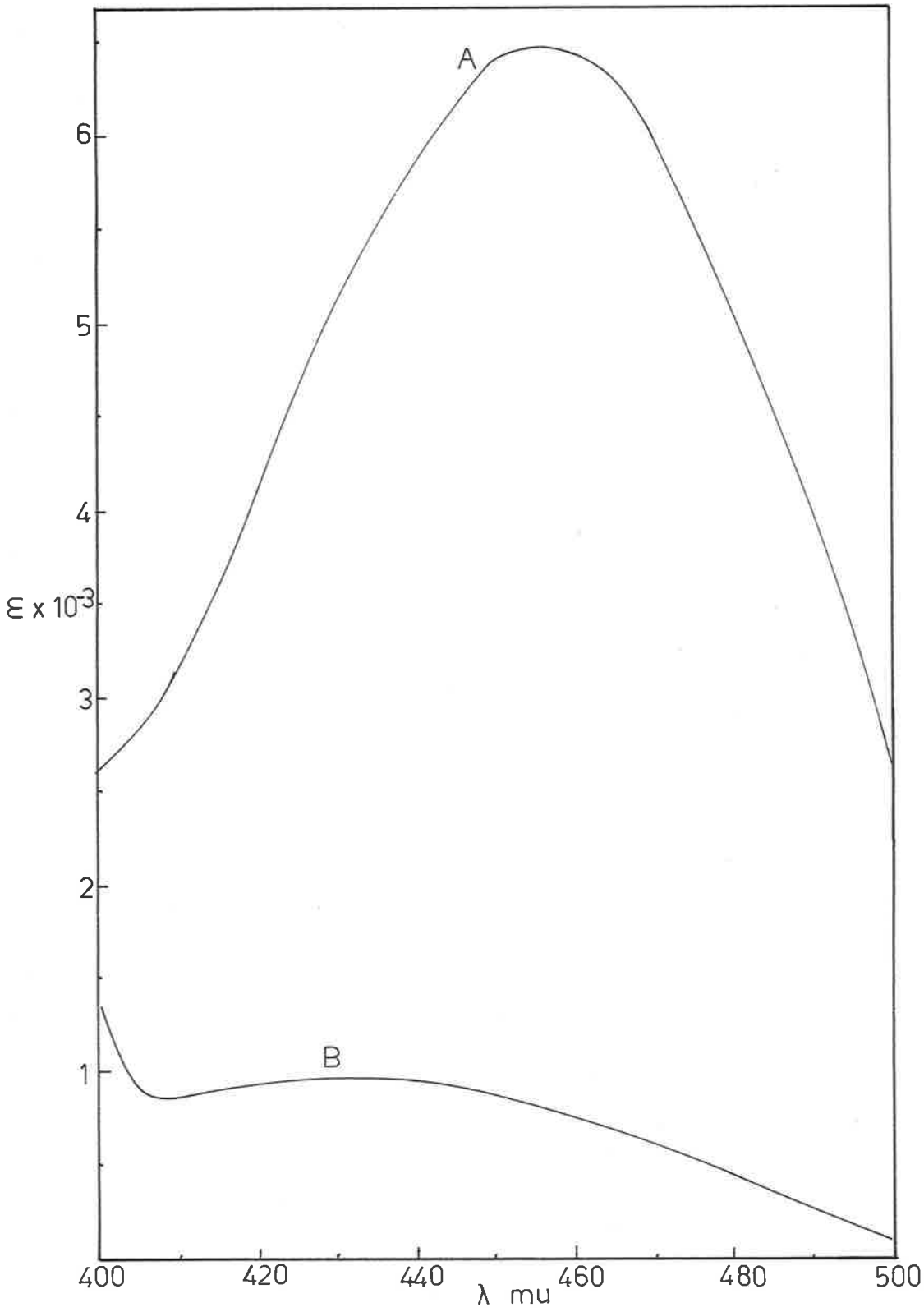


Fig. VIa - Absorption spectra (nπ* band) in acetic anhydride; (A) azobenzene, (B) 4-chloroazobenzene, (C) 2-methylazobenzene, (D) 2,6-dichloroazobenzene, and (E) 2,6,2',6'-tetrachloroazobenzene.



Absorption spectra (nπ* band) of 4-methoxyazobenzene in (A) acetic anhydride-hydrochloric acid solution, and (B) in acetic anhydride.

