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JOHN EDWARD MOIR, B.Sc(HONS.)

Department of Organic Chemistry

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SUMMARY

Irradiation of trans-azobenzene in acetyl chloride is known[101] to yield N,N'-diacetyl-4-chlorohydrazobenzene in high yield. In this thesis the examination of the photoinduced reactions of various azonaphthalenes with acetyl chloride is described, the investigation having been directed toward obtaining more information concerning the scope and mechanism of the reaction.

Irradiation of trans-1-phenylazonaphthalene, 2-phenylazonaphthalene, and 2,2'-azonaphthalene in acetyl chloride afforded mixtures of chloro-N,N'-diacetyl hydrazonaphthalenes. Hydrolysis* - oxidation of the crude photoproduct from each reaction has been shown to yield a chloroazonaphthalene and the parent azo compound as the main products, trace amounts of one or more other chloroazonaphthalenes also having been detected. A crystalline chloro-N,N'-diacetyl hydrazonaphthalene was isolated from each photoreaction; and subsequent hydrolysis-oxidation of the compound gave the non-chlorinated parent azonaphthalene in each case. Some possible modes of formation of the non-halogenated compound are discussed.

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* The hydrolysis was carried out under alkaline conditions; and the hydrazo compound so formed was spontaneously oxidized by atmospheric oxygen present in the reaction mixture.

trans-1,2'-Azonaphthalene has been found to undergo a photoreaction with acetyl chloride to give a mixture of ≠x-chloro-N,N'-diacetyl-1,2'-hydrazonaphthalenes and 4-chloro-N,N'-diacetyl-1,2'-diamino-1',2-binaphthyl. The mixture of hydrazo compounds yielded 1,2'-azonaphthalene and ≠x'-chloro-1,2'-azonaphthalene when subjected to alkaline hydrolysis; and a small quantity of 4-chloro-1,2'-azonaphthalene was also present in the hydrolysis mixture.

Irradiation of trans-1,1'-azonaphthalene in acetyl chloride has been shown to lead to the formation of 4 -chloro-N,N'-diacetyl-1,1'-diamino-2,2'-binaphthyl in high yield. Treatment of the crude photoreaction mixture with ethanolic potassium hydroxide gave a small yield of 4-chloro-1,1'-azonaphthalene.

The nature of the hydrolysis products in all of the reactions mentioned above is discussed in relation to the compounds present in the photochemical reaction mixture. Some possible mechanistic pathways to the photoproducts are outlined in each case.

≠ The terms x and x' are used to indicate unknown positions of chlorine substitution. x' defines positions in the phenyl ring when phenylazonaphthalenes are discussed; and in a naphthalene ring attached to the azo linkage at the 2'-position when azonaphthalenes are described.

cis-2-Phenylazonaphthalene, 1-phenylazonaphthalene, 2,2'-azonaphthalene, 1,2'-azonaphthalene, and 1,1'-azonaphthalene have been shown to react with acetyl chloride in the absence of light to form in each case a complex mixture of compounds. Hydrolysis - oxidation of these mixtures gave essentially the same products as were formed when the respective photoreaction mixtures were hydrolysed. The possible structures of the dark reaction products are discussed in terms of the hydrolysis products. In all of these reactions an intense blue-purple colouration occurred as soon as the reactants were mixed. Attempts to characterize the dark blue compound responsible for this effect were unsuccessful. Each compound was too unstable to permit its isolation in a pure state. The observed colour change provides a simple test to distinguish between the cis- and trans-isomers of the azo compounds. The significance of the dark reaction of the cis-isomers with acetyl chloride when related to the photochemical reactions of the trans-isomers is discussed.

Irradiation of trans-2-phenylazonaphthalene, 1-phenylazonaphthalene, 2,2'-azonapthalene, and 1,2'-azonaphthalene in different acid chlorides and subsequent hydrolysis - oxidation of the photoproducts have been shown to give widely varying yields of products. Attempts to correlate these variations with the ionizability and structures of the acid chlorides are made.

trans-2-Phenylazonaphthalene has been shown to yield x-chloro-

N-oxalyl-2-phenylazonaphthalene (as the major product) when irradiated in oxalyl chloride. This product readily formed an ethyl and methyl ester when treated with the respective alcohol. Hydrolysis - oxidation of either of the pure esters yielded mainly 2-phenylazonaphthalene. Treatment of the crude photoproduct under the same conditions gave 2-phenylazonaphthalene, 2-(4'-chlorophenylazo)naphthalene and 2-(2'-chlorophenylazo)naphthalene. Conclusions are drawn concerning the possible precursors of these compounds. A similar sequence of reactions has been extended to trans-azobenzene.

trans-2-Phenylazonaphthalene and trans-azobenzene have been irradiated separately in malonyl dichloride; and the photoproduct from each reaction was treated with ethanol. The same product was shown to be formed in each reaction sequence. This compound has not been identified; but its possible nature is discussed in terms of the available data. A similar reaction sequence was carried out using methanol instead of ethanol. It has not been possible to determine the part played by the azo compound in the photoreaction.

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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.

JOHN EDWARD MOIR.

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INTRODUCTION

Aromatic azo compounds are known to undergo a variety of reactions under conditions of photoactivation. Azobenzene and substituted azobenzenes have been subjected to detailed examination under diverse reaction conditions.

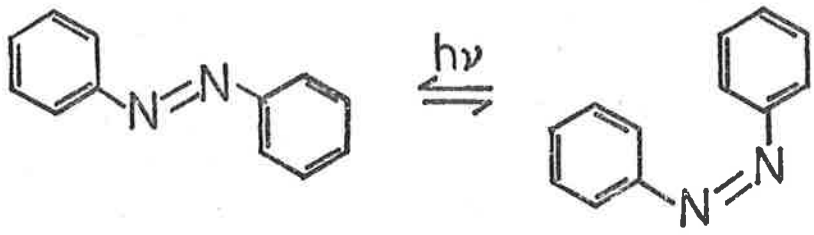
Well-documented accounts of the trans ⇌cis photoisomerization, and of the photocatalysed cyclodehydrogenation of these compounds in acidic media, can be found in the literature. Other aromatic azo compounds, such as azonaphthalenes and phenylazonaphthalenes, have to a lesser extent been the subject of similar studies. Photoinduced rearrangements have also been shown to occur with azoxybenzenes[73-81] and azoxynaphthalenes.[69-73] A novel photoreaction of azobenzenes with acid chlorides has been reported by Lewis and Mayfield.[101-105]

The following is a brief account of these photocatalysed reactions of azobenzene and substituted azobenzenes. The azonaphthalenes and phenylazonaphthalenes are also discussed where appropriate examples are available.

cis⇋trans Photoisomerization of Azo Compounds.

Hartley[1,2] was the first to show that the irradiation of solutions of azobenzene gives a mixture of cis (2) and trans (1) isomers. Continued irradiation leads to a photostationary state wherein a fixed percentage of each isomer is maintained by photoinduced trans⇌cis

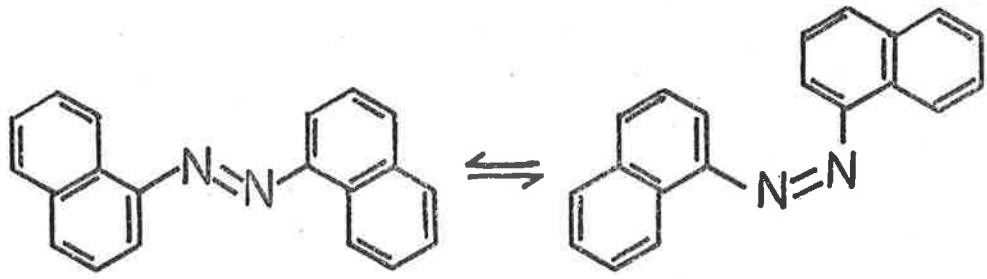
and thermal cis → trans isomerization. The proportion of each isomer in the equilibrium mixture is dependent on the wavelength of the incident light.[3-5]



(1) (2)

Initial attempts[6,7] to isolate the cis-isomers of azonaphthalenes and phenylazonaphthalenes were unsuccessful. It was not until 1955 that Frankel et al.[10] reported that they had isolated the cis-isomers of 1,1'-azonaphthalene (6), 2,2'-azonaphthalene (7), and 1,2'-azonaphthalene (8) from mixtures obtained by the irradiation of the respective trans-azonaphthalenes (3-5) in chloroform solution. They showed that solutions of azonaphthalenes formed photostationary mixtures on prolonged exposure to ultraviolet radiation. In 1955 Fischer et al.[3] published results which showed that photoequilibria in the isomerization of 1,2'-, 1,1'-, and 2,2'-azonaphthalene were dependent on the wavelength of the incident light.

Substituted azobenzenes are known to photoisomerize[6-11] and many



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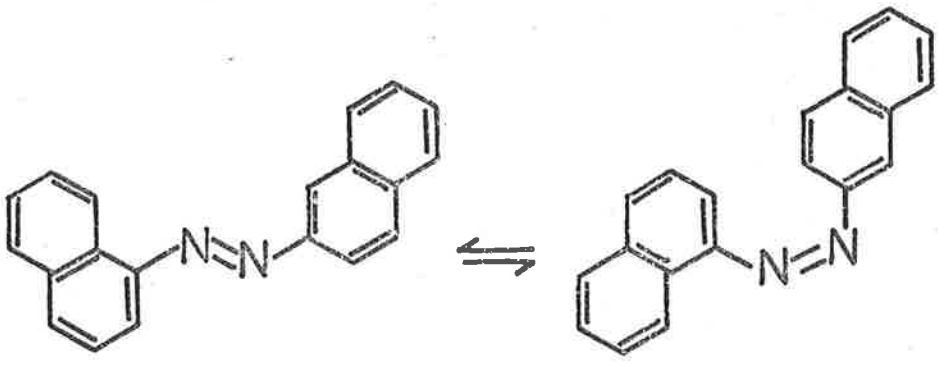

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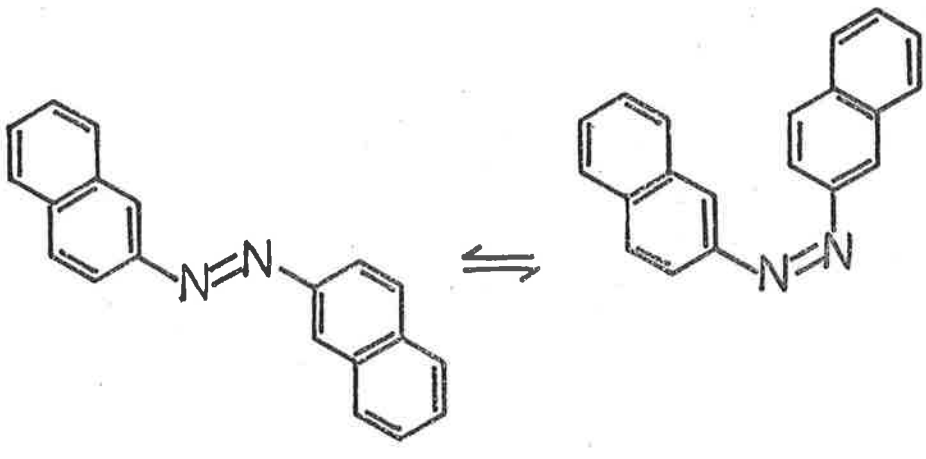


(4) (7)

of the more stable cis-isomers have been isolated from the cis⇌trans mixtures and characterised.[6,8,9] However photoisomerization has not been reported for any substituted azonaphthalenes; and only one account of a substituted phenylazonaphthalene[7] exhibiting this phenomenon appears in the literature.

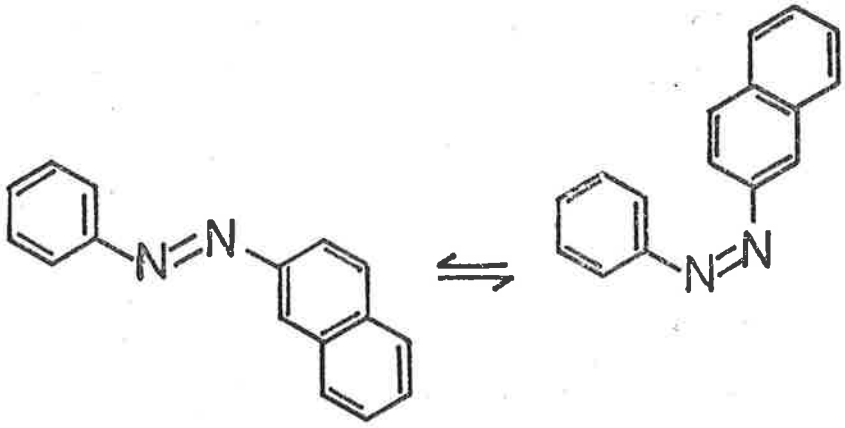
Hartley's results[2] for the thermal cis→trans conversion of azobenzene in benzene solution indicated half-lifetime values of $\tau_{\frac{1}{2}}$ = 150 min (56.5°) and $\tau_{\frac{1}{2}}$ = 21 min (76.6°), E_A = 23 k.cal.mole^{-1}. Comparison of these values with those obtained for cis-1,1'-, 2,2'-, and 1,2'-azonaphthalene[10] (Table I) shows the slightly greater thermal instability of these cis-isomers when compared with cis-azobenzene.

Table I.

Azonaphthalene	Temp. (°C)	$\tau_{\frac{1}{2}}$ (min)	Temp (°C)	$\tau_{\frac{1}{2}}$ (min)	E_A, k.cal.mole^{-1}
1,1'-	0	173	12.5	29.5	22 ± 2
2,2'-	29.0	150	47.0	19	22 ± 2
1,2'-	18.5	104	45.0	5	21 ± 2

As a consequence of this thermal instability the effect of ultraviolet radiation on solutions of these three ordinary azonaphthalenes at room temperature is short-lived; and a comparatively rapid thermal reversion to the trans form takes place.

Both 1-phenylazonaphthalene[13,14] and 2-phenylazonaphthalene[13] have been observed to undergo distinct spectral changes when irradiated with ultraviolet light at temperatures low enough to minimise thermal reversion. The spectral changes have been attributed to the establishment of photostationary states resulting from cis⇌trans photoisomerization; (9)⇌(11) and (10)⇌(12).



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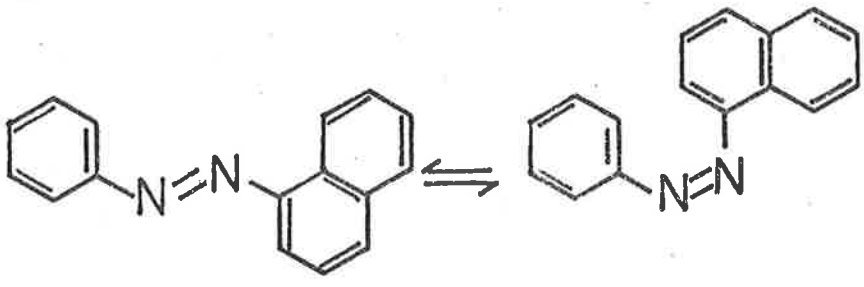
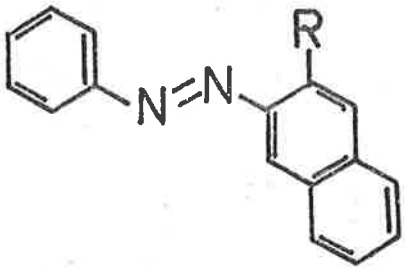


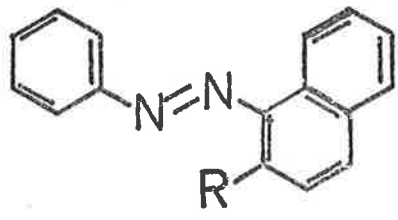
(9) (11)

Several substituted phenylazonaphthalenes, namely 3-hydroxy- and 3-methoxy-2-phenylazonaphthalene (13) and 2-methoxy-1-phenylazonaphthalene (14), were also found to attain photoisomeric equilibrium when irradiated.[13] All spectral changes observed were thermally



R= -OH , $-OCH_3$

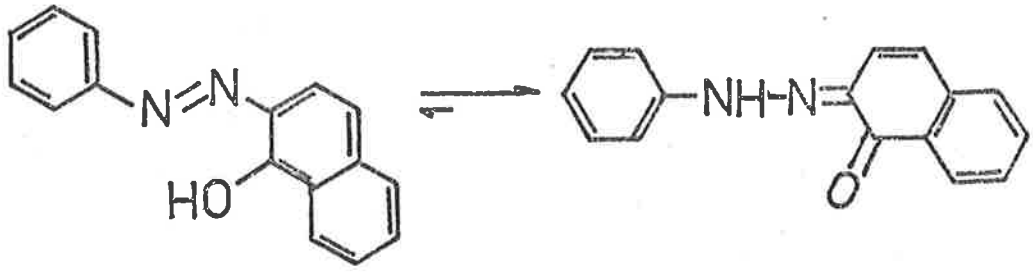
(13)



R= $-OCH_3$

(14)

reversible. The cis-isomers were not isolated, their presence being shown spectroscopically. 1-Hydroxy-2-phenylazonaphthalene (15) was an exception with no isomerization occurring on irradiation. The predominance of the hydrazo tautomer (16) in solution was held to be responsible for the cis-isomer of compound (15) not being formed.



(15) (16)

Much of the work done during the last two decades on cis-azobenzenes has been directed towards obtaining a better understanding of the mechanism of photoisomerization[3,14,16-24] and of the thermally induced cis→trans isomerization[9,25-29] of azobenzene.

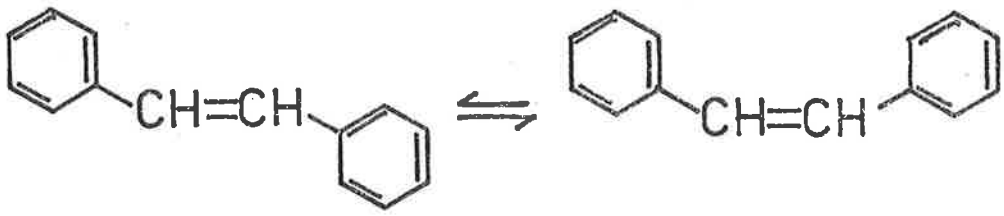
Many ideas have been forwarded to explain the mechanism of photoisomerization. Lewis et al.[31] suggested that photoisomerization involved the molecule changing from its electronically excited state into one at a high vibrational level of the ground excited state. Here energy is available for rotation which leads to cis or trans molecules in their ground states once the surplus energy has been lost to the medium. According to several other workers[2,25,27,30] photo-isomerization involves an intermediate state common to both cis- and trans-isomers where no energy barrier exists between the two forms. Both of these hypotheses were found to contradict the experimental results of Zimmermann[18] and Fischer.[14,19]

Zimmermann[18] determined the quantum yields, ϕ_t, for the trans→cis, and ϕ_c, for the cis→trans isomerizations of azobenzene at several wavelengths in iso-octane as solvent. The sum $(\phi_t + \phi_c)$ was found to deviate from unity (0.52-0.82) in all cases and no fluorescence was observed from either isomer. This evidence excludes the possibility of a common excited state being formed when either the cis- or trans-isomer is irradiated. The explanation advanced by them was that photo-isomerization takes place as an ordinary thermal reaction of an

electronically excited state, where thermal interconversion of excited cis* and trans* molecules occurs across an (hypothetical) energy barrier.