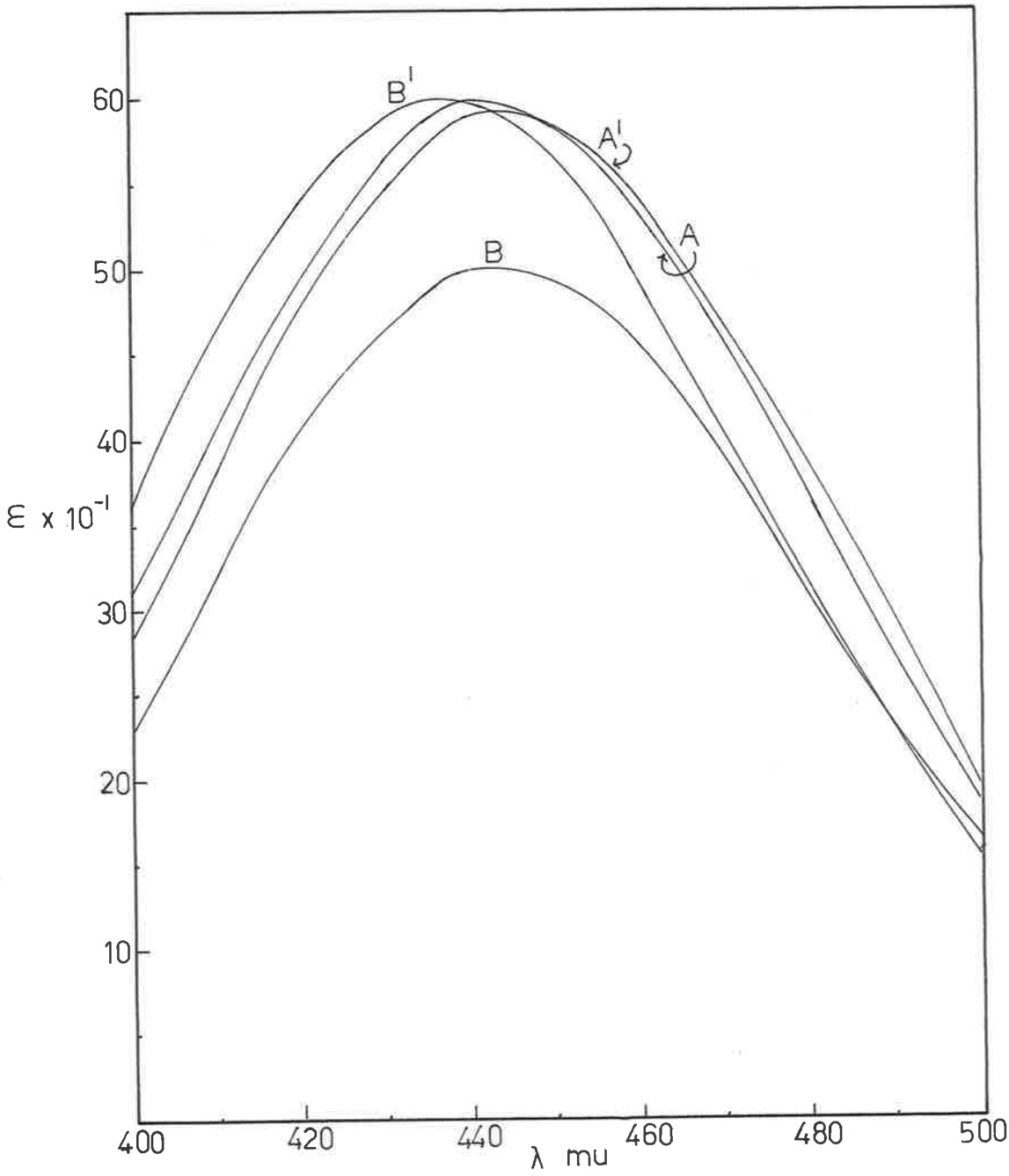


Fig. VII - Absorption spectra (nπ* band) in acetic anhydride; (A) 4-bromoazobenzene, and (B) 3-methylazobenzene. Absorption spectra (nπ* band) in acetic anhydride-hydrochloric acid solution; (A') 4-bromoazobenzene, and (B') 3-methylazobenzene.

(c) MASS SPECTRA OF SOME AZOBENZENES AND PHOTOPRODUCTS

All peaks greater than 5% of the base peak (100%) are shown.

Compound (52)	*m/e*	73	74	75	84	85	108	109	110	111	143
	I(%)	12	41	27	15	7	12	68	16	21	23

144	145	146	147	149	173	175	177	179	181	183	207	209	211
12	100	15	70	12	66	46	6	48	47	15	30	28	9

352(M)	354(M+2)	356(M+4)
15	25	16

Compounds (53 and 54) (mixture)	*m/e*	43	61	62	74	124	161	163	165	168	195	197
	I(%)	90	12	15	12	15	100	61	8	9	49	48

199	203	318	320	322
13	11	9	18	15

Compounds (53 and 54) (mixture)	*m/e* (>300 20eV)	316	318	320	322	324	352	354	356
	I(%)	35	59	98	100	42	14	31	37

358	362(M)	364(M+2)	366(M+4)	368	378	380	382	396(M)	398(M+2)
19	79	95	45	11	24	43	27	12	19

400(M+4)
12

Compound (55)	*m/e*	43	145	147	160	161	162	179	181	194	196	319
	I(%)	100	8	6	33	7	10	5	5	6	6	5

321	353	354	355	356	357	358	396	398	400	438(M)
6	5	31	28	40	12	32	27	34	27	<0.2

Compound (61)	*m/e*	43	163	176	178	191	193	198	218	233	235
	I(%)	43	9	66	42	100	65	14	8	87	56

276(M)	278(M+2)
13	9

Compound (62)	*m/e*	43	52	63	108	123	142	144	157	159	199
	I(%)	100	10	11	16	23	49	17	59	19	25

201	241(M)
9	3

Compound (63)	*m/e*	43	51	52	63	65	78	79	114	116	142
	I(%)	41	11	18	14	15	12	11	16	6	100

144	156	157	159	164	199(M)	201(M+2)
34	11	69	23	20	25	9

Compound (65)	*m/e*	50	51	52	53	57	62	63	64	65	75
	I(%)	7	9	7	5	5	5	30	24	5	8

76	77	78	79	80	92	98	107	108	111	113	126	127	128
8	68	13	6	6	37	8	100	12	11	7	27	7	10

135	136	138	141	142	143	169	171	276(M)	277(M+1)	278(M+2)	279(M+3)
58	7	5	38	7	14	24	10	70	15	28	5

Compound (71)	*m/e*	50	51	63	64	75	77	78	98	105	107	111
	I(%)	10	41	32	8	10	100	12	8	11	9	15

113	128	141	143	169	171	246(M)	248(M+2)
7	8	41	15	33	12	32	12

Compound (75)	*m/e*	43	44	50	51	52	53	61	62	63	64
	I(%)	88	6	22	44	24	7	6	12	31	9

65	73	75	76	77	78	79	87	90	91	92	93	99	101
16	10	11	16	14	44	17	9	19	9	10	23	27	9
108	113	114	115	116	123	126	127	128	129	142	144	145	157
8	7	70	8	26	6	16	9	10	9	99	71	7	100
158	159	199(M)	200(M+1)	201(M+2)									
26	73	90	17	40									

Compound (76)	*m/e*	43	51	52	63	64	65	77	78	79	92
	I(%)	81	12	10	7	6	13	28	11	10	19

93	94	95	108	111	120	121	122	123	126	129	142	154	156
19	13	10	11	10	14	7	15	14	11	6	7	7	13
157	158	277	278	279	320	321	322	362					
10	6	100	26	36	48	10	17	8					

Compound (77)	*m/e*	50	51	52	53	62	63	64	65	75	76	77
	I(%)	14	38	11	6	8	42	31	11	13	24	100

78	79	80	92	93	98	100	106	107	108	111	112	113	114
30	79	6	65	13	16	6	7	13	12	63	11	45	7
115	120	121	123	126	127	128	135	136	141	142	154	156	157
10	30	10	13	68	10	27	67	17	6	10	17	8	14
169	170	171	276(M)	277(M+1)	278(M+2)								
61	10	24	39	8	15								

Compound (88)	*m/e*	50	51	52	62	63	64	75	76	77	78	93
	I(%)	16	49	6	7	30	9	18	15	100	10	11

98	105	106	111	113	126	128	154	169	171	246(M)	248(M+2)
10	27	26	37	27	36	12	7	25	9	20	7

Compound (80)												
m/e	50	51	52	63	64	65	75	76	77	78	79	92
I(%)	25	31	7	20	25	6	28	10	100	16	40	40
m/e	93	111	113	120	121	127	139	140	141	142	246(M)	247(M+1)
I(%)	7	43	21	20	13	12	32	23	13	8	31	6
m/e	249(M+2)											
I(%)	12											