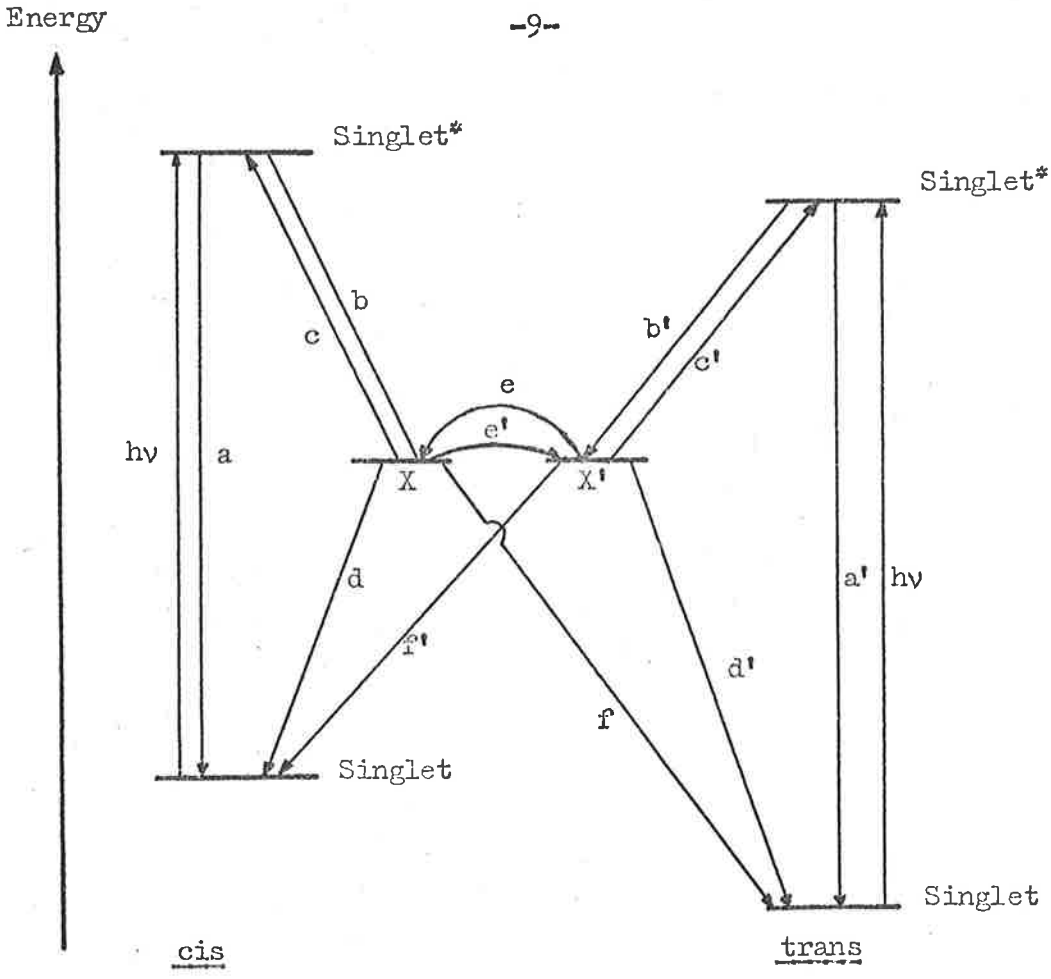
Two papers, one by Fischer[19] and another by Malkin and Fischer,[14] describe results obtained for ϕ_c and ϕ_t of azobenzene, 1-phenylazonaphthalene, 1,1'-, 1,2'-, and 2,2'-azonaphthalene measured in the temperature range of + 20° to -183°. Both ϕ_c and ϕ_t were found to change as the temperature was lowered. ϕ_t decreased markedly, whereas the decrease in ϕ_c was much less, suggesting that the trans→cis conversion requires a larger activation energy than for the cis→trans conversion.

Malkin et al.[14] also noted a similar temperature dependence of ϕ_t and ϕ_c for the photoisomerization of stilbene (17).



(17) (18)

A general reaction scheme for the photoisomerization of aromatic azo compounds was postulated[14] (Scheme I). In the scheme, processes a-f and a'-f' are all thermal reactions. Insufficient data are



Scheme I.

available to decide which of the processes is responsible for the observed temperature dependent effects. The nature of the intermediate states X and X' is unknown; and they may be separate states (cis*, trans*) or one common state(s). The latter possibility is discounted

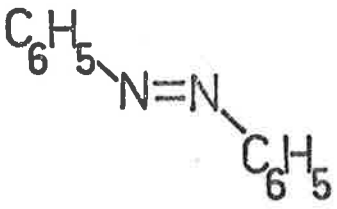
$$\underline{\text{cis}} \overset{I_o}{\rightleftharpoons} \underline{\text{cis}}^* \rightleftharpoons \underline{\text{trans}}^* \overset{I_o}{\rightleftharpoons} \underline{\text{trans}}$$

$$\underline{\text{cis}} \overset{I_o}{\rightleftharpoons} S \overset{I_o}{\rightleftharpoons} \underline{\text{trans}}$$

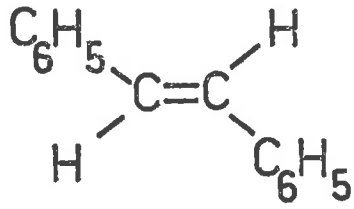
by Zimmermann,[18] who found that $(\phi_c + \phi_t)$ for azobenzene was less than unity, rather than equal to one which would be the case if there was a common state. Malken et al.[14] suggested that the fact that this value is less than unity may be attributed to the competing reactions a and a' (see Scheme I).

Kearns[21] adopted a theoretical approach to explaining the qualitative results obtained for the photoisomerization of aromatic azo compounds. He considered isomerization in the excited molecule as occurring by rotation about the N-N bond axis. Using molecular orbital calculations he determined the dependence of the excited state ($n-\pi^*$) and ($\pi-\pi^*$) energies on the angle of rotation about the N-N bond axis. On the basis of his results, he concluded that an activation energy was required to convert azobenzene from the planar to the perpendicular conformation when in its lowest ($\pi-\pi^*$) singlet or triplet state, or lowest ($n-\pi^*$) singlet state. No energy barrier existed if isomerization occurred when the molecule was in its lowest ($n\pi^*$) triplet state. This implied that the most efficient means of promoting isomerization would be the most efficient process for populating the $n\pi^*$ triplet state. His calculations also predicted that lowering the temperature would cause a smaller decrease in the quantum yield for cis→trans photoisomerization than for trans→cis photoisomerization. These conclusions are compatible with the observed behaviour of azo compounds as reported by Zimmermann[18] and Fischer.[14,19]

The "lateral shift mechanism" is an alternative method of trans⇌cis interconversion that has been proposed[26,33] in an attempt to explain the very low activation energies required for the isomerization of azobenzene[9,25,26] and imines.[32,33] This mechanism requires the movement of one substituent from one side of the molecule, via a linear transition state, to the other. Rotation is not involved, and the mechanism can only apply to molecules such as azobenzene (19) and imines (20), but not stilbenes (21).



(19)



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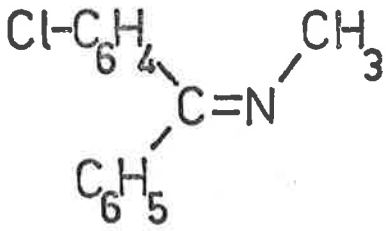


(20)

The study of the photosensitized isomerization of azobenzene has been undertaken by several workers[23,24] in an effort to learn more concerning the excited states involved in the transformation. Using triphenylene, β-acetonaphthone, and 3-acetylpyrene as triplet sensitizers, Jones and Hammond[23] established that energy transfer to

the azobenzene occurred. A photostationary state resulted in which 1.5-1.8 percent of the cis-isomer was present. The decay ratio of 60 obtained from this percentage was in sharp contrast to the value of 4 obtained by Zimmermann et al.[18] for the non-sensitized photoisomerization of azobenzene using light of wavelength 315 mμ. Photoisomerization was suggested to occur through excited singlet states.

Recent work by Fischer[24] involving use of naphthalene and triphenylene as triplet donors indicated a decay ratio of 4 for the photostationary state. This corresponded to an approximate cis-isomer content in the photoequilibria mixture of 20 percent. These results did not agree with those obtained by Jones and Hammond[23] but were identical with values published by Zimmermann et al.[18] for direct photoisomerization. Fischer suggested on the basis of his results that a crossing of paths in the triplet sensitized isomerization and the direct photoisomerization may occur. However, energy transfer involving a state other than a triplet state cannot be eliminated completely.

The photoisomerization of azobenzenes, and in particular azobenzene itself, has been the subject of most studies directed towards a more detailed knowledge of the mechanism of this transformation. With the exception of work by Fischer et al.[14] and Fischer,[19] the phenylazonaphthalene and azonaphthalene photoisomerizations have received much less attention.

The complete mechanism of the trans⇌cis thermal- and photo-isomerization of the aromatic azo compounds is still undetermined. Further work needs to be done on this problem.

Studies of the Conjugate Acids of cis and trans Aromatic Azo Compounds.

The relative basicities and possible structures of the conjugate acids of cis- and trans-azobenzenes have been studied by many workers. Unfortunately very little is known about the conjugate acids of the cis- and trans-azonaphthalenes. As a consequence of this, conclusions regarding the azonaphthalenes must be drawn by analogy from what is known about the azobenzenes as indicated in the following outline.

Detailed spectroscopic examination of the conjugate acids[34-47] and related metal halide complexes[48-52] of azobenzenes has yielded useful information concerning the basicities and structures of these species. Large changes have been observed to occur in the electronic absorption spectra of cis- and trans-azobenzenes as the acidity of the solvent medium is increased. This has been attributed to the protonation of one or both of the nitrogen atoms at the azo linkage, resulting in a reorganization of the energy levels involved in the electronic transitions.

Badger et al.,[81] on the basis of their results for the oxidation of cis- and trans-azobenzene, were the first to suggest that cis-azobenzene was more basic than trans-azobenzene. This prediction was

verified by later workers who determined spectroscopically the basicities of both isomers in aqueous sulphuric acid,[35] ethanolic sulphuric acid[34,36-38] and acetic acid-perchloric acid.[39] Their results showed the cis-isomer to be the stronger base by a factor of 10. This result has been shown to be generally true for substituted azobenzenes,[39] with the exception of compounds where strongly electron-attracting (-M) substituents are present in the para position.

The basic strengths of the conjugate acids of cis- and trans-azonaphthalenes have not been determined. If we assume that the results observed for the azobenzenes may be applied in general to other azo compounds, then the cis-isomers of such compounds should be appreciably more basic than the trans-isomers.

The difference in the basic strengths between cis- and trans-azobenzene has been related to the marked difference in molecular geometry of the two isomers. trans-Azobenzene has been shown to be a planar molecule.[83] This allows extensive conjugation of π -electrons throughout the molecule, thus decreasing the electron density at the azo linkage by delocalization of the π -electrons in this bond. The partial double bond character of the C-N bonds was shown from electron diffraction studies. The C-N bond was found to be shorter than a true C-N single bond.[53] The orbitals of the nitrogen lone pair electrons lie in the nodal plane of the π -electrons in the aromatic rings. As a consequence of this, steric interaction by bulky substituents in the

ortho position restricts access by protons[35] and other species to these electrons.

The geometry of the trans-azonaphthalene molecules would be expected to be similar to that of trans-azobenzenes, with both the phenyl and naphthalene rings being in one plane and extensive conjugation existing between them through the π-electrons in the azo linkage. The greater conjugating ability of the naphthalene rings[54,55] decreases the bond order, and hence the electron density, at the azo linkage. This would render the trans-azonaphthalenes less basic than trans-azobenzene. Steric interactions[54,55] may also effect the basic strengths of azonaphthalenes by restricting protonation at the azo group nitrogen atoms.

In contrast to trans-azobenzene, cis-azobenzene is known (from X-ray diffraction studies) to be non-planar in the solid state.[56,57] This was verified by calculations[57] which showed that the phenyl rings are turned 56° out of the nodal plane of the π-electrons in the azo linkage. This non-planarity is caused by steric repulsions between ortho hydrogen atoms. Recently, Beveridge and Jaffe[40] published calculations which indicated that the geometry of the cis-azobenzene giving the most consistent interpretation of the electronic spectrum is the "propellor shaped" conformation, wherein the phenyl rings are rotated approximately 30° out of the plane. The fact that the rings are not co-planar with the rest of the molecule is thought to account

for the greater basicity of cis-azobenzene[40] when compared to trans-azobenzene. The molecule being non-planar would result in much less overlap of the azo and phenyl π-orbitals. Delocalization of the azo linkage π-electrons would then be less extensive resulting in the localized electron density at the azo linkage being much greater than in the planar trans-isomer. Because of this the basicity of the cis-isomer would be greater than that of the trans-isomer. X-ray diffraction measurements of the C-N bond length in cis-azobenzene show that it is a normal single bond.[56,57]

The same studies have not been extended to the cis-azonaphthalenes, but it is reasonable to assume that these molecules will also exist in the non-planar "propellor shaped" conformation. However, the difference in basicities of the cis- and trans-isomers may be much larger because of the lower electron density at the azo linkage of trans-azonaphthalenes when compared with trans-azobenzene.[56,57] If the basicities of the cis-isomers of azobenzene and azonaphthalenes have similar values then this would suggest a larger difference in the basic strengths of the cis- and trans-azonaphthalenes.

Other azobenzene derivatives which have been examined in detail as their conjugate acids are those containing a second basic centre.[35,41-46,63] Here the main aim has been to determine where protonation first occurs, viz. at the azo linkage or at the second basic centre. The first protonation occurs at the amino group[35] in dilute acid, while protonation

of the azo group takes place only at fairly high concentration of acid. As the acidity of a solution of 4-aminoazobenzene increases several species can be detected spectroscopically.[46] A concept of tautomerism has been used by Sawicki[46] and later workers[41] to explain this. The monoxides and dioxides of N,N-dimethyl-4-aminoazobenzene also undergo protonation first at the dimethylamino group and then at the azo linkage[63] as the acidity increases.

The related aminoazonaphthalenes have not been examined in relation to this problem and definite conclusions cannot be drawn regarding the order of protonation in such compounds.

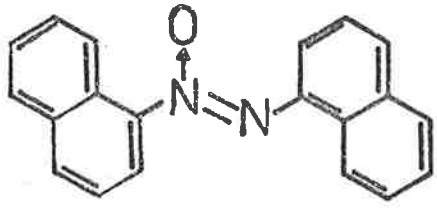
Structurally the conjugate acids of cis- and trans-azobenzene exist in the cis and trans conformations[34,47] with the proton attached to one of the nitrogen atoms. The conjugate acids were also reported[34] to undergo photoisomerization resulting in a photostationary state being formed containing 55 percent of the cis-isomer. This work disproved an earlier proposal by Jaffe et al.[38,39] who suggested that the cis and trans conjugate acids had a common structure where the phenyl rings were in a cis conformation and the proton was shared by the two nitrogen atoms.

By analogy, protonation of the phenylazonaphthalenes and azonaphthalenes would give structures of a similar form. The trans $\rightleftharpoons$ cis photoisomerization of the conjugate acids may occur but to what extent we cannot be certain. It was suggested by Badger et al.[98] that the

photoequilibrium favoured the trans-isomer. This they postulated to account for the non-cyclisation of 1,1'-azonaphthalene, 1,2'-azonaphthalene, 2,2'-azonaphthalene, and 2-phenylazonaphthalene when each was irradiated in strong acid solution. However the ready formation of naphtho-[1,2-c]cinnoline from 1-phenylazonaphthalene, under similar conditions, indicates that irradiation of the conjugate acid of this compound yields a relatively stable cis-isomer.

The Photoinduced Rearrangement of Azoxybenzenes, Phenylazoxynaphthalenes, and Azoxynaphthalenes.

The photochemical rearrangements of the azoxybenzenes and azoxynaphthalenes have been extensively studied during the past fifty years. In 1923 it was first reported[69] that exposure of yellow 1,1'-azoxynaphthalene (22) to ultraviolet light rapidly converted it to a red compound (23). A similar change was observed with 2,2'-azoxynaphthalene.[70]



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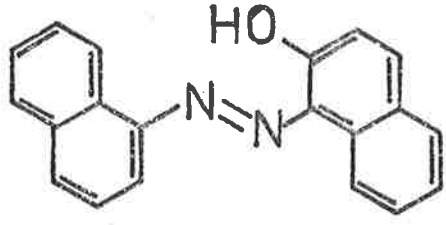
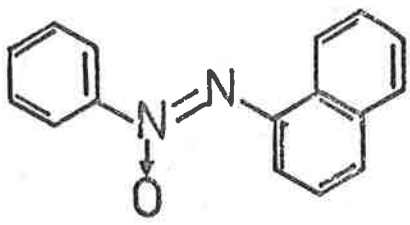


(23)

The photoproducts were later shown[71,72] to be the respective hydroxyazonaphthalenes arising from rearrangement. This was confirmed by Badger and Buttery,[73] who also used the unsymmetrical phenylazoxynaphthalenes to demonstrate that oxygen migration occurred from the nitrogen to the non-adjacent ring, e.g. (24)⟶(25). Experiments



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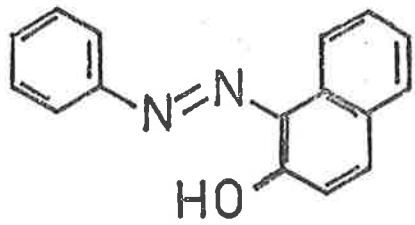
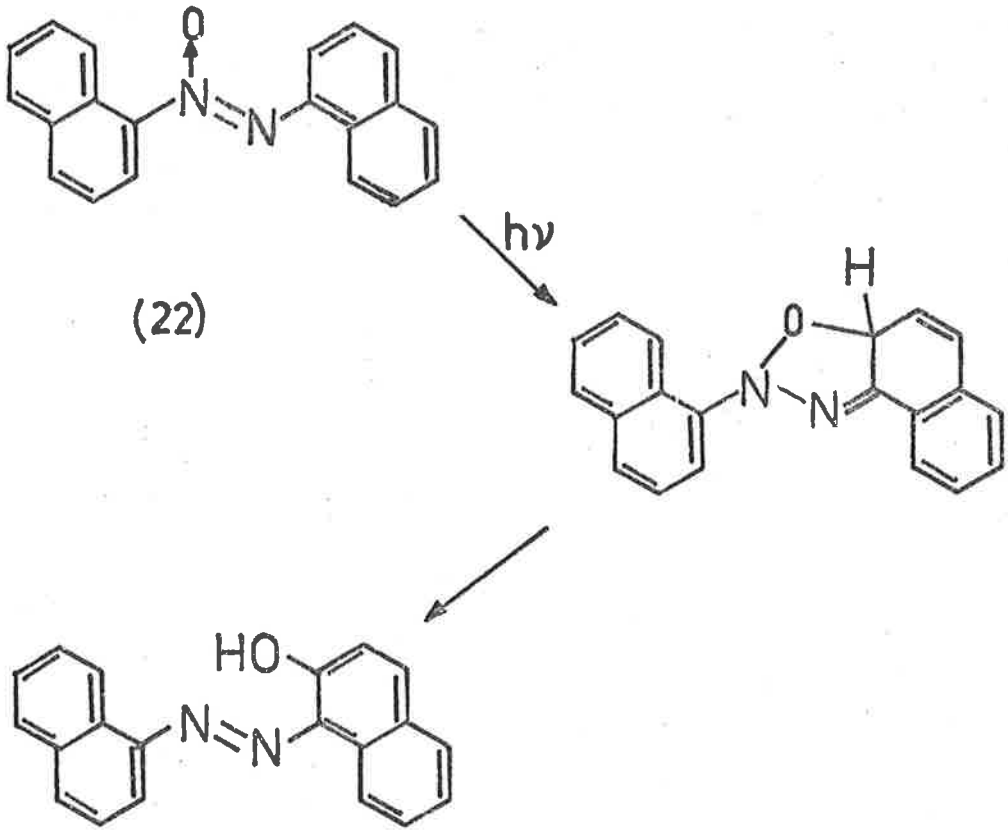


(25)

using labelled (N^{15})-azoxybenzene[74] and (^{18}O)-azoxy compounds[75] proved this to be true for other azoxy compounds.