Compound (83)												
m/e	50	51	63	64	66	75	76	77	92	98	107	108
I(%)	7	12	33	27	12	10	12	70	41	8	100	11
m/e	111	113	126	128	135	141	142	143	169	178	193	207
I(%)	15	8	20	7	15	65	7	24	11	14	12	22
m/e	276(M)	277(M+1)	278(M+2)									
I(%)	41	7	14									

Compound (84)												
m/e	63	64	77	78	92	107	108	111	126	128	135	141
I(%)	17	12	36	5	21	100	9	6	14	5	18	38
m/e	142	143	169	276(M)	277(M+1)	278(M+2)						
I(%)	6	13	10	48	9	18						

Compound (88)												
m/e	39	50	51	53	54	75	76	77	78	92	107	108
I(%)	5	10	10	16	25	25	9	49	6	35	100	10
m/e	111	112	113	135	139	140	141	246(M)	247(M+1)	248(M+2)		
I(%)	82	7	30	11	33	5	10	40	7	14		

Compound (89)												
m/e	50	51	62	63	64	75	76	77	78	98	105	106
I(%)	8	22	5	19	5	10	9	100	12	9	29	5
m/e	111	113	126	128	139	141	142	143	169	171	175	246(M)
I(%)	13	7	17	7	6	61	7	21	12	5	6	63

247(M+1)	248(M+2)
11	24

Compound (91)	*m/e*	75	76	111	112	113	139	141	152	160	250(M)
	I(%)	25	8	100	8	35	34	11	8	5	29

252(M+2)
18

Compound (92)	*m/e*	50	51	75	76	111	112	113	139	141	152
	I(%)	6	5	28	7	100	8	34	39	13	7

250(M)	252(M+2)
22	14

Compound (93)	*m/e*	51	74	75	77	78	105	109	145	147	152
	I(%)	19	5	5	100	8	30	8	31	20	7

173	175	250(M)	251(M+1)	252(M+2)
9	6	29	5	19

Compound (96)	*m/e*	51	63	65	75	91	92	111	113	119	139
	I(%)	6	5	21	11	100	9	33	11	17	9

230(M)	232(M+2)
26	8

Compound (97)	*m/e*	50	51	63	77	79	89	90	99	105	125	126
	I(%)	7	30	12	100	11	19	5	6	22	52	5

127	153	155	165	230(M)	232(M+2)
17	18	5	5	20	7

Compound (101)											
m/e	50	51	63	64	75	76	77	92	111	112	
I(%)	15	7	7	6	36	22	6	12	100	8	
113	122	139	140	141	150	195	261(M)	262(M+1)	263(M+2)		
33	28	43	5	14	10	7	31	8	13		

Compound (102)											
m/e	50	51	63	64	74	75	76	77	90	111	
I(%)	21	8	7	7	5	49	30	5	13	100	
112	113	122	139	141	150	152	261(M)	262(M+1)	263(M+2)		
8	33	50	54	18	21	6	42	7	16		

Compound (103)											
m/e	50	51	55	56	57	63	64	65	69	71	
I(%)(>10)	19	23	19	17	25	15	12	29	19	17	
75	76	77	78	83	85	91	92	93	103	104	105	108	111
31	27	44	12	12	12	23	67	25	13	14	25	12	69
112	210	122	127	139	141	166	167	180	183	195	196	231	261
23	23	21	25	38	17	15	12	12	25	48	12	23	25
262	263	277	278	303	304	458(M)	460(M+2)						
29	12	38	21	100	25	4	3						

Compound (104)* indirect entry at T >400°.						
m/e	458	460	462	474(M)	476(M+2)	478(M+4)
I(%)	100	72	22	91	70	16

* The base peak of this spectrum was really *m/e* 45, but the largest peak for *m/e* >100 was *m/e* 104 where I = 6%. The molecular ion (M) and the (M-16) peaks were <2% of the base peak.

Compound (119)										
m/e	53	54	55	75	77	78	92	105	139	197
I(%)	5	5	9	5	56	7	9	100	5	21

217	322(M)	
5	*c*.1	

Compound (129)	*m/e*	51	65	77	78	79	103	105	106	133	182
	I(%)	15	6	73	9	16	9	100	11	9	5

209	210(M)	211(M+1)
8	35	7

Compound (131)	*m/e*	77	79	103	104	105	106	133	238(M)
	I(%)	19	14	8	5	100	11	5	14

Compound (132)	*m/e*	50	73	74	75	84	85	109	110	111	124
	I(%)	8	6	21	21	8	7	46	11	16	5

145	146	147	148	149	173	174	175	177	318(M)	320(M+2)	322(M+4)
100	9	68	5	11	84	7	54	10	18	23	12

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