Azoxybenzene[76,77] and substituted azoxybenzenes have been photochemically rearranged to the corresponding o-hydroxyazobenzenes.[73,100] Recent work[78] has indicated that other rearrangement products are formed in addition to the major o-hydroxy product.

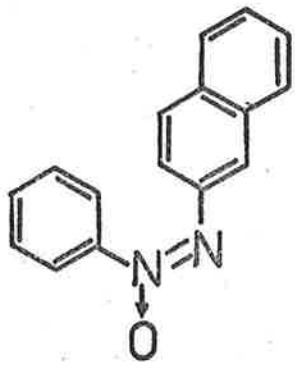
To explain the results accumulated for this rearrangement, an intramolecular cyclic mechanism was proposed.[73,78] The rearrangement of 1,1'-azoxynaphthalene (22) is used as an example in Scheme 11.



Scheme II.

Photoisomerization of azoxybenzenes is known to occur,[79] and cis-azoxybenzenes have been prepared by oxidation of the corresponding cis-azobenzenes[80,81] and by photoisomerization of trans-azoxybenzenes.[79] Although cis-phenylazoxynaphthalenes (e.g. 26) and cis-azoxynaphthalenes (e.g. 27) have not been synthesized, it is likely that photoequilibration of the cis- and trans-isomers does occur. However

participation of the cis-isomer as a rearrangement intermediate is unlikely because of its unfavourable structural geometry.



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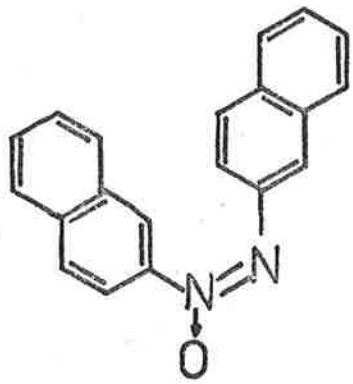
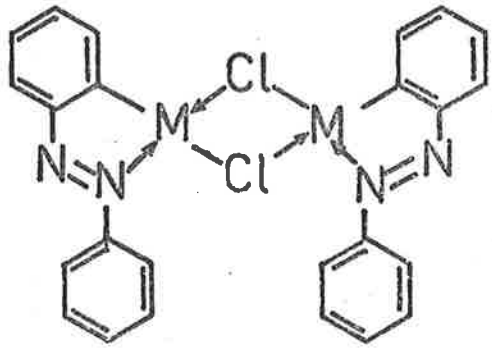


(27)

It is of interest to note that a similar type of mechanism can be suggested for the non-photochemical reaction of azobenzene with palladium and platinum halides[57] to give a complex having the structure (28). Initial acceptance of electrons from a nitrogen atom by the metal could then be followed by intramolecular nucleophilic substitution at an ortho position of the phenyl ring furthest from the nitrogen atom attached to the metal. Treatment of the palladium

(28)



M = Pt, Pd

complex with chlorine gas[97] yields a mixture of mono-, di-, tri-, and tetra-chloroazobenzenes, where the chloro group occupies positions ortho to the azo linkage.

Photocatalysed Cyclodehydrogenations of Azonaphthalenes, Phenylazonaphthalenes, and Azobenzenes.

Photocatalysed cyclodehydrogenation of 1,2-diarylethylenes to the corresponding phenanthrenes are well documented in the literature.[84-89,91]

In 1960 Lewis[92] found that azobenzene underwent a similar type of reaction when irradiated in strong acid solution to give the cyclised product benzo[c]cinnoline. Irradiation of solutions of azobenzene in acetic acid in the presence of ferric chloride was shown by Hugelshofer et al.[83] to yield the same product. In the next decade many other workers examined the photocyclization of a large number of substituted azobenzenes.[93-96]

A mechanism was advanced by Badger et al.[99] which involved the initial photoinduced formation of the cis conjugate acid and subsequent ring closure of this species to yield the appropriate benzo[c]cinnoline.

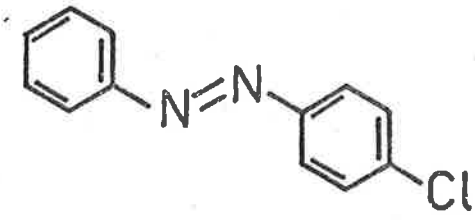
All attempts to convert by photochemical means 1,1'-azonaphthalene, 2,2'-azonaphthalene, 1,2'-azonaphthalene, and 2-phenylazonaphthalene into the respective cinnolines were unsuccessful.[98] It was suggested that the photoequilibria for the protonated species favoured the trans form which could not cyclise. However, this does

not satisfactorily explain why 1-phenylazonaphthalene was found to be readily converted into naphtho[1,2-c]cinnoline under the same conditions.[98] The isolation of the cis-isomers of azonaphthalenes and phenylazonaphthalenes from photoisomeric mixtures of cis- and trans-isomers has been achieved.[10] If the parent azonaphthalenes are readily photoisomerized, then an argument based on the non-photoisomerization of the protonated species does not seem credible. Further investigation of the above-mentioned azonaphthalenes is obviously needed.

Photoinduced Reactions of Azobenzenes with Acid Chlorides.

Solutions of trans-azobenzene (1) in acetyl chloride were shown by Lewis and Mayfield[101,102] to be almost completely decolourized on exposure to sunlight or ultraviolet radiation. They identified the major product as 4-chloro-N,N'-diacetylhydrazobenzene (29). A trace of the 2-chloro isomer (31) was also detected in the reaction mixture.[104] They converted the major photoproduct into 4-chloroazobenzene[101,102] (30) using basic hydrolysis followed by oxidation.

The isolation of 4-chloro-N,N'-diacetylhydrazobenzene from the reaction of cis-azobenzene with acetyl chloride in the absence of light,[103] established that the cis-isomer was involved in the photochemical reaction of trans-azobenzene with acetyl chloride. The photodependent step in the reaction is thought to be the isomeriza-



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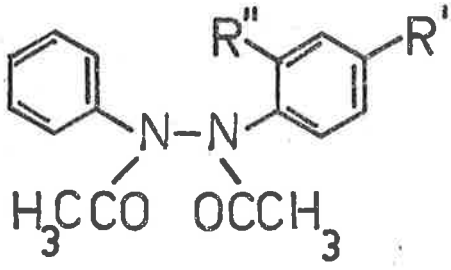


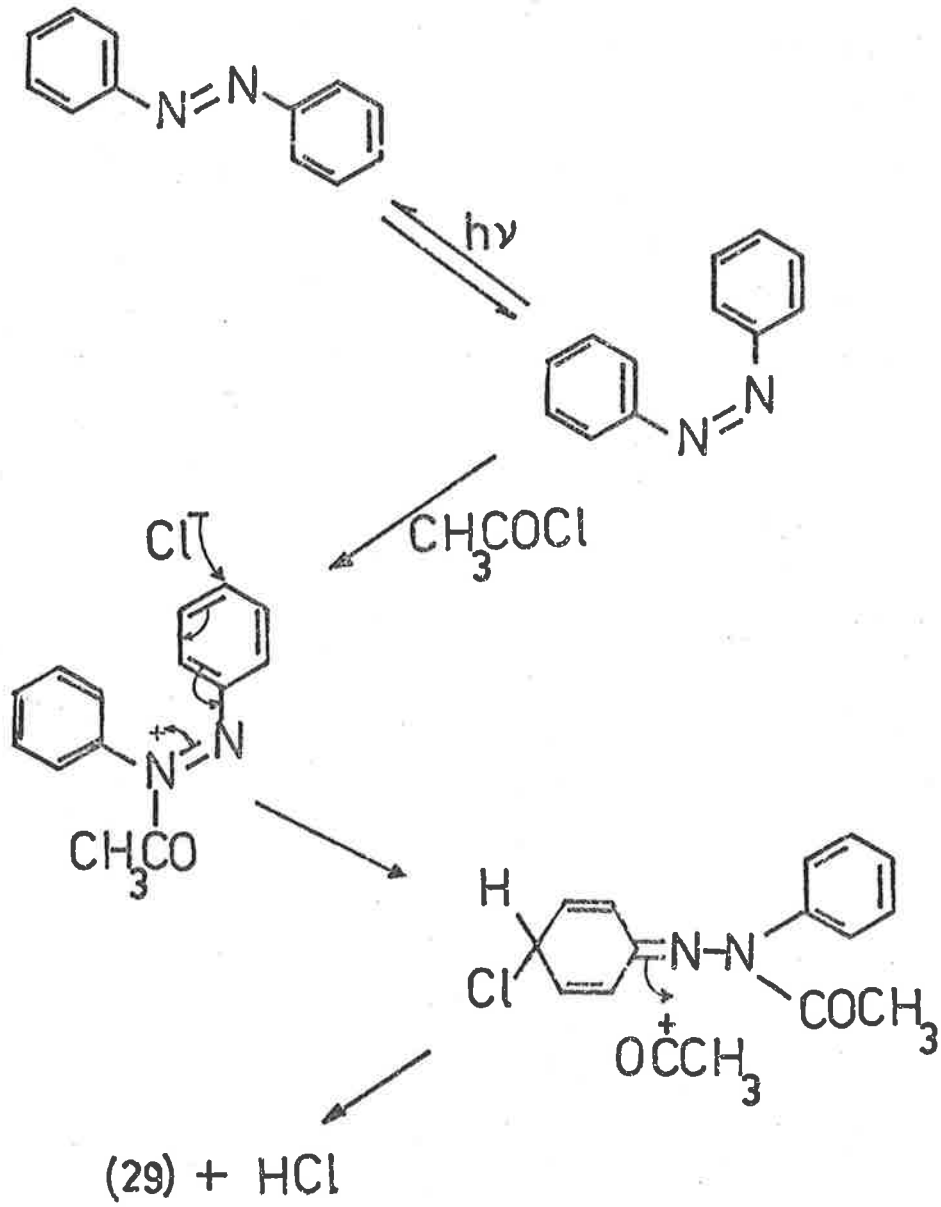
(29) R''=H, R'=Cl

(31) R''=Cl, R'=H

tion of trans- to cis-azobenzene. The cis-azobenzene then undergoes a non-photochemical reaction with acetyl chloride to yield the observed photoproducts. On the basis of these results a mechanistic pathway involving acetylium ions and chloride ions was proposed to account for the reaction observed (Scheme 111).

An interesting colouration developed when cis-azobenzene was added to acetyl chloride,[104] providing a sensitive test for distinguishing between cis- and trans-isomers of azobenzene. The addition of acetyl chloride to cis-azobenzene results in an intense blue-purple colouration, whereas trans-azobenzene under similar conditions forms a

red-orange solution.



Scheme III.

Using several substituted azobenzenes Mayfield[171] determined

the quantum yields for trans→cis photoisomerization (ϕ_t) in acetic anhydride, and for the photoinduced reaction of the azobenzenes in acetic anhydride-hydrochloric acid solution (ϕ). It was found that the values of ϕ_t and ϕ were generally in reasonable agreement. From this it was concluded that the rate determining step in the photochemical reaction of these azo compounds with acetyl chloride was the rate of trans→cis isomerization. This supported the postulated mechanism[103] which requires an initial slow trans→cis photoisomerization followed by a rapid non-photochemical reaction of the cis azo compound with acetyl chloride. In some cases ϕ_t and ϕ values did not agree.[171] The rate determining step in these reactions was suggested to be the non-photochemical step involving the reaction of the cis-isomer with acetyl chloride. This was attributed to the very slow reaction of these cis-isomers with acetyl chloride making the photoisomerization step the faster of the two.

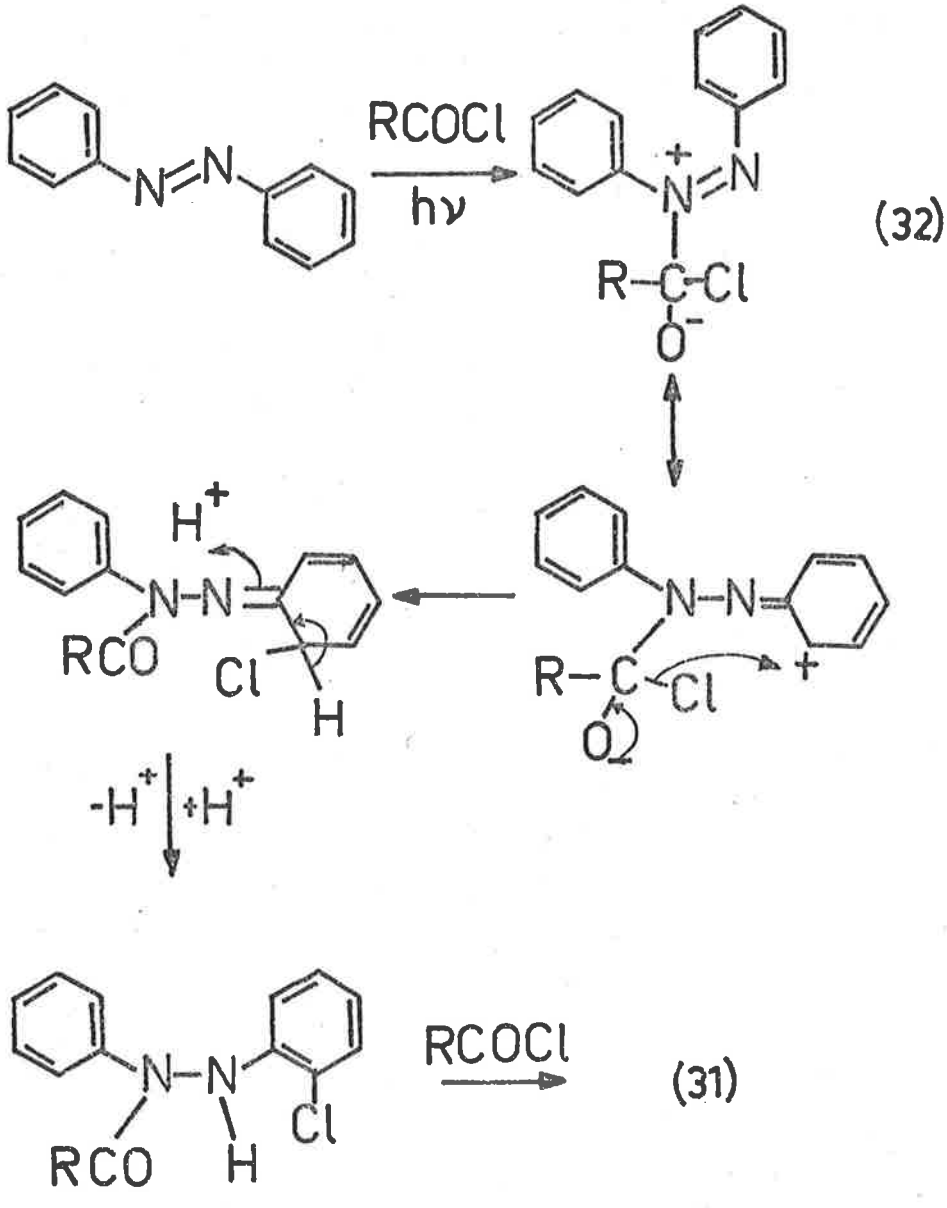
The proposal that ionic species were involved in the mechanism, was justified by further work involving several acid chlorides of widely differing ionizabilities[104] and the use of benzene or cyclohexane as inert solvents in the reaction. From their observations they concluded that ortho substitution was increased when ionization of the acid chloride to the corresponding acylium/aroylium ions and chloride ions was suppressed. This was achieved by having electron-attracting substituents in the acid chlorides, or by using non-polar

inert solvents such as benzene. A mechanism was proposed[104] (Scheme IV) involving non-ionized acid chloride molecules and the intramolecular rearrangement of an intermediate (32) to give the ortho substituted product (31).

Hydrolysis of 4-chloro-N,N'-diacetylhydrazobenzene (29) and subsequent oxidation of the product so formed was reported by Lewis and Mayfield[101,102] to be a convenient method of preparing 4-chloroazobenzene (30). An analogous reaction sequence was used by the same workers[105] to prepare di-, tri-, and tetra-chloroazobenzenes from mono-, di-, and tri-chloroazobenzenes respectively.

4-Bromoazobenzenes could be prepared in a similar fashion from azobenzene and acetyl bromide, but all attempts to introduce the cyano, fluoro, and iodo groups into the benzene nucleus were unsuccessful.[172]

The examination of the reactions of other azo compounds when subjected to ultraviolet radiation in acid chloride solutions was a logical extension of the studies carried out by Lewis and Mayfield.[101-105] The azonaphthalenes and phenylazonaphthalenes were the chosen compounds, and research in our laboratories was directed toward determining what type of photoinduced reactions occurred between azonaphthalenes and acyl halides. It was thought that such a study might provide convenient synthetic routes to many chloroazonaphthalenes and in addition yield further information regarding the mechanism of the



Scheme IV.

photocatalyzed reaction described by Lewis and Mayfield.

The Absorption Spectra of Azobenzenes, Phenylazonaphthalenes, and Azonaphthalenes.

Three main regions of absorption have been shown to exist in the electronic spectra of aromatic azo compounds.[55,106,107] The shorter wavelength absorption occurs at 210-270mμ as one or more bands. At higher wavelength absorption occurs at 320-370mμ (K-band) and at 440-470mμ (R-band). The latter band can be seen in azobenzene, but is difficult to distinguish in the spectra of azonaphthalenes and phenylazonaphthalenes.

The band or bands at 210-290mμ are thought to be due to absorption by the aromatic rings, and the intense absorption at 320-370mμ is ascribed to conjugation between the N=N group and the aromatic nucleus. It has been reported[55,106,107] that this absorption band shifts to longer wavelength with increasing conjugation. This is apparent from the work of Badger and Buttery[55] with phenylazonaphthalenes and azonaphthalenes (Table II). For these compounds the K-band is at a longer wavelength than for azobenzene. The wavelength maximum also shifts, depending on the conjugating power of the ring position to which the azo linkage is attached.[55]

Table II.

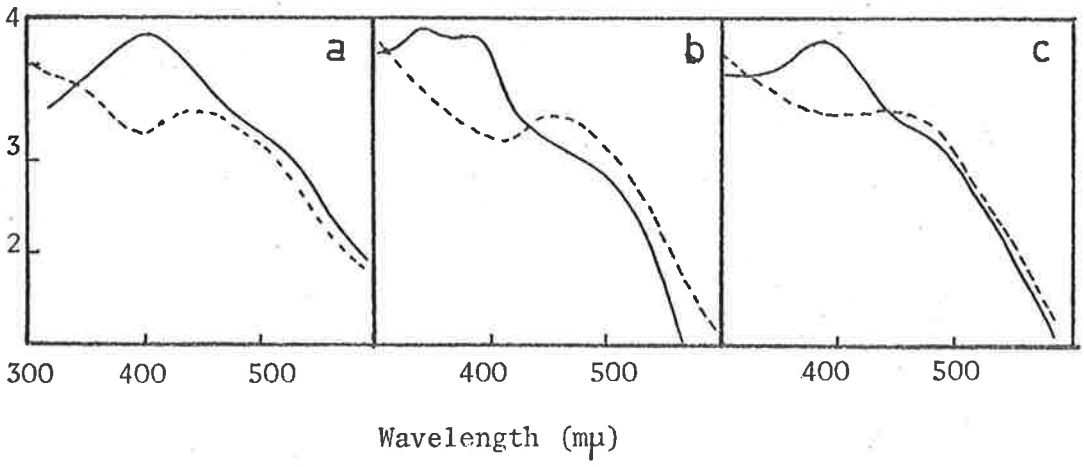
Positions of maxima (mμ) and corresponding log ε values (solvent, ethanol).

Compound	Region I		Region IA		Region II (K-band)
Azobenzene	-	229(4.11)	-	-	318(4.32)
2-Phenylazonaphthalene	219(4.48)	265(4.13)	277(4.13)	287(4.13)	328(4.28)
2,2'-Azonaphthalene	214(4.57)	262(4.39)	278(4.28)	290(4.18)	335(4.37)
1-Phenylazonaphthalene	219(4.58)	266(4.03)	273(4.03)	290(3.94)	372(4.10)
1,2'-Azonaphthalene	216(4.76)	264(4.35)	-	310(4.02)	381(4.24)
1,1'-Azonaphthalene	214(4.87)	266(4.26)	-	-	400(4.21)

The spectra of cis- and trans-phenylazonaphthalenes and azonaphthalenes[10,14,55,93] are shown in Figure I.

Recent calculations[40,108] based on molecular orbital theory have enabled an interpretation of the electronic spectrum of azobenzene in terms of electron-level diagrams. Assignments of electronic transitions responsible for these absorptions have been made on the basis of these calculations. Similar assignments can be made to partially account for the observed absorption spectra of cis- and trans-azonaphthalenes and cis- and trans-phenylazonaphthalenes.

In both isomers the K-band is a result of the lowest $\pi\ \pi^*$ transition. For the cis-isomer this is much less intense and occurs at a shorter wavelength than for the trans-isomer. The $\pi\ \pi^*$ transition



a. 1,1' - Azonaphthalene

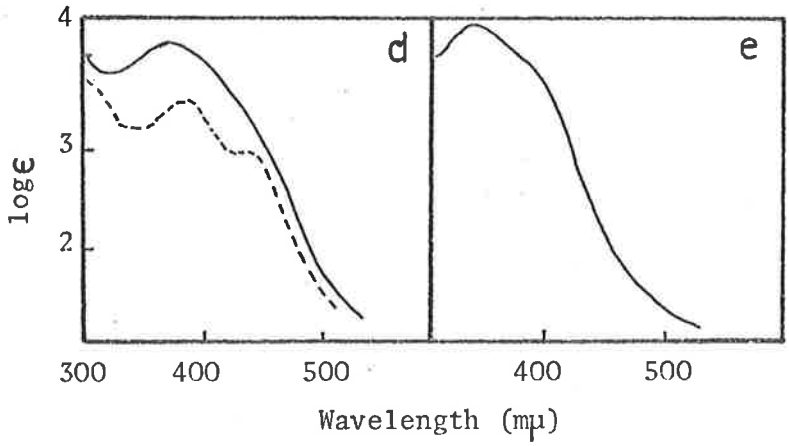
b. 2,2' - Azonaphthalene

c. 1,2' - Azonaphthalene

trans ———

cis ------

Solvent : toluene



d. 1 - Phenylazonaphthalene
(Solvent: isohexane - methylcyclohexane (1:1))

e. 2 - Phenylazonaphthalene
(Solvent: ethanol)

trans ———

cis ------

Figure 1.

has been shown[108,114] to be restricted to the atoms linking the aromatic rings because the π and π^* energy levels change as the types of atoms in the linkage are altered.

The electronic absorptions at shorter wavelength (Region I) are due to transitions ($\sigma\sigma^*$) between levels which are localized in the aromatic rings. The single peak at 220mμ corresponds to a peak at 221mμ in the spectrum of naphthalene.[109] Skulski[111] considered the intense band at 219mμ in the spectrum of phenylazonaphthalenes as being due to a weak benzenoid chromophore fully overlapped by another band due to the naphthalenic chromophore. The one to three bands at 265, 275, and 290mμ are thought to correspond to the three bands in the spectrum of naphthalene at 265, 275, and 290mμ. Increased conjugation in the case of 1,1'-azonaphthalene disturbs the electronic configuration and only one absorption maximum appears in this region.

A weak R-band absorption observed in the 440-470mμ region for azobenzene, is usually present only as a point of inflexion in the spectra of azonaphthalenes and phenylazonaphthalenes. These bands are associated with one or more $n\pi^*$ transitions involving the non-bonded electrons in the azo linkage.

The geometry of the cis molecules must place the phenyl and naphthalene rings in positions where their π -electron clouds interact. This would result in the arrangement of the energy levels becoming more complex. The consequences of such interactions have been

observed in the spectra of cis-azobenzenes and these spectra have been interpreted.[110]

The protonation of cis and trans-azobenzene causes the $\pi\pi^*$ transition to undergo a marked bathochromic shift to 420mμ together with a large increase in the intensity.[67] On protonation a quaternary nitrogen atom is created in the molecule, and this is responsible for the lowering of the π^* energy level and thereby causing the shift to longer wavelength. For the same reason, protonation of the cis- and trans-isomers of azonaphthalenes and phenylazonaphthalenes would be expected to produce a large bathochromic shift of the $\pi\pi^*$ absorption. This has been observed for both substituted[112,62] and unsubstituted[123-125] phenylazonaphthalenes and azonaphthalenes.

For the azobenzenes, phenylazonaphthalenes, and azonaphthalenes protonation of the azo linkage will compress the n level even more than the π^* level, forcing the $n\pi^*$ absorption to undergo a considerable hypsochromic shift. The lower wavelength absorptions due to transitions localized in the aromatic rings, would be virtually unchanged by protonation of either isomer.

Substituents exert little effect on the $n\pi^*$ transitions of cis- and trans-azobenzenes,[108] and similar behaviour has been observed for substituted phenylazonaphthalenes and azonaphthalenes. For these $n\pi^*$ absorptions electron-donating substituents would cause minor bathochromic shifts and electron-withdrawing substituents small hypsochromic

shifts. The $\pi\,\pi^*$ transitions are very sensitive to substituent effects. Electron-donating groups (NH_2, OR, OH) cause large bathochromic shifts,[113,162] while electron-attracting groups have little effect.

RESULTS AND DISCUSSION

I. PHOTOINDUCED REACTIONS IN ACETYL CHLORIDE.

1. trans-2-Phenylazonaphthalene.

Irradiation of trans-2-phenylazonaphthalene (10) in acetyl chloride and subsequent recrystallization of the crude photoproduct gave x-chloro-N,N'-diacetyl-2-phenylhydrazonaphthalene (40). The structure was established on the basis of elementary analysis and the infrared and ultraviolet spectra. Alkaline hydrolysis and subsequent oxidation of the pure photoproduct afforded 2-phenylazonaphthalene (10) (as the main product) and 2-(4'-chlorophenylazo)naphthalene (33).

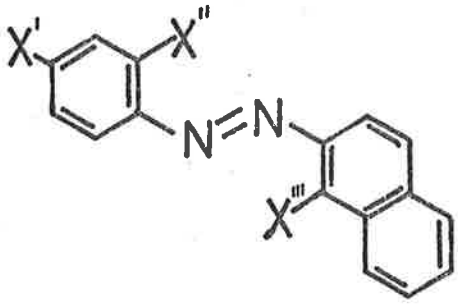
The combined mother liquors from the recrystallization of the crude photoproduct could not be separated into their components by a combination of column chromatography and recrystallization. The mixture was therefore subjected to hydrolysis and aerial oxidation in ethanolic potassium hydroxide. The hydrolysis mixture was resolved into 2-phenylazonaphthalene (10), 2-(4'-chlorophenylazo)naphthalene (33), and 1-chloro-2-phenylazonaphthalene (35). The major product was (10). Qualitative gas chromatography showed that a very small amount of 2-(2'-chlorophenylazo)naphthalene (34) was present in the crude product.

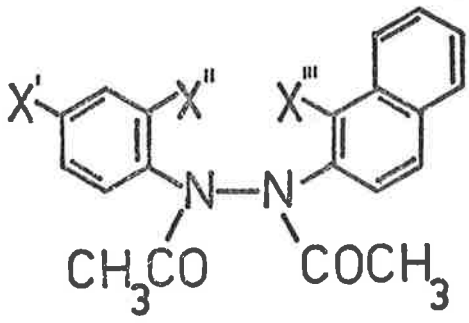
Compounds (10), (33), (34), and (35) were identified by comparison with authentic samples. Synthesis of isomers (33) and (34) was accomplished by sodium hydroxide fusions of 2-naphthylamine with 4-chloronitrobenzene and 2-chloronitrobenzene respectively.

Compound (35) was prepared by condensation of nitrobenzene with 1-chloro-2-naphthylamine.

As compounds (33) and (35) were isolated from the hydrolysed photochemical reaction mixture it was concluded that the corresponding compounds, 2-(N,N'-diacetyl-4'-chlorophenylhydrazo)naphthalene (37) and 1-chloro-2-(N,N'-diacetylphenylhydrazo)naphthalene (39), were probably formed in the photoreaction. Similarly the gas chromatographic identification of 2-(2'-chlorophenylazo)naphthalene suggested that the N,N'-diacetyl compound (38) was also present. The possibility of the products (33) and (35) being obtained from mono-acetylated photo-products was discounted because the infrared spectrum of the crude photoreaction mixture did not show the N-H stretching absorption at c. 3300 cm^{-1} which is characteristic of an N-acetylphenylhydrazonaphthalene. However, attempts to separate the N,N'-diacetyl isomers (37) and (39) were unsuccessful.

The formation of 2-phenylazonaphthalene (10) by hydrolysis-oxidation of x-chloro-2-(N,N'-diacetylphenylhydrazo)naphthalene (40) was unexpected. The most obvious compound to yield 2-phenylazonaphthalene upon hydrolysis was 2-(N,N'-diacetylphenylhydrazo)naphthalene (36), but such a structure disagreed with the analytical data obtained for the photoproduct. The formation of compound (36) would require radical addition of two acetyl groups across the azo linkage. Radical addition to the azo group in azobenzene is known to occur.[12,58,90]





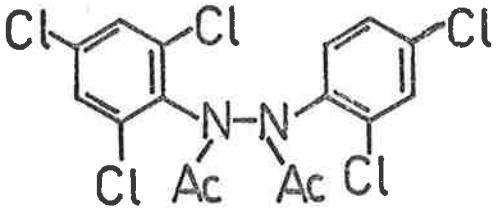
	X'	X''	X'''
(10)	H	H	H
(33)	Cl	H	H
(34)	H	Cl	H
(35)	H	H	Cl

	X'	X''	X'''
(36)	H	H	H
(37)	Cl	H	H
(38)	H	Cl	H
(39)	H	H	Cl

Karasch et al.[12] obtained N-benzoylhydrazobenzene in 80% yield when azobenzene was treated with benzaldehyde in the presence of t-butyl peroxide. The irradiation of trans-azobenzene in ethyl acetate solution has been reported[58] to give products which are supposed to arise from attack of acetyl radicals, generated by irradiation of ethyl acetate, on the molecules of azobenzene. The radiation source was a medium pressure mercury lamp and a quartz reactor was used. The photo-induced reaction of azobenzene with cumene using light of wavelength greater than 400mμ has been proved[90] to yield N,N'-diphenyl-N-(1-methyl-1-phenylethyl)hydrazine via a radical intermediate. However

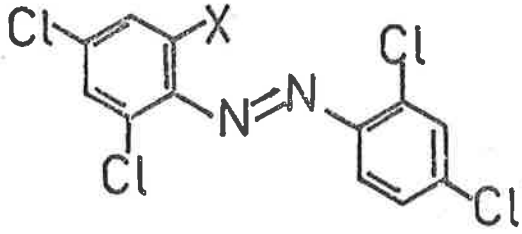
the conditions used in the photoreaction of 2-phenylazonaphthalene with acetyl chloride would not be expected to lead to radical formation.

From the available information it was concluded that the photoproduct (40) was a chloro-2-(N,N'-diacetylphenylhydrazo)naphthalene, in which the chloro group was substituted in one of the aromatic rings, and that dechlorination of that compound occurs under the alkaline hydrolysis conditions. In a related reaction Mayfield[179] found that the deacetylation of N,N'-diacetyl-2,4,6,2',4'-pentachlorohydrazobenzene (41) under alkaline conditions yielded a mixture of 2,4,6,2',4'-pentachloroazobenzene (43) and 2,4,2',4'-tetrachloroazobenzene (42).



(41)

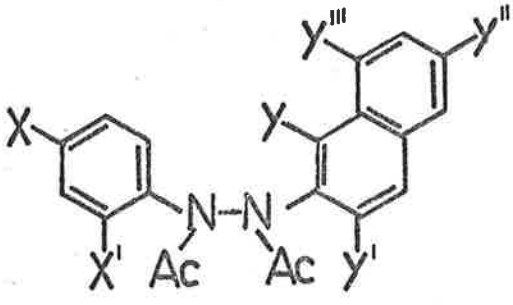
Ac = $COCH_3$



(42) X=H

(43) X=Cl

On mechanistic grounds six possible chloro-N,N'-diacetyl compounds (44), (45), (46), (47), (48), and (49) could have been formed in the photoreaction. The crystalline photoproduct (40) had a sharp melting point; and this suggested that it was not a mixture

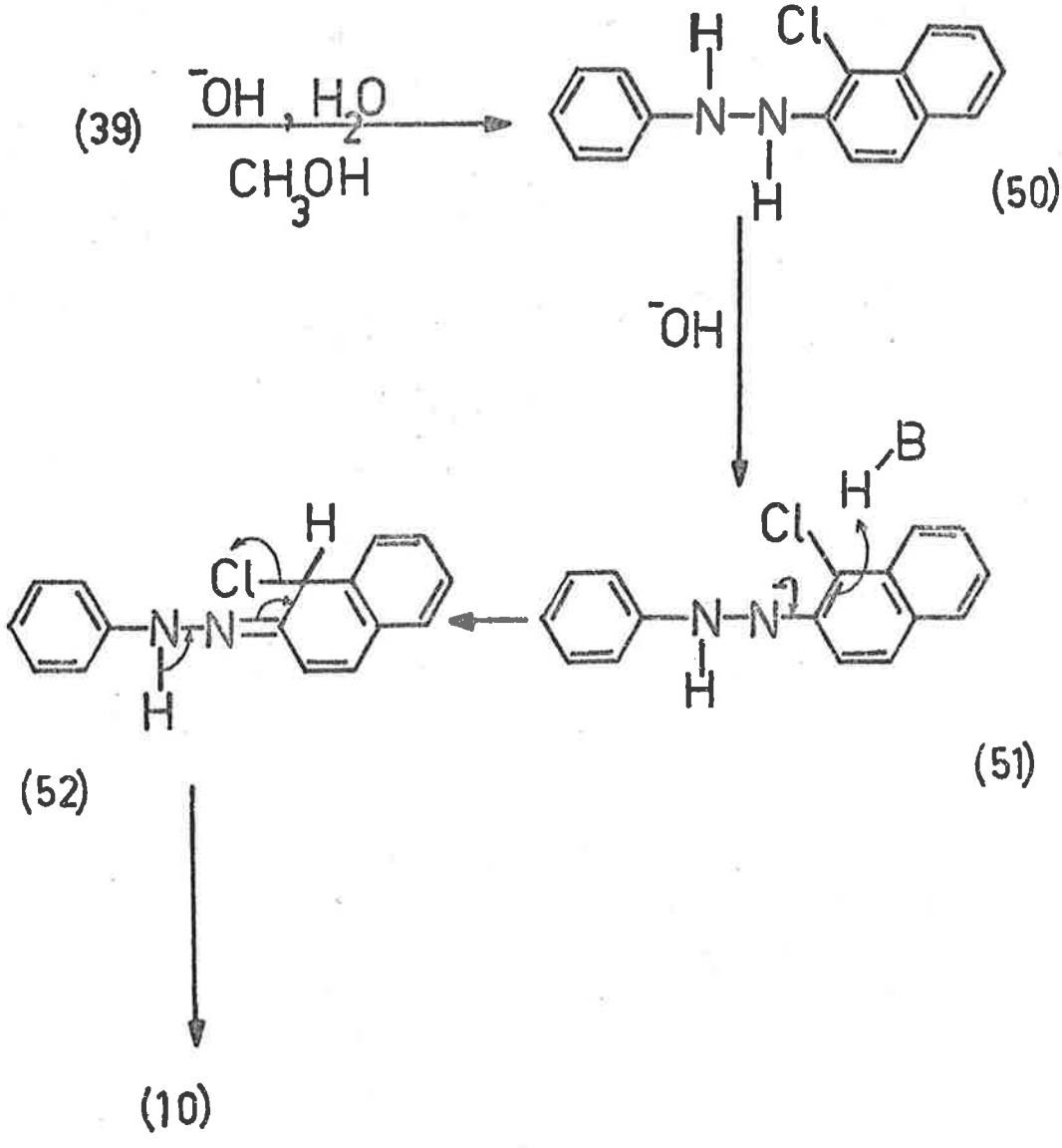


	X	X'	Y	Y'	Y''	Y'''
(44)	Cl	H	H	H	H	H
(45)	H	Cl	H	H	H	H
(46)	H	H	Cl	H	H	H
(47)	H	H	H	Cl	H	H
(48)	H	H	H	H	Cl	H
(49)	H	H	H	H	H	Cl

of N,N'-diacetyl compounds. The isolation of 2-(4'-chlorophenylazo)-naphthalene (33) from the hydrolysis of this compound led to the conclusion that 2-(N,N'-diacetyl-4'-chlorophenylhydrazo)naphthalene (37) was the compound undergoing dechlorination. This was proved to be false when an authentic sample of compound (37) was subjected to hydrolysis-oxidation. An almost quantitative yield of 2-(4'-chlorophenylazo)naphthalene was obtained. The presence of a small quantity of 2-phenylazonaphthalene in the mixture was established by the use of gas chromatography. This indicated that dechlorination of the N,N'-diacetyl compound (37) was possible, but only to a very minor extent. A similar reaction using an authentic sample of 2-(N,N'-diacetyl-2'-chlorophenylhydrazo)naphthalene (38) showed that this compound was not the precursor of 2-phenylazonaphthalene. The corresponding N-acetyl compounds and hydrazo compounds were also subjected to ethanolic potassium hydroxide, but once again none of

the dechlorinated product (10) was formed. From these results it was concluded that the crystalline photoproduct (40) consisted of an N,N'-diacetyl compound which was chlorinated in the naphthalene ring, together with a small quantity of 2'-(N,N'-diacetyl-4'-chlorophenylhydrazo) naphthalene. The dechlorination reaction previously investigated by Mayfield[179] involved the loss of a chloro group ortho to the azo linkage. If this is typical of all such dechlorination reactions which involve azo compounds, then it is possible that the photoproduct (40) contains a chloro group which is attached to a carbon atom of the naphthalene ring, which is adjacent to the azo linkage, viz. the 1 or 3 position. The irradiation of 2,2'-azonaphthalene and subsequent hydrolysis of the photoproduct yielded 2,2'-azonaphthalene and a chlorinated azonaphthalene (see Part I.3). Although it has not been conclusively proven, the latter compound is thought to be chlorinated in the 6 or 8 position of the naphthalene ring. The unsubstituted azonaphthalene could arise from hydrolysis-oxidation of 1- and/or 3-chloro-N,N'-diacetyl-2,2'-hydrazonaphthalene. This further suggests that the chloride ion lost comes from a position adjacent to the azo linkage.

A reaction pathway from (40) to (10) is shown in Scheme V. 1-Chloro-2-(N,N'-diacetylphenylhydrazo)naphthalene (39) is used as an example in the sequence, but the participation of this species and the intermediacy of (50) have not been proven.



Scheme V.

Konaka et al.[178] have shown that the oxidation of hydrazobenzenes under alkaline conditions involves the formation of a dianion resulting from the removal of both "hydrazo" hydrogen atoms. If this result can be applied to the oxidation of phenylhydrazonaphthalenes, then the alternative oxidation (39)⟶(10) could occur resulting in the loss of a chloride ion. Mayfield[179] postulated a similar mechanism (see Part III.1); and it was suggested that the presence of three electron-attracting chloro groups (-I effect) would facilitate the removal of a proton from the nitrogen atom adjacent to the trisubstituted phenyl ring. The reason for the loss of a chloride ion from the naphthalene ring is not as obvious. The conjugating ability of naphthalene rings is greater than that of phenyl rings. This property of the naphthalene ring could stabilize the anion formed on a nitrogen atom attached to the naphthalene ring; and thereby lead to specific removal of a chloro group from that ring. The reasons for the apparent ease of dehalogenation are not known. If a cage effect were present then the preferential loss of a chloro group "ortho" to the azo linkage would be expected.

No dark reaction was detected when solutions of 2-phenylazonaphthalene (1C) in acetyl chloride were boiled under reflux for long periods in the absence of light.

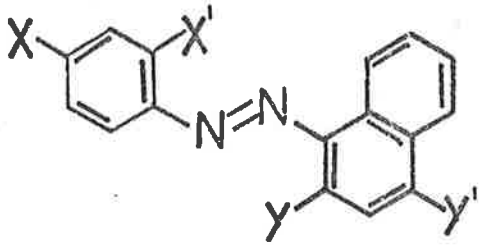
A solution of 2-phenylazonaphthalene in acetic acid-hydrochloric acid was irradiated with a high pressure mercury lamp, and this led

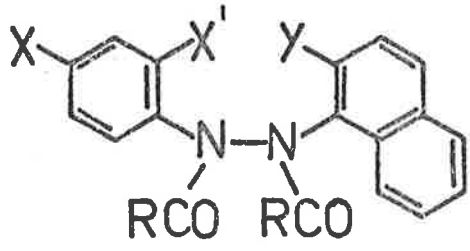
to the formation of the same compound (40) as that obtained in the experiment with acetyl chloride.

2. trans-1-Phenylazonaphthalene.

A solution of trans-1-phenylazonaphthalene (9) in acetyl chloride was irradiated until the initially red-orange solution had almost completely faded. Examination of the crude reaction mixture by thin-layer chromatography revealed that several compounds had been formed. However, the mixture of N,N'-diacetylhydrazonaphthalenes could not be resolved by column chromatography. Recrystallization of the major fraction eluted from the column yielded a white crystalline solid which was subsequently identified as x-chloro-N,N'-diacetyl-1-phenylhydrazonaphthalene (59). The structure was established on the basis of the elementary analysis and the infrared, n.m.r., and mass spectra. Alkaline hydrolysis in the usual manner afforded 1-phenylazonaphthalene (9) (major product) and 1-(4'-chlorophenylazo)naphthalene (52). The product (59) possessed a sharp melting point and this suggested that the crystalline material consisted mainly of one compound. The nature of the photoproduct cannot be conclusively stated on the basis of the information available. Authentic samples of 1-(N,N'-diacetyl-4'-chlorophenylhydrazo)naphthalene (56) and 1-(N,N'-diacetyl-2'-chlorophenylhydrazo)naphthalene (57) could not

be prepared, and it is therefore not known whether these compounds give rise to 2-phenylazonaphthalene under alkaline conditions. However if the results and arguments described for the photoreaction involving 2-phenylazonaphthalene can be applied in this case, then the compound undergoing dechlorination is not (56) or (57), but rather an N,N'-diacetyl compound with a chloro group in the naphthalene ring, viz. (58). A suggested structure for the crystalline photoproduct (59) is 2-chloro-1-(N,N'-diacetylphenylhydrazo)naphthalene (58) where the chloro group occupies a position "ortho" to the azo linkage.





R=CH$_3$

	X	X'	Y	X'
(10)	H	H	H	H
(52)	Cl	H	H	H
(53)	H	Cl	H	H
(54)	H	H	Cl	H
(55)	H	H	H	Cl

	X	X'	Y
(56)	Cl	H	H
(57)	H	Cl	H
(58)	H	H	Cl

All of the possible N,N'-diacetyl compounds need to be prepared and subsequently hydrolysed; in this way the exact nature of the compound (59) undergoing dechlorination could be determined.

The combined mother liquors obtained from recrystallization of the photoproduct were treated with ethanolic potassium hydroxide. The main products isolated were 1-(4'-chlorophenylazo)naphthalene (52) and 1-phenylazonaphthalene (9); 1-(2'-chlorophenylazo)naphthalene (53) was shown by gas chromatography to be present in small amounts. The infra-red spectrum of the chromatographed photoproduct showed two carbonyl and no N-H stretching absorptions; this indicated that no mono-acetylated product was present in the mixture. The formation of compounds (52) and (53) in the hydrolysis/oxidation reaction suggested that corresponding amounts of the N,N'-diacetyl compounds (56) and (57) were present in the photoreaction product.

The structures of compounds (9) and (52) were confirmed by direct comparison with authentic samples. A sample of 1-(2'-chloro-phenylazo)naphthalene exhibited an identical retention time to compound (53) which appeared as a single peak in the gas chromato-gram of the hydrolysis mixture. 1-(4'-Chlorophenylazo)naphthalene (52) and 1-(2'-chlorophenylazo)naphthalene (53) were prepared by condensation of 1-naphthylamine with the respective chloronitro-benzene.

A small quantity of 4-chloro-1-phenylazo naphthalene (55) was prepared from 4-amino-1-phenylazo naphthalene using a Sandmeyer reaction. However gas chromatographic analysis of the crude hydrolysis-oxidation mixture did not show the presence of compound (55).

trans-1-Phenylazonaphthalene (9) was recovered unchanged after being heated under reflux with acetyl chloride in complete darkness. This showed that photoactivation was necessary before the reaction described above would occur.

The product obtained after irradiation of 1-phenylazonaphthalene (9) in acetic acid-hydrochloric acid solution was found to be identical with that formed in the photoreaction of (9) with acetyl chloride. Crystallization of the crude photoproduct yielded a crystalline compound which was shown to be identical with a previously isolated sample of x-chloro-N,N'-diacetyl-1-phenylhydrazonaphthalene (59).

3. trans-2,2'-Azonaphthalene.

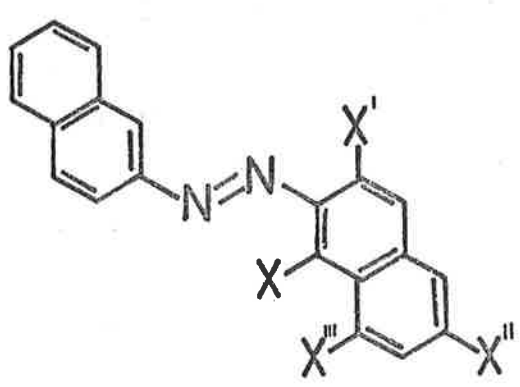
The product obtained after irradiation of 2,2'-azonaphthalene (4) in acetyl chloride was passed through a column of alumina. Only one broad band was eluted from the column and the pale yellow glass isolated from this fraction was crystallized to yield x-chloro-N,N'-diacetyl-2,2'-hydrazonaphthalene (60). Alkaline hydrolysis and oxidation of compound (60) yielded 2,2'-azonaphthalene (4). Qualita-

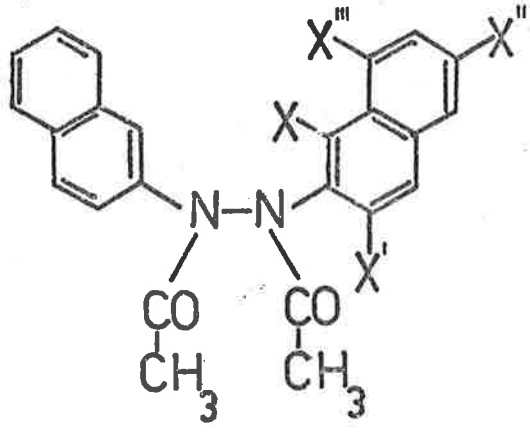
tive gas chromatography showed that a small quantity of a second compound was present in the crude mixture. The retention time of this compound was identical to that of a sample of x-chloro-2,2'-azonaphthalene (69) which was isolated from the hydrolysis of the crude photoreaction mixture.

The structure of compound (60) was established from elementary analysis and infrared, n.m.r., and mass spectra. 2,2'-Azonaphthalene (4) was identified by direct comparison with an authentic sample.

Ritter and Ritter[59] have reported that N-acetyl-hydrazobenzene was readily cleaved with phenylhydrazine to yield aniline and acetanilide. A similar attempt to cleave x-chloro-N,N'-diacetyl-2,2'-hydrazonaphthalene (60) was unsuccessful.

The position of the chloro group in compound (60) has not been determined; and it is this group which is presumably lost under alkaline hydrolysis conditions to yield 2,2'-azonaphthalene. The chloro group could be present in any of four positions, viz., the 1, 3, 6, and 8 positions.





	X	X'	X''	X'''
(4)	H	H	H	H
(61)	Cl	H	H	H
(62)	H	Cl	H	H
(63)	H	H	Cl	H
(64)	H	H	H	Cl

	X	X'	X''	X'''
(65)	Cl	H	H	H
(66)	H	Cl	H	H
(67)	H	H	Cl	H
(68)	H	H	H	Cl

In a separate reaction, the photoproduct isolated from the photoinduced reaction of 2,2'-azonaphthalene (4) with acetyl chloride was chromatographed; and the major fraction eluted from the column was subjected to hydrolysis and aerial oxidation. A combination of column chromatography and fractional recrystallization resolved the mixture into 2,2'-azonaphthalene (4) and x-chloro-2,2'-azonaphthalene (69). The structure of compound (69) was established on the basis of the microanalytical data and the mass spectra.

The presence of (4) in the mixture suggests that an equivalent

amount of the crystalline product (60) was formed in the photoreaction. However the possibility that more than one compound is undergoing dechlorination cannot be ignored. It is assumed that the precursor (70) of x-chloro-2,2'-azonaphthalene (69) is an N,N'-diacetyl compound and that this compound (70) does not undergo dechlorination during the hydrolysis/oxidation reaction. The infrared spectrum of the mixture before hydrolysis showed two strong carbonyl and no N-H stretching absorptions. Attempts to obtain a pure sample of (70) by preparative techniques were completely unsuccessful. Elemental analysis of the chromatographed photoproduct showed that the compounds in the photoreaction mixture were isomeric.

If the argument presented in Part I.1, which indicated preferential loss of a chloride ion from a position "ortho" to the azo linkage, is correct then the crystalline compound (60) could be 1- or 3-chloro-N,N'-diacetyl-2,2'-hydrazonaphthalene (65 or 66). Similarly, suggested structures for the hydrolysis product (69) would be 6- or 8-chloro-2,2'-azonaphthalene (64 or 63). In an attempt to prove or disprove these postulated structures x-chloro-2,2'-azonaphthalene (69) was subjected to hydrogenolysis, but the expected naphthylamines could not be isolated or otherwise characterized. Attempted synthesis of 1-chloro-2,2'-azonaphthalene by the condensation of 1-chloro-2-naphthylamine with 2-nitronaphthalene was unsuccessful.

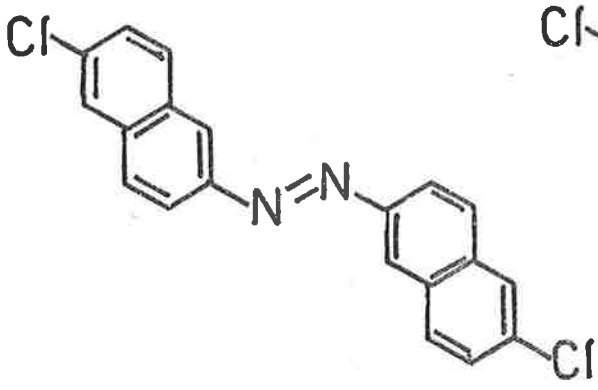
It was thought that if x-chloro-2,2'-azonaphthalene (69) was irradiated in acetyl chloride, then the photoreaction might lead to chlorine substitution in the corresponding position in the second naphthalene ring; the possible directing effect of the existing chloro group was assumed to be small. The hydrolysis of such a product would yield a symmetrical dichloroazonaphthalene and hydrogenolysis of this compound would yield a single chloronaphthylamine.

Irradiation of x-chloro-2,2'-azonaphthalene (69) in acetyl chloride gave a photoproduct which was eluted from a column of silica as one broad band. This compound was crystallized and yielded a crystalline solid (71) which melted over a range of seven degrees. Attempts to purify this compound by column chromatography and fractional crystallization were unsuccessful. The microanalytical data agreed with the calculated values for a structure such as x,y-dichloro-N,N'-diacetyl-2,2'-hydrazonaphthalene (72); and it was concluded that the crystalline material was a mixture of positional isomers. The infrared, n.m.r., and mass spectra were in agreement with the expected characteristics of a structure such as (72). After the usual procedure of hydrolysis and oxidation of the solid product (71), a mixture of compounds was obtained and was shown to consist of x,y-dichloro- and x-chloro-2,2'-azonaphthalene (73 and 69). Gas chromatography showed that no other compounds were present in the hydrolysis mixture. From this it was concluded that the photoproduct

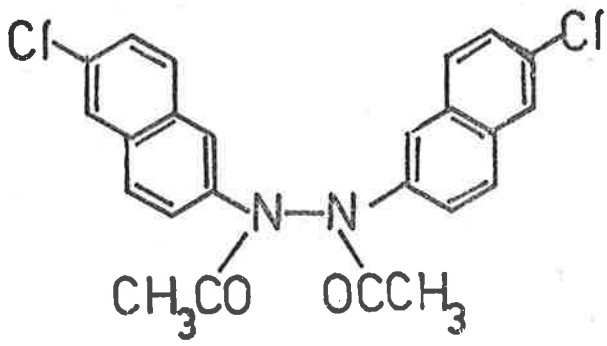
consisted of a dichloro-N,N'-diacetyl-2,2'-hydrazonaphthalene, which did not undergo dehalogenation under alkaline conditions, and one or more isomeric dichloro-N,N'-diacetyl compounds, which did lose a chloro group. Compound (73) is not 1,1'-dichloro-2,2'-azonaphthalene as this is a known compound,[61] m.p. 170-171° (cf. 73, m.p. 272-273°).

Hydrogenolysis of the purified x,y-dichloro-2,2'-azonaphthalene (73) with stannous chloride-hydrochloric acid solution gave a crystalline solid (74) which melted over a range of four degrees (116-120°). On the basis of the elemental analysis, melting point, infrared, and mass spectra it was concluded that this compound was 6-chloro-2-naphthylamine (75). The melting points of 6-chloro-, 8-chloro-, and 1-chloro-2-naphthylamine are 120°,[60] 70°,[60] and 59°[133] respectively. A corresponding value for 3-chloro-2-naphthylamine could not be found in the literature. None of the authentic compound was available for direct comparison; and an insufficient quantity of pure (74) was obtained to form a usable derivative.

If the two chloro groups are symmetrically substituted in the azonaphthalene, then compound (73) could be 6,6'-dichloro-2,2'-azonaphthalene (76) and the monochloro compound (69) would therefore be 6-chloro-2,2'-azonaphthalene (63). In the photoreactions the corresponding N,N'-diacetyl compounds (77 and 67) would be formed. Further work is required to substantiate these suggested structures.



(76)



(77)

Dark reactions were found not to occur when solutions of 2,2'-azonaphthalene (4) and x-chloro-2,2'-azonaphthalene (69) in acetyl chloride were heated in complete darkness for long periods.

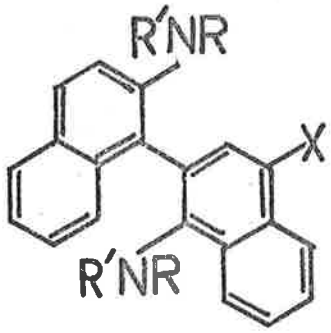
4. trans-1,2'-Azonaphthalene.

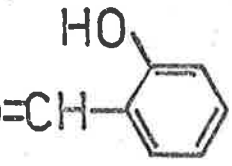
Irradiation of 1,2'-azonaphthalene (5) in acetyl chloride solution gave a mixture of photoproducts. 4-Chloro-N,N'-diacetyl-1,2'-diamino-1',2-binaphthyl (80) crystallized directly from the reaction mixture. This photoproduct was characterized by elemental analysis and infrared and mass spectra. The structure was confirmed by direct comparison with an authentic sample. When hydrolysed under acidic or alkaline conditions the photoproduct yielded 4-chloro-1,2'-diamino-1',2-binaphthyl (79) as the major product. The crude diamino compound was converted to bis-salicylidene-4-chloro-1,2'-

diamino-1',2-binaphthyl (82) by treatment with salicylaldehyde. The structure of the bis-salicylidene anil was confirmed by elemental analysis, infrared, and mass spectra, and by direct comparison with an authentic sample. The formation of a bis-salicylidene anil proved that the photoproduct had a benzidine-type structure and not a semidine-type structure.

The position of attachment of the two naphthalene rings in the binaphthyl (80) was assumed to be from the 1-position of one ring to the 2-position of the other. This was based on the results of Shine et al.[149] and others[82] who isolated 1,2'--diamino-1',2-binaphthyl (78) as the major rearrangement product of 1,2'-hydrazonaphthalene (83) in acidic media. However in the photoreaction the rearrangement is thought to occur via the 4-chloro-N-acetyl-1,2'-hydrazonaphthalene; and it is not known whether the presence of a chloro group would alter the preferred position of attachment. Consequently, the supposed 4-chloro-1,2'-diamino-1',2-binaphthyl (79) was dechlorinated using a Grignard reaction (in decalin as the solvent and with iso-propanol as the initiator). The mass spectrum of the product suggested that the mixture contained unchanged compound (79), 1,2'-diamino-1',2-binaphthyl (78) and 4-iso-propoxy-1,2'-diamino-1',2-binaphthyl (81). However attempts to isolate and characterize the dechlorinated product by column chromatography, by chemical means, and by gas chromatography, were unsuccessful. The proposed positions (1'-2) of

ring attachment in the diamino compound (79) and the N,N'-diacetyl photoproduct (80) have therefore not been conclusively proven.



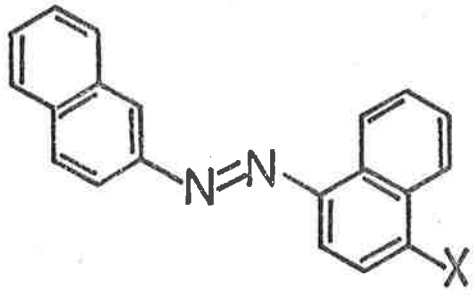
	R	X	R'
(78)	H	H	H
(79)	H	Cl	H
(80)	$-COCH_3$	Cl	H
(81)	H	$-OCH(CH_3)_2$	H
(82)		Cl	-

The photoproduct which remained after removal of the N,N'-diacetylbinaphthyl (80) was chromatographed and thereby separated into two main fractions. One fraction afforded 4-chloro-N,N'-diacetyl-1,2'-diamino-1',2-binaphthyl (80), the structure of which was confirmed by comparison with a previously characterized sample. The major product (87) was obtained as a colourless glass. All attempts to crystallize this product were unsuccessful. Alkaline hydrolysis of the distilled photoproduct yielded a mixture containing 1,2'-azonaphthalene (5) and 4-chloro-1,2'-azonaphthalene (84). The identities of these compounds were established by direct comparison with authentic samples. On the basis of the hydrolysis/oxidation products, elementary analysis, and infrared, n.m.r., and mass spectra it was

concluded that the product (87) consisted of a mixture of isomeric x-chloro-N,N'-diacetyl-1,2'-hydrazonaphthalenes. This mixture could not be resolved into its components.

One of the compounds formed in the photoreaction is obviously 4-chloro-N,N'-diacetyl-1,2'-hydrazonaphthalene (86). Because this compound could not be isolated in pure form, it was not possible to determine whether it loses chlorine upon hydrolysis. The precursor of 1,2'-azonaphthalene in the hydrolysis reaction could be any of several compounds where the chloro group is in one of several positions of either of the two rings. This problem needs to be investigated further in order to determine the exact nature of these compounds.

The treatment of the crude photoproduct with ethanolic potassium hydroxide afforded a similar mixture of azo compounds. In addition, the possibility of a third azo compound being present was shown by gas chromatographic analysis of the hydrolysis product.



(5) X= H

(84) X= Cl

(85) X= NH_2

(86)

4-Chloro-1,2'-azonaphthalene (84) was synthesised from 4-amino-1,2'-azonaphthalene (85) by means of a Sandmeyer reaction. In addition to the required compound (84) a second compound was formed in the reaction. From the microanalytical data and the mass spectrum it was deduced that the additional product was a dichloroazonaphthalene (88). Because of the reactants used it was assumed that one of the halogeno groups was in the 4-position. The position (x) of the second group is not known and it could be in one of several positions of either ring.

The mode of formation of this compound, x,4-dichloro-1,2'-azonaphthalene (88), is not fully understood. The diazotisation of the amine (85) is apparently a necessary part of its formation because if this step was carried out with t-butyl nitrite (or n-amyl nitrite), instead of with sodium nitrite, then none of the dichloro compound was formed. 4-Chloro-1,2'-azonaphthalene (84) remained unaltered when treated with cuprous chloride-hydrochloric acid solution. This removed the possibility that dichlorination was a simple halogenation of the Sandmeyer product. It is suggested that a particular compound may be formed in the diazotisation step which is chlorinated under the Sandmeyer conditions used.

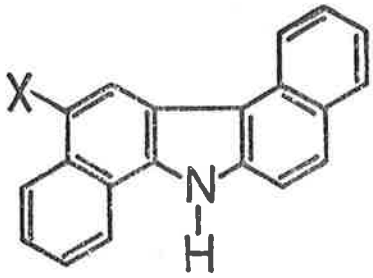
Authentic 4-chloro-1,2'-diamino-1',2-binaphthyl (79) was prepared from 4-chloro-1,2'-azonaphthalene (84) by rearrangement in acidic media of the 4-chloro-1,2'-hydrazonaphthalene derived from (84). The

bis-salicylidene anil (82) and 4-chloro-N,N'-diacetyl-1,2'-diamino-1',2-binaphthyl (80) were synthesised by treating compound (79) with salicylaldehyde and acetyl chloride respectively.

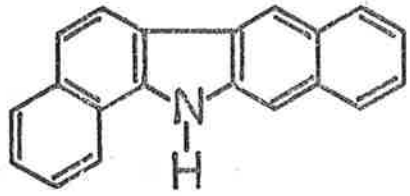
Two samples of 4-chloro-1,2'-diamino-1',2-binaphthyl (79) were converted to dibenzocarbazoles in order to prove that the two amino groups were in positions "ortho" to the bond linking the two rings. One sample was authentically prepared and the other was derived from the N,N'-diacetylated photoproduct (80). In strongly acidic solution these diamino compounds readily underwent cyclisation with loss of ammonia to form a dibenzocarbazole. The product in each case was not fully characterised. However the ultraviolet-visible and infrared spectra of the products were similar to those of an authentic sample of 7H-dibenzo[a,g]carbazole (89). Ethanolic solutions of the products exhibited strong blue fluorescence which is characteristic of dibenzocarbazoles. Mass spectrometry was found to be an excellent method for the detection of dibenzocarbazoles. These compounds undergo a very simple and distinctive fragmentation in the mass spectrometer. The base peak in the spectrum was always the parent molecular ion. If the dibenzocarbazole was non-chlorinated then the next ion resulted from loss of HCN (M-28); if chlorinated then the fragmentation first involved loss of Cl (M-35) followed by loss of HCN. Doubly charged ions always appeared at m/2e values for all of the fragments. The

species described were the only ones that appeared in the mass spectra.

Shine et al.[67] have prepared 7H-dibenzo[a,g]carbazole (89) from 1,2'-diamino-1',2-binaphthyl (78) under similar conditions; the other possible dibenzocarbazole (91) was not formed. From this it was concluded that 4-chloro-1,2'-diamino-1',2-binaphthyl afforded 12-chloro-7H-dibenzo[a,g]carbazole (90) in acidic media.



(89) X= H
(90) X= Cl



(91)

A portion of the crude N,N'-diacetyl binaphthyl (80) from the photoreaction was deacetylated and the mixture so obtained was heated with sulphuric acid. The mass spectrum of the product indicated that a chlorinated and non-chlorinated dibenzocarbazole had been formed; this implied that a mixture of the corresponding diamino compounds had originally been present. A probable explanation is that a chloro-N,N'-diacetylhydrazonaphthalene was present in the crude compound (80) and that this was hydrolysed under the acidic conditions

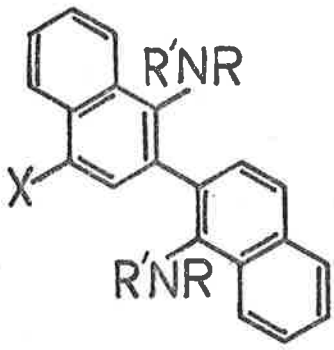
to give non-chlorinated hydrazonaphthalene, which then rearranged to form a diaminobinaphthyl. If this suggestion is correct, then it would seem that dechlorination occurs upon hydrolysis of chloro-N,N'-diacetylhydrazo compounds in acidic and alkaline media.

5. trans-1,1'-Azonaphthalene.

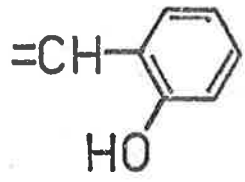
The photoinduced reaction of 1,1'-azonaphthalene (3) with acetyl chloride, unlike the previously described reactions, resulted in virtually complete formation of a naphthidine-type rearrangement product. No dark reaction occurred when 1,1'-azonaphthalene was heated in acetyl chloride solution in complete darkness for a long period.

The major product from the photoreaction was 4-chloro-N,N'-diacetyl-1,1'-diamino-2,2'-binaphthyl (94). The identity of this compound was established by elementary analysis, infrared and mass spectra, and comparison with an authentic sample.

The photoproduct (94) was deacetylated in basic or acidic media to yield 4-chloro-1,1'-diamino-2,2'-binaphthyl (93). This compound was converted into bis-salicylidene-4-chloro-1,1'-diamino-2,2'-binaphthyl (95) by treatment with salicylaldehyde. The structure of the bis-salicylidene anil was shown from microanalytical data, infrared and mass spectra, and by comparison with an authentic sample. The formation of a bis-salicylidene anil showed the presence



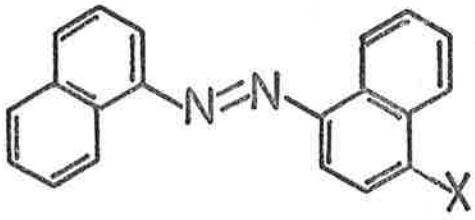
	X	R	R'
(92)	H	H	H
(93)	Cl	H	H
(94)	Cl	$-COCH_3$	H
(95)	Cl	=CH-	



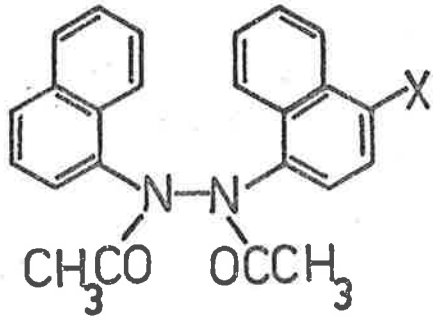
of two primary amino groups in the compound (93).

1,1'-Hydrazonaphthalene has been reported[67] to undergo rearrangement in acidic media to form 1,1'-diamino-2,2'-binaphthyl (92). No reported instance of rearrangement leading to other binaphthyl compounds could be found. This led to the conclusion that rearrangement in the photoreaction resulted in bonds being formed between the β-positions of the two naphthyl rings.

In a separate photoreaction the complete crude product was treated with ethanolic potassium hydroxide. Chromatography of the mixture so formed yielded small quantities of 4-chloro-1,1'-azonaphthalene (96) (0.5%) and 1,1'-azonaphthalene (3). The structures of these hydrolysis products were confirmed by comparison with authentic samples. The isolation of compound (96) suggested that a corresponding quantity of the N,N'-diacetyl compound (98) was formed in the photoreaction. It is not known whether the 1,1'-azonaphthalene isolated is unchanged starting material or comes from dechlorination



(3) X=H
(96) X=Cl
(97) X=NH_2



(98)

of a chloro-N,N'-diacetylhydrazo compound during the hydrolysis reaction.

Other fractions afforded quantities of oils which could not be crystallized or resolved into components. Examination of these products was not pursued further.

The mechanism postulated for the formation of the rearrangement product (94) (see II.6) requires protons to be present. A possible source of protons would be the hydrogen chloride dissolved in the acid chloride. It was thought possible that if the concentration of hydrogen chloride was diminished then more of the N,N'-diacetylhydrazonaphthalene might form in preference to rearrangement product. Accordingly 1,1'-azonaphthalene (3) was irradiated at -35° under an atmosphere of nitrogen in degassed acetyl chloride; and the crude photoproduct was subjected to hydrolysis-oxidation in the usual way. Chromatography of the hydrolysis mixture yielded 4-chloro-

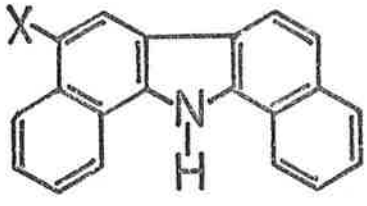
1,1'-azonaphthalene (96) in 11% yield. The presence of 1,1'-azonaphthalene (3) was detected by gas chromatography and a small quantity of 4-chloro-N,N'-diacetyl-1,1'-diamino-2,2'-binaphthyl (94) was also isolated. The yield of compound (96), and hence of the corresponding N,N'-diacetyl compound (98), was much greater (11% cf. 0.5%) than that for the "normal" irradiation. This indicated that the presence of dissolved hydrogen chloride was indeed a factor which aided formation of the rearrangement product (94).

4-Chloro-1,1'-azonaphthalene (96) was prepared from 4-amino-1,1'-azonaphthalene (97) by a Sandmeyer reaction. A second azo compound, x,4-dichloro-1,1'-azonaphthalene (99), was also formed in the reaction. The structure of both products was established from the elemental analysis and mass spectrum. The position (x) of the second halogeno group has not been determined. It could be in either naphthyl ring. When n-amyl nitrite was used in place of sodium nitrite as the diazotising agent none of the dichloro compound was formed. A similar result has been described for the reaction of 4-amino-1,2'-azonaphthalene under similar conditions (see I.4).

4-Chloro-1,1'-diamino-2,2'-binaphthyl (93) was prepared by rearrangement of 4-chloro-1,1'-hydrazonaphthalene under acidic conditions. The compound (93) was used to prepare 4-chloro-N,N'-diacetyl-1,1'-diamino-2,2'-binaphthyl (94) and bis-salicylidene-4-chloro-1,1'-diamino-2,2'-binaphthyl (95).

4-Chloro-N,N'-diacetyl-1,1'-diamino-2,2'-binaphthyl (94) obtained from the photoreaction was deacetylated; and the diamino compound (93) so formed was converted into 5-chloro-13H-dibenzo[a,i]carbazole (101) by treatment with sulphuric acid. The compound (101) was not fully characterised, but its structure was established from its mass (see I.4), ultraviolet-visible, and infrared spectra. An identical product was obtained when an authentically prepared sample of (93) was treated under the same conditions. The product in each case exhibited blue-purple fluorescence. The ultraviolet-visible and infrared spectra were similar to those of an authentic sample of 13H-dibenzo[a,i]carbazole (100). The compound (100) was prepared from 1,1'-hydrazonaphthalene via 1,1'-diamino-2,2'-binaphthyl (92).

The formation of 5-chloro-13H-dibenzo[a,i]carbazole (101) proved the "ortho" relationship of the amino groups to the positions of attachment of the two naphthyl rings.



(100) X=H
(101) X=Cl

6. N.M.R. Spectra of some Chloro-N,N'-diacetylhydrazonaphthalenes.

Table III.

Methyl Group Proton-Resonances.

	Compound	δ (ppm)
(37)	2-(4'-chloro-N,N'-diacetylphenylhydrazo)-naphthalene	2.0
(38)	2-(2'-chloro-N,N'-diacetylphenylhydrazo)-naphthalene	2.0
(40)	2-(x-chloro-N,N'-diacetylphenylhydrazo)-naphthalene	2.0
(29)	4-chloro-N,N'-diacetylhydrazobenzene	1.97[101]
(59)	1-(x-chloro-N,N'-diacetylphenylhydrazo)-naphthalene	1.86, 1.92, 1.97
(86)	x-chloro-N,N'-diacetyl-1,2'-hydrazonaphthalene	1.83, 1.86, 1.90, 1.95, 2.0
(72)	x,y-dichloro-N,N'-diacetyl-2,2'-hydrazonaphthalene	2.0
(60)	x-chloro-N,N'-diacetyl-2,2'-hydrazonaphthalene	2.0

The n.m.r. spectra of N,N'-diacetylhydrazonaphthalenes yielded some unexpected results. The spectra of compounds in which only the β-position of the naphthyl ring was involved in the hydrazo linkage (37, 38, 40, 72, and 60), or where only phenyl rings were present (29),

gave a single peak at δ2.0 ppm for the methyl protons in the acetyl groups. A marked difference was observed when a naphthyl ring was attached through its α-position to the hydrazo bridge (59 and 86, see Table III); in such cases several sharp singlets appeared in the region δ1.8-2.0 ppm.

The compounds (37) and (38) were conventionally prepared samples. Compounds (40) and (59) were obtained from photoreactions, and these were pure crystalline solids. Compounds (60) and (72) were photoproducts. Compound (86) was a mixture of two isomeric x-chloro-N,N'-diacetylhydrazonaphthalenes and this would account to some degree for the complexity of the signals in this case. The value of δ for (29) was obtained from work published by Lewis and Mayfield.[101]

A possible explanation of the results listed in Table III is based on conformational effects. Tetra-alkylhydrazines,[62] N,N'-diaryl-N,N'-dialkylhydrazines,[64] N,N'-diaryl-N,N'-diacylhydrazines,[65] and nitrosoamines[66] have been shown to undergo temperature-dependent conformational changes. These alterations in conformer population have been examined by variable temperature n.m.r. spectroscopy; and the results were interpreted in terms of a substantial barrier to rotation about the N-N bond. Rapid inversion also occurs at each nitrogen atom but the energy barrier is thought to be too small to account for the observed changes in the n.m.r. spectra. At temperatures low enough to prevent coalescence some of the individual conformers have a

sufficiently long life for their individual proton-resonances to be recorded. At high temperatures the signals coalesced.

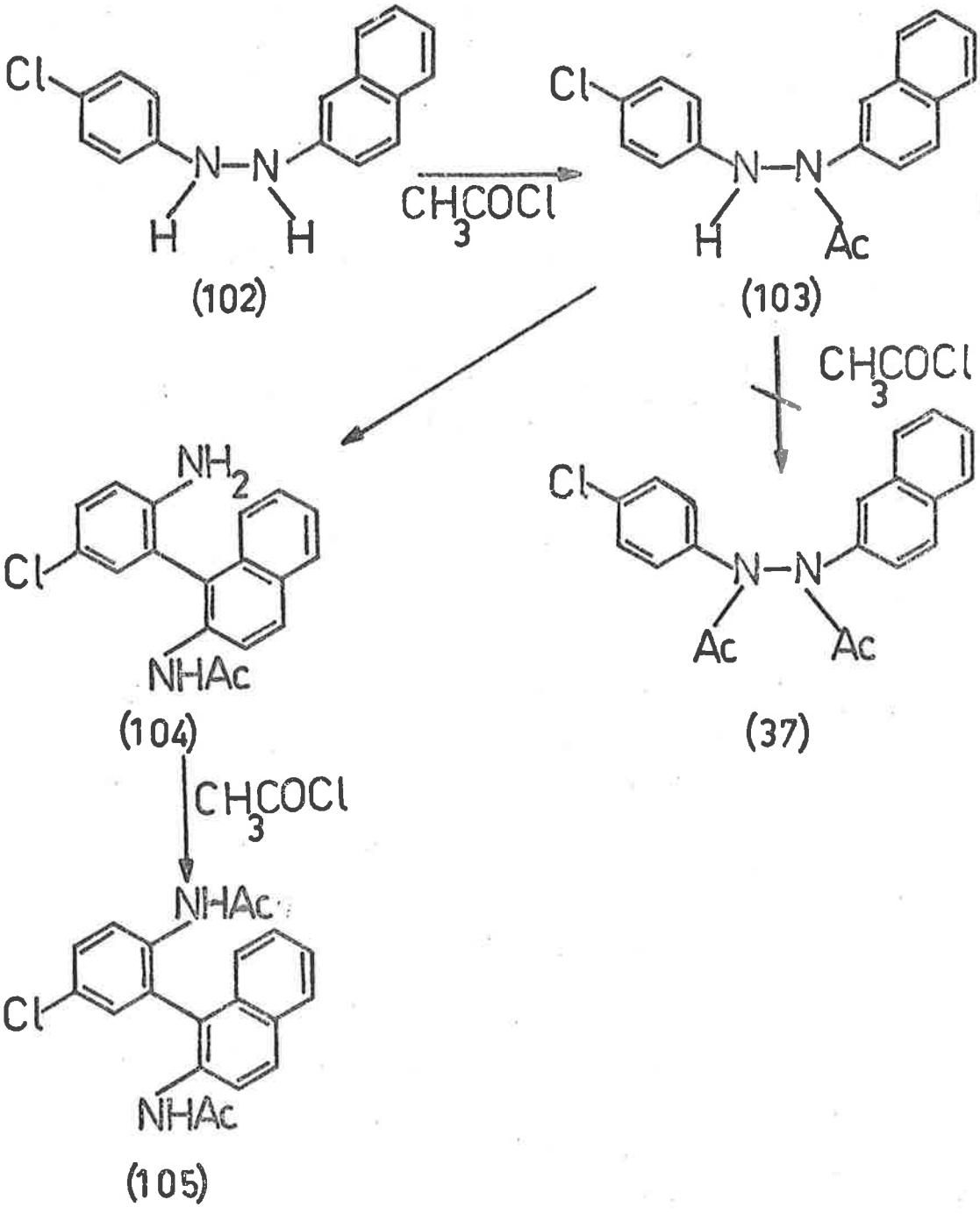
The eight compounds noted in Table III can be considered as tetra-substituted hydrazines. It is suggested that the single signal obtained for the methyl groups in (37), (38), (40), (72), (60), and (29) is a consequence of signals from all of the possible conformers coalescing. In compounds (86) and (72) the rotational energy barrier for the N-N bond may be large enough to give some of the different conformers sufficient lifetimes to enable registration of the individual resonances in the n.m.r. spectra for the acetyl groups. The possibility of protons in a particular methyl group being non-equivalent (rather than the methyl groups in themselves being non-equivalent) is considered unlikely because of the low barrier to rotation about a C-C bond.

Further investigation of the temperature dependence of these n.m.r. spectra is required in order to determine whether conformational differences are in fact responsible for the observed spectra. Why the phenomenon which was described above should occur only with compounds containing α-naphthyl rings is not known. Hydrogen bonding between the peri-hydrogen atom in the naphthyl ring and the oxygen atom of the acetyl group on the nitrogen atom adjacent to that ring, might result in restriction of rotation about the N-N bond.

7. Approaches to the Syntheses of N,N'-Diacetylhydrazonaphthalenes.

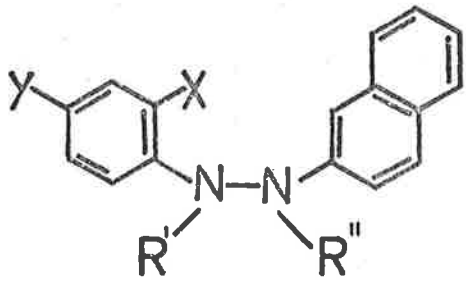
Acetylation of the various hydrazonaphthalenes was attempted with different acetylating agents. The hydrazobenzenes are known to readily form N,N'-diacetylhydrazo compounds when heated with acetyl chloride.[101] However, similar attempts with substituted and unsubstituted azonaphthalenes yielded products which were evidently derived from an initially formed N-acetylhydrazo compound. What is thought to be a typical reaction sequence, (102) to (105), is depicted in Scheme VI.

The final composition of each reaction mixture was established from infrared and mass spectral data, and the fact that on alkaline hydrolysis only a small quantity of the parent azonaphthalene was isolated. The N-acetylhydrazo compounds could be isolated if the reactions were carried out at room temperature and short reaction times were involved. All attempts to acetylate these compounds further with acetyl chloride, N,N'-dimethyl aniline-acetyl chloride, and pyridine-acetyl chloride were unsuccessful. In acetyl chloride at room temperature the mono-acetylhydrazo compounds were found to be slowly converted into "benzidine-type' rearrangement products; authentic samples of N,N'-diacetylhydrazo compounds were recovered unchanged after being treated under the same conditions. This suggested that in photoreactions where acetyl chloride was present as a solvent, any N-acetylhydrazo compounds formed would eventually undergo rearrangement.


Cl
N–N
H H
(102)
CH3COCl
Cl
N–N
H Ac
(103)
CH3COCl
NH2
Cl
NHAc
(104)
CH3COCl
Cl
N–N
Ac Ac
(37)
NHAc
Cl
NHAc
(105)

Scheme VI.

The N,N'-diacetylhydrazo compounds (37), (38), and (106) were obtained when acetyl chloride-pyridine/dichloromethane was used as the acetylating medium. A superior method involved the use of acetic anhydride[176] (which was completely free of acidic impurities) as the acetylating agent.



	Y	X	R"	R'
(107)	H	H	H	H
(108)	Cl	H	H	H
(109)	H	Cl	H	H
(106)	H	H	Ac	Ac
(37)	Cl	H	Ac	Ac
(38)	H	Cl	Ac	Ac

In all of these preparations the mono-acetylhydrazonaphthalenes were first isolated and purified. Ritter and Ritter[137] have mono-acetylated a number of unsymmetrically substituted hydrazobenzenes; and in most instances a mixture of the two possible isomeric N-acetyl compounds was obtained. The exception to this occurred when an ortho substituent was present. In this case exclusive acetylation was observed to occur at the nitrogen atom furthest from the substituted ring. The n.m.r. spectra of the products isolated from the mono-acetylation of the hydrazonaphthalenes (107), (108), and (109) indicated that mixtures had been formed (see Table IV).

Table IV.

Mono-acetylation Products

Hydrazo Compound	Acetylation Position	Methyl Proton-Resonances δ (ppm)
2-(4'-chlorophenylhydrazo)naphthalene (108)	* N,N'	2.27, 2.30
2-(2'-chlorophenylhydrazo)naphthalene (109)	N'	2.27
2-phenylhydrazonaphthalene (107)	N,N'	2.27, 2.30

* (N and N' indicate nitrogen atoms adjacent to the phenyl and naphthyl rings respectively.)

The presence of two sharp singlets at δ2.27 and 2.30 ppm (integrated peak areas in the ratio of 1:1) in the n.m.r. spectra of the products derived from (108) and (107) indicated that a mixture of the corresponding N-acetyl and N'-acetyl compounds had been formed in approximately equal quantities. The product obtained from mono-acetylation of compound (109) showed only one singlet at δ2.27 ppm in its n.m.r. spectrum. Here acetylation apparently had yielded only one of the two possible isomers. It was thought that the acetyl group would be attached to the nitrogen atom adjacent to the naphthalene ring because of steric hindrance by the ortho chloro group to the approach of the acetylating species to the other nitrogen atom. This

would also be compatible with the results reported by Ritter and Ritter[137] for the acetylation of ortho substituted hydrazobenzenes. These authors also reported a convenient test to distinguish between N-acetylhydrazobenzenes containing the acetyl group on a nitrogen atom adjacent to a substituted ring (N), and those with the acetyl group on a nitrogen next to an unsubstituted phenyl ring (N'). Upon treatment with potassium dichromate the former compounds yielded a deep red or violet coloured solution and the latter a brown solution. The single 2-(2'-chloro-N-acetylphenylhydrazo)naphthalene which had been isolated was treated in a similar way and a dark brown solution was obtained. It is tentatively suggested that this result may indicate that the acetyl group is on the nitrogen atom (N') which is adjacent to the naphthalene ring. However it must be emphasized that the applicability of the test of Ritter and Ritter[137] to the hydrazonaphthalenes has not been proven.

Authentically prepared samples of 2-(2'-chloro-N,N'-diacetyl-phenylhydrazo)naphthalene (38), 2-(4'-chloro-N,N'-diacetylphenyl-hydrazo)naphthalene (37), and the corresponding N-acetyl and parent hydrazo compounds were treated with ethanolic potassium hydroxide. In no instance was the reaction product found to contain non-chlorinated 2-phenylazonaphthalene. This eliminated the possibility that one or more of these compounds was the precursor of the 2-phenylazonaphthalene which was isolated from the hydrolysis-oxidation of the product from the photoreaction of trans-2-phenylazonaphthalene with acetyl chloride.

II. DARK REACTIONS OF cis-PHENYLAZONAPHTHALENES AND cis-AZONAPHTHALENES WITH ACETYL CHLORIDE.

In Part I a description was given of the photoactivated reactions between trans-azonaphthalenes and acetyl chloride. In separate experiments it was shown that no appreciable reaction occurred between trans-azonaphthalenes and acetyl chloride at room temperature (and at 55°) in the complete absence of light. From this it was concluded that a photoexcited form of each trans-azonaphthalene was responsible for the products which were formed in each photoreaction. trans-Azobenzene[1,2] and trans-azonaphthalenes[10,13,14] are known to undergo photoisomerization when irradiated in solution, to give an equilibrium mixture of the cis- and trans-isomers. Lewis and Mayfield[104] have shown that the products obtained from the photoreaction of trans-azobenzene with acetyl chloride were directly derived from the dark reaction of cis-azobenzene with the acid chloride. In order to show that the cis-isomers were the reactive species in the photodependent reactions involving trans-azonaphthalenes it was necessary to examine the dark reactions between cis-azonaphthalenes and acetyl chloride.

When the cis-azonaphthalenes and cis-phenylazonaphthalenes were individually treated with acetyl chloride, a rapid reaction occurred and hydrogen chloride was evolved. A deep blue-purple solution was formed in each case. With one exception, it was found that when the reaction mixtures were left to stand the blue-purple colour gradually

faded until after a period of *c.* 1 min only a red-orange colour remained. The exception was the reaction mixture derived from *cis*-1,1'-azonaphthalene. In this case the blue-purple colour also faded, but a grey coloured suspension was formed. The colours of the red solutions and the grey suspension did not alter when the mixtures were exposed to direct sunlight or allowed to stand in the dark for several days. *trans*-1- and 2-Phenylazonaphthalenes, and *trans*-2,2'-, 1,2'-, and 1,1'-azonaphthalenes all give orange or red-orange solutions in acetyl chloride. In each case the colour fades when the solution is exposed to light. Hence the colourations formed by the *cis*-isomers in acetyl chloride provide a test for differentiating between *cis*- and *trans*-azonaphthalenes and between *cis*- and *trans*-phenylazonaphthalenes. The test can also be applied to the series of azobenzene compounds.[104]

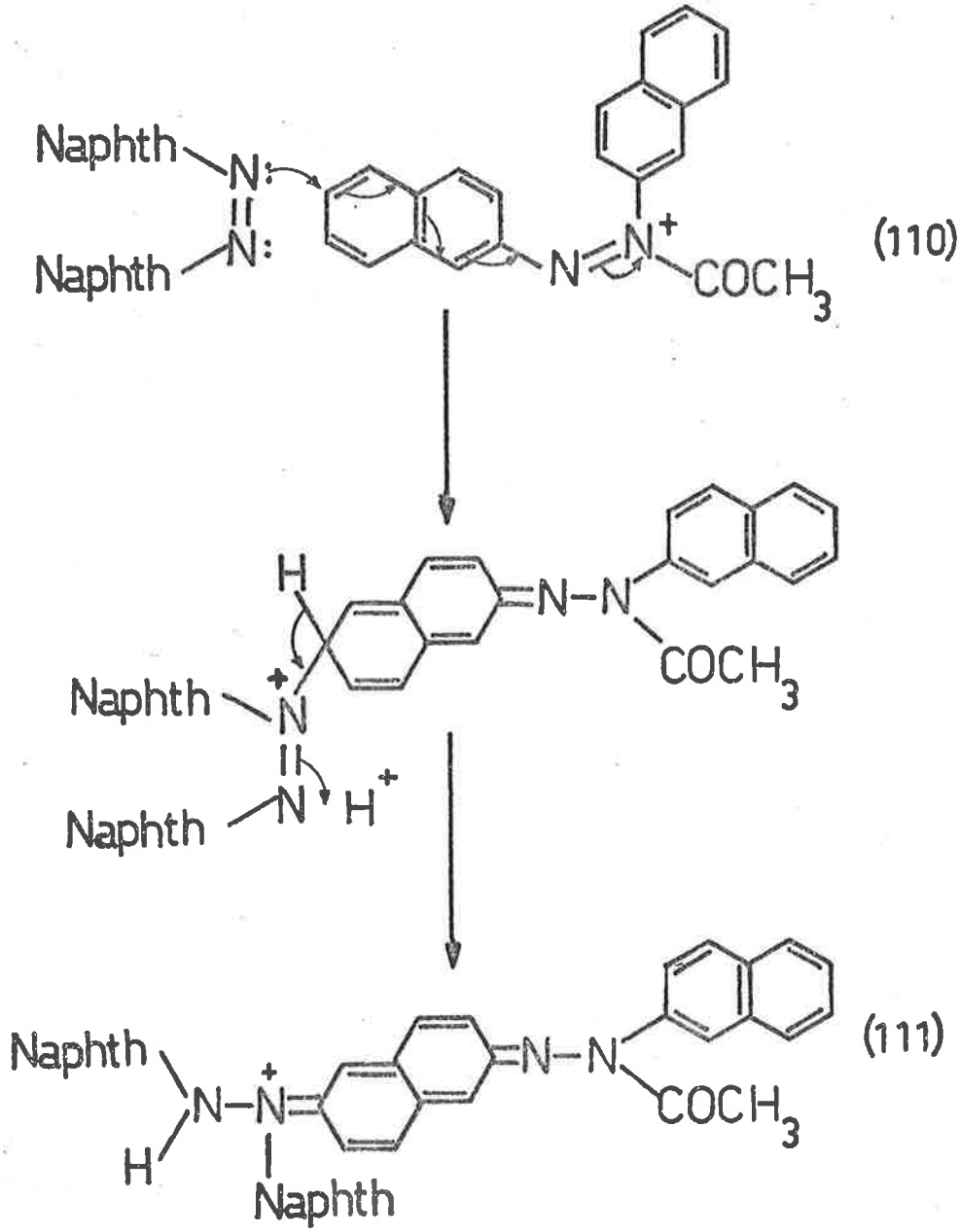
Attempts were made in each case to isolate the compound which was responsible for the observed blue-purple colouration. Very small quantities of impure blue-black resinous materials were obtained from the reaction mixtures. Thin-layer chromatography of these products indicated that they contained several compounds. The blue-black compounds which were apparently causing the observed colourations could not be isolated and purified. The blue-black mixture on all occasions gradually decomposed on standing either in or out of solution. It was unstable in neutral, acidic, or basic aqueous media and in organic solvents. The decomposition products could not be identified. Efforts

to recrystallize the resins resulted in decomposition. Meaningful infrared and n.m.r. spectral data could not be obtained because of the complexity of the mixtures and the limited amounts of material available. Solutions of the crude resins in ethanol exhibited broad absorptions in the region 590-640mμ.

Lewis and Mayfield[104] postulated a structure for the blue compound formed when cis-azobenzene was treated with acetyl chloride. If their suggestion and arguments are assumed to be correct then similar types of structures can be written for the blue compound formed in each of the reactions of the cis-azonaphthalenes with acetyl chloride Scheme VII depicts a possible pathway, (110)⟶(111), to such a compound (111) derived from cis-2,2'-azonaphthalene.

The pathway involves nucleophilic attack of cis-2,2'-azonaphthalene on the cation (110) to form structure (111), which by comparison with dyestuffs having similar structures would be expected to be blue-black in colour.

If such compounds are formed by a process similar to that shown in Scheme VII, then the cis-azonaphthalenes are acting as nucleophiles in competition with chloride ions. This was demonstrated by adding the cis-azonaphthalenes to large quantities of acetyl chloride. Here very little blue coloured material was formed, indicating that the formation of this compound was dependent upon the concentration of the cis-isomer. This dependence is also thought to be responsible for the colouration not being formed in the photoreactions of the trans-


Naphth
N:
Naphth
N:
N
N+
COCH3
(110)
H
N–N
COCH3
Naphth
N
N
H+
Naphth
Naphth
N–N
H
N
Naphth
N–N
COCH3
(111)

Scheme VII.

isomers. The cis-isomer formed would immediately react thereby preventing the concentration of this isomer from reaching a high level.

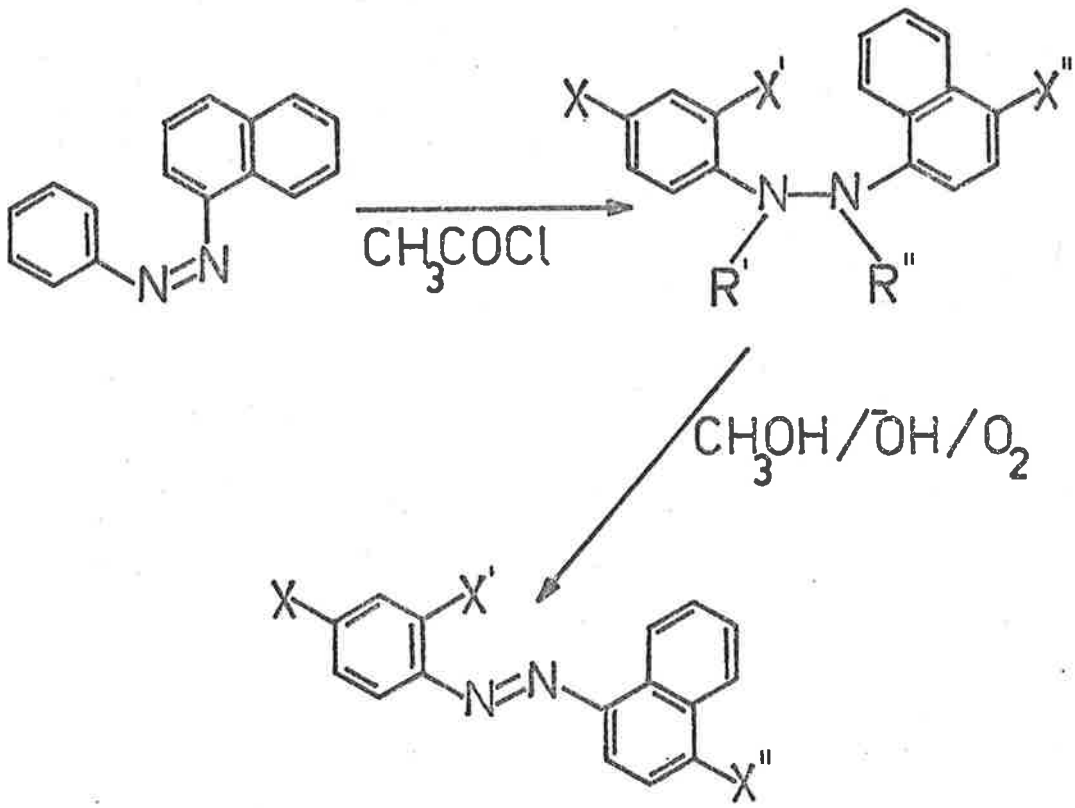
It has been described in Part I how in the photoreactions involving the trans-isomers nucleophilic attack by the chloride ion occurs at several positions on the aromatic rings. Similarly it would be expected that the blue colourations formed by the cis-isomers would be caused by a mixture of several isomeric compounds arising from nucleophilic substitution at several positions.

Reaction Products.

1. cis-1-Phenylazonaphthalene.

cis-1-Phenylazonaphthalene (11) and excess acetyl chloride were mixed; and after c. 1 min the reaction was quenched by the addition of water. The mixture so obtained was extracted; and evaporation of the solvent gave a dark coloured residue. This material was chromatographed; and the first fraction afforded trans-1-phenylazonaphthalene.

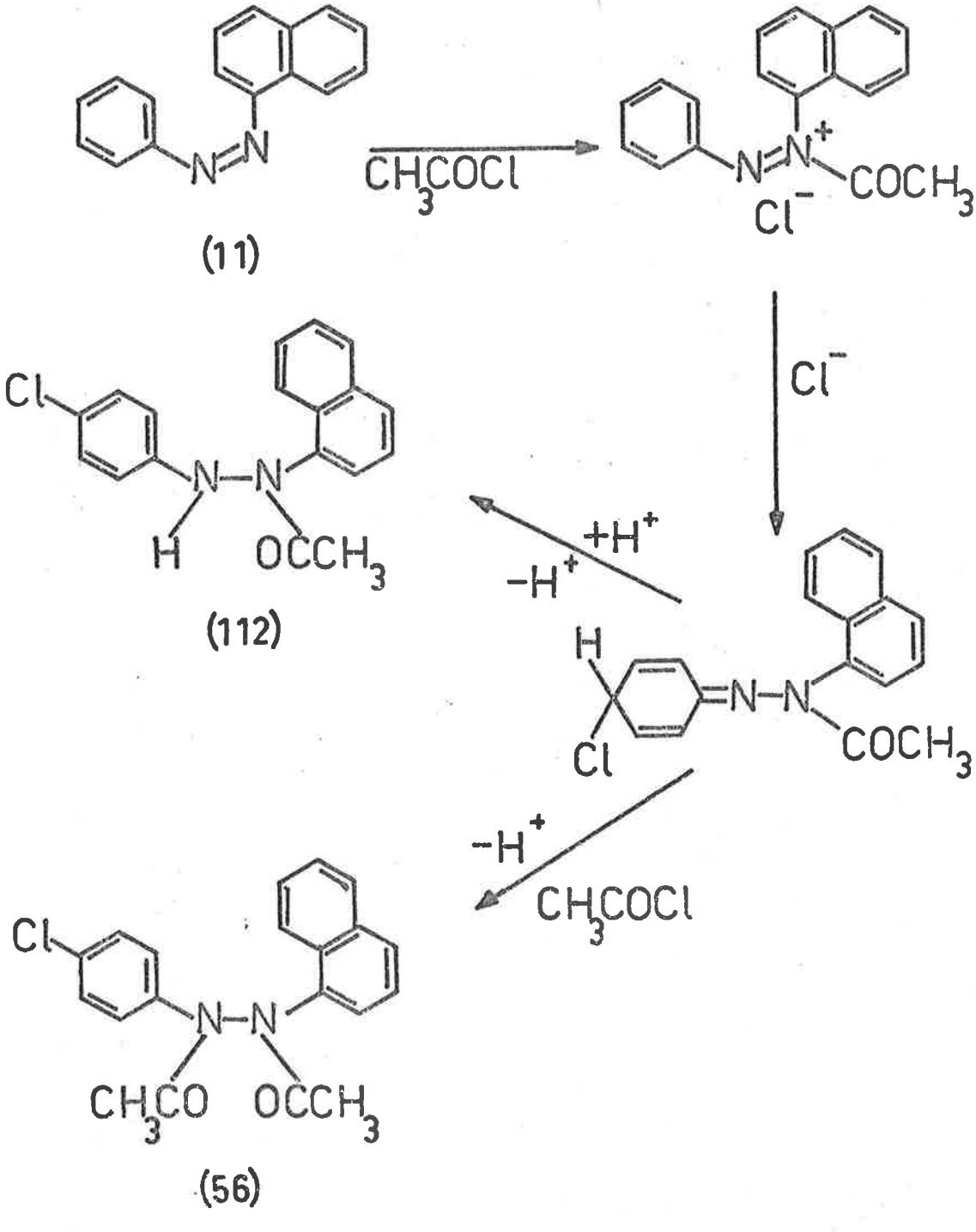
From the second and third fractions mixtures of N-acetyl- and N,N'-diacetylhydrazonaphthalenes were obtained. This was established on the basis of the infrared spectra and the fact that these mixtures yielded phenylazonaphthalenes under alkaline hydrolysis conditions. Gas chromatography was used to show that the hydrolysis/oxidation reaction product contained 1-phenylazonaphthalene (9), 1-(4'-chlorophenylazo)naphthalene (52), 4-chloro-1-phenylazonaphthalene (55), and 1-(2'-chlorophenylazo)naphthalene (53). The first three compounds (9), (52), and (55) were present in the approximate ratio of 1:4:2. Compound (53) was present in only trace amounts. The formation of these compounds in the hydrolysis reaction indicates that the corresponding N-acetyl and/or N,N'-diacetyl compounds, were present in the original reaction mixture. In addition a chloro-N-acetyl and/or chloro-N,N'-diacetyl compound is present which gives 1-phenylazonaphthalene upon hydrolysis. The separate N-acetyl and N,N'-diacetyl compounds could not be isolated and characterised.



	X	X'	X"	R'	R"
(112)	Cl	H	H	H	Ac
(56)	Cl	H	H	Ac	Ac
(113)	H	Cl	H	H	Ac
(57)	H	Cl	H	Ac	Ac
(114)	H	H	Cl	Ac	H
(115)	H	H	Cl	Ac	Ac
(52)	Cl	H	H		
(53)	H	Cl	H		
(55)	H	H	Cl		
(9)	H	H	H		

Comparison with the photoreaction involving the trans-isomer showed that the dark reaction between cis-1-phenylazonaphthalene and acetyl chloride yielded similar types of products. However, in the dark reaction a much larger quantity of N-acetyl compounds was formed. This is attributed to the much higher concentration of hydrogen chloride in the non-photochemical reaction mixture. This allows protons to compete favourably with the acetyl chloride (or acetylium ions) in attacking the nitrogen atom adjacent to the substituted phenyl or naphthyl rings, thereby forming a mixture of mono- and di-acetylated products. A mechanistic pathway to illustrate this is shown in Scheme VIII. Similar pathways can be drawn which involve chloride attack at other positions on the rings. In the photoreaction of trans-1-phenylazonaphthalene in acetyl chloride, the N,N'-diacetyl compounds are formed exclusively because of the low concentration of hydrogen chloride in the reaction mixture. This is partly due to the volume of acetyl chloride used in this reaction being much larger. In addition, because the photochemical reaction occurs at a much slower rate (probably at the rate of trans→cis isomerization) the hydrogen chloride concentration cannot build up to a level which would result in an appreciable amount of mono-acetyl compound being formed.

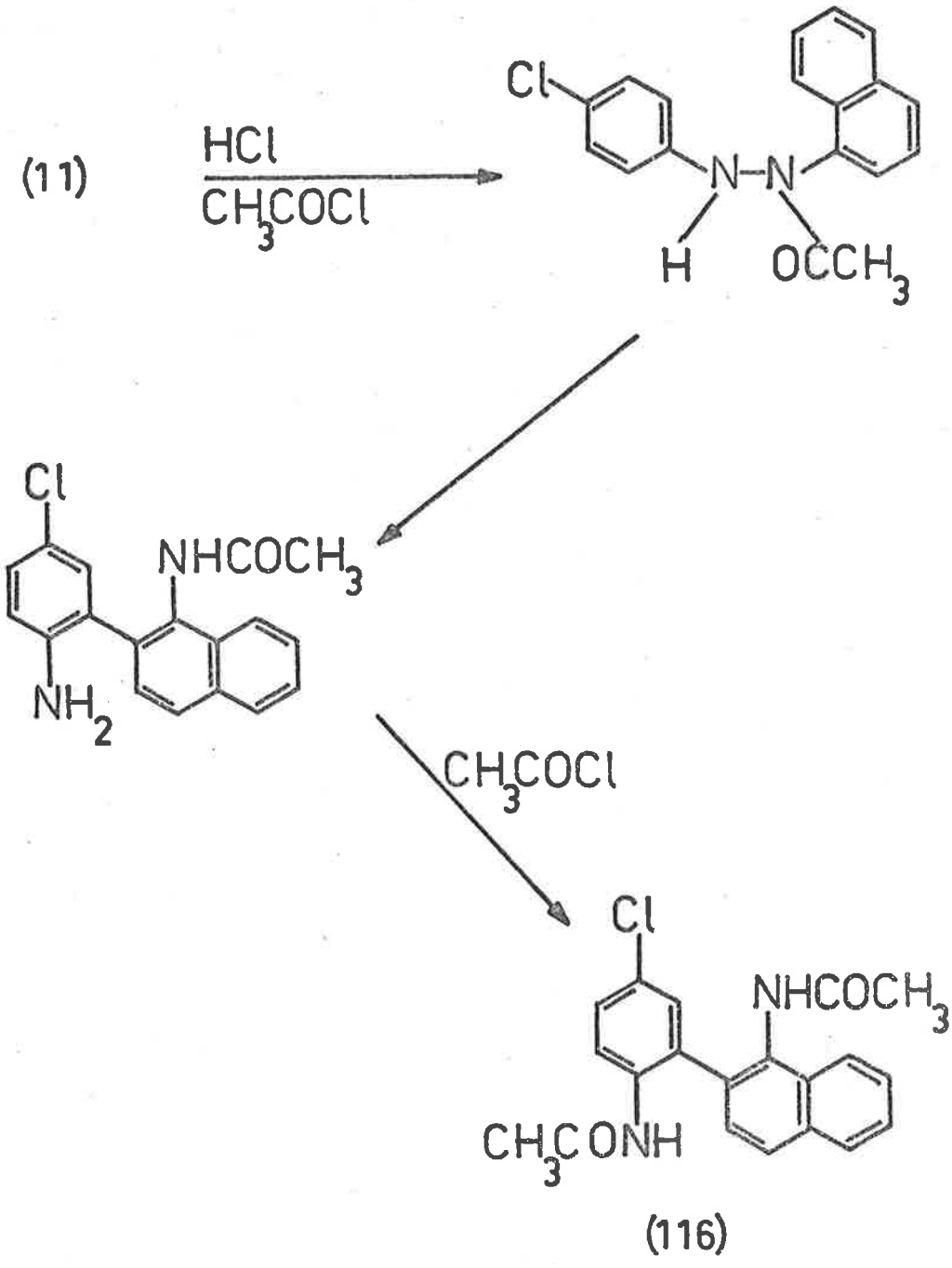
The relative yields of the various isomers (determined from the yields of the hydrolysis products) were noticeably different to those obtained for the photoreaction. The main feature was a very large yield of the 4-chloro compound (115) where chlorination had



Scheme VIII.

occurred in the naphthalene ring. This was in contrast to the photo-reaction in which only minute amounts of that isomer were formed. It is not known why this difference should exist.

Chromatography of the dark reaction product also afforded mixtures of products which showed bands at c. 3230 and 1695 cm^{-1} in their infrared spectra. These mixtures did not form azo compounds when subjected to alkaline hydrolysis-oxidation and were recovered unchanged at the end of the reaction. It has already been shown (Part I.7) that N-acetyl-2-phenylhydrazonaphthalenes undergo naphthidine-type rearrangements under acidic conditions, viz., in acetyl chloride solution. On the basis of these facts it was concluded that the material isolated comprised a mixture of products arising from re-arrangement of the N-acetyl compounds. A plausible mechanistic path-way to one of these compounds (116) is shown in Scheme IX. The indi-vidual compounds could not be isolated from what was evidently a complex mixture and therefore the postulated structures could not be verified.

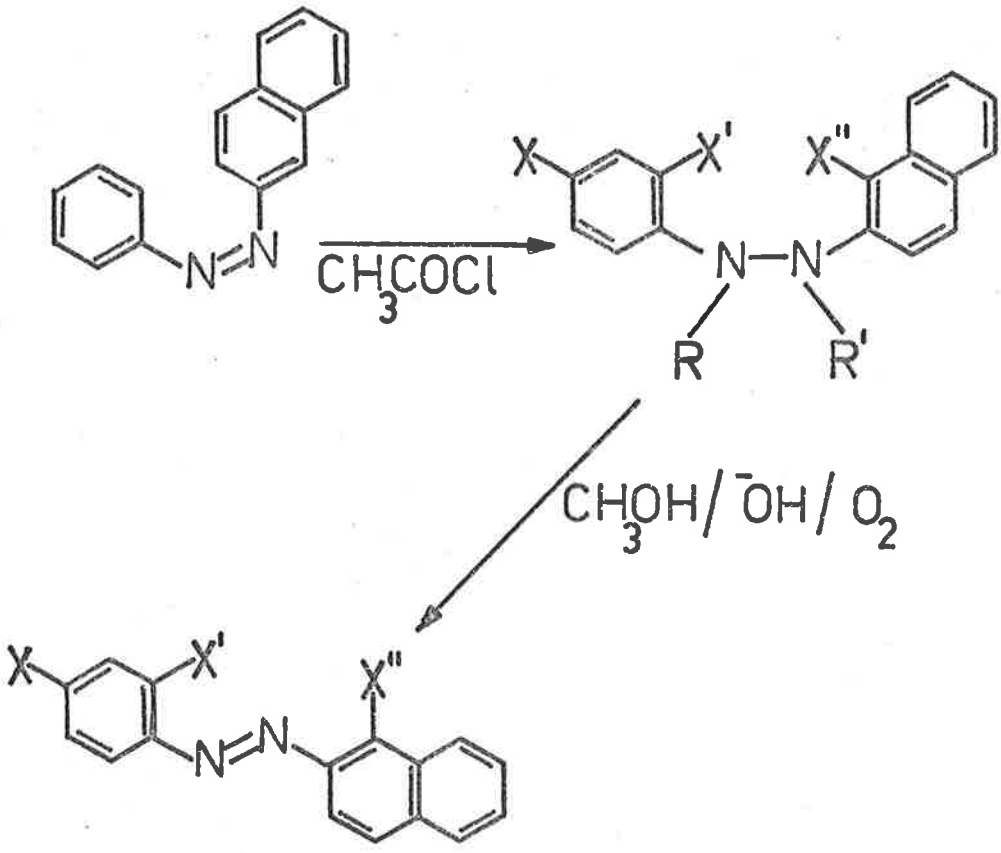

(11)
HCl
CH3COCl
Cl
N–N
H
OCCH3
Cl
NHCOCH3
NH2
CH3COCl
Cl
NHCOCH3
CH3CONH
(116)

Scheme IX.

2. cis-2-Phenylazonaphthalene.

cis-2-Phenylazonaphthalene (12) was treated with acetyl chloride; and, following the usual working-up procedure, the final reaction mixture was chromatographed on a column of silica. trans-2-Phenylazonaphthalene (10) was isolated from the first fraction.

The second and third fractions were collected; and thin-layer chromatography indicated that a complex mixture of products was present in each fraction. From the infrared spectra of the mixtures it was concluded that each fraction contained both N-acetyl and N,N'-diacetyl compounds. Attempts to resolve these mixtures into their components by column chromatography and recrystallization were unsuccessful. Accordingly the combined material from the two fractions was heated with ethanolic potassium hydroxide; and the product so obtained was chromatographed. A single broad band was eluted. The material in this fraction was examined by qualitative gas chromatography. In this way it was shown that 2-phenylazonaphthalene (10), 2-(4'-chlorophenylazo)naphthalene (33), 2-(2'-chlorophenylazo)naphthalene (34), and 1-chloro-2-phenylazonaphthalene (35) had been formed in the hydrolysis-oxidation reaction. The compounds were insufficiently resolved for accurate comparative yields to be determined. However compounds (10) and (33) were obviously the major products and were present in approximately the same quantities. It is reasonable to assume that equivalent quantities of the N-acetyl and/or N,N'-diacetylhydrazonaphthalenes were formed in the dark reaction of cis-2-phenylazo-



	X	X'	X''	R	R'
(117)	Cl	H	H	H	Ac
(37)	Cl	H	H	Ac	Ac
(118)	H	Cl	H	H	Ac
(38)	H	Cl	H	Ac	Ac
(119)	H	H	Cl	Ac	H
(39)	H	H	Cl	Ac	Ac
(33)	Cl	H	H		
(34)	H	Cl	H		
(35)	H	H	Cl		

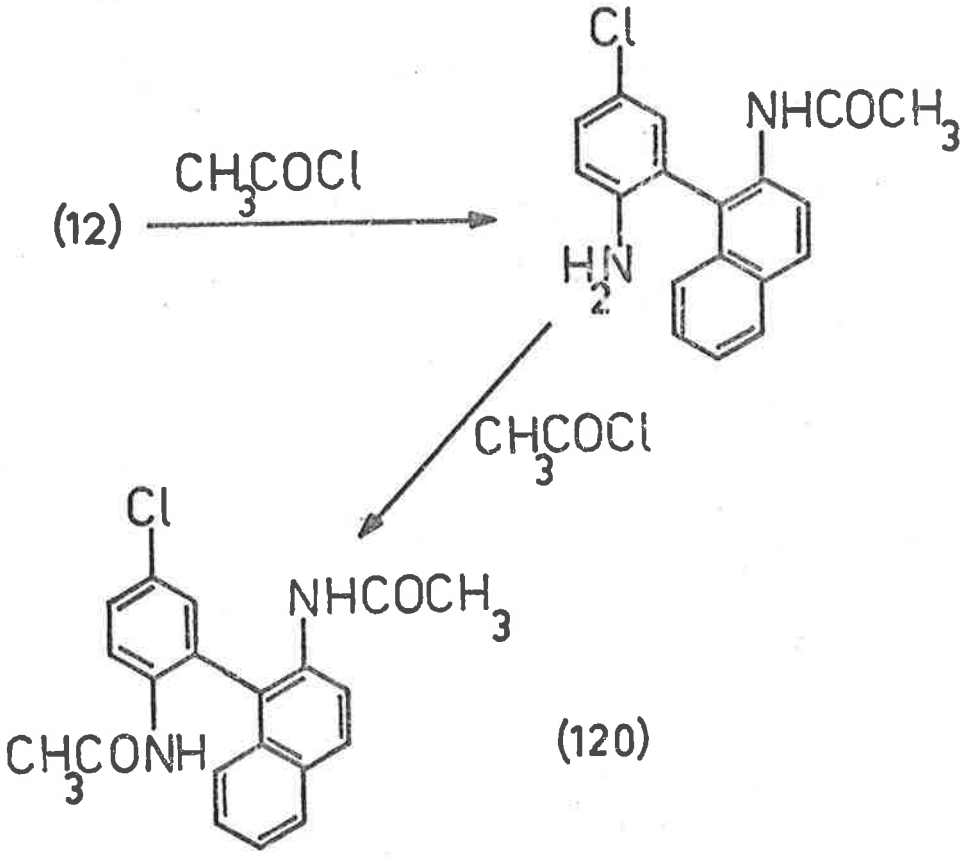
naphthalene with acetyl chloride. It is not known whether a particular position of substitution favours mono-acetylation rather than diacetylation. A similar argument and mechanistic pathway to those described in Part III.1 can be applied to this reaction to account for the formation of N-acetyl and N,N'-diacetylhydrazo compounds.

Presumably a product is formed in the dark reaction which undergoes dechlorination under alkaline hydrolysis conditions. It is probably the same N,N'-diacetyl compound (40) as that isolated from the photoreaction of trans-2-phenylazonaphthalene in acetyl chloride. It might alternatively be an N-acetylhydrazo compound. An instance of a mono-acetylated hydrazonaphthalene losing a chloro group upon hydrolysis is described in Part III.1. x-Chloro-N-oxalyl-2-phenylhydrazonaphthalene was shown to lose a chloro group in such a reaction.

The values for the relative amounts of the different phenylazonaphthalenes in the hydrolysis product were similar to those obtained for the mixture arising from the hydrolysis of the photoreaction product. This indicated that chlorine substitution in both cases occurred in the same positions in the rings and with a similar preference for individual positions.

Chromatography of the crude dark reaction mixture also yielded a fourth fraction. The residue obtained after evaporation of the solvent was found not to be converted into an azonaphthalene when subjected to alkaline hydrolysis-oxidation. This result, together with

the infrared and mass spectral data, led to the conclusion that this fraction contained a mixture of naphthidine-type rearrangement products [e.g. (120)]. These compounds could not be individually isolated



(120)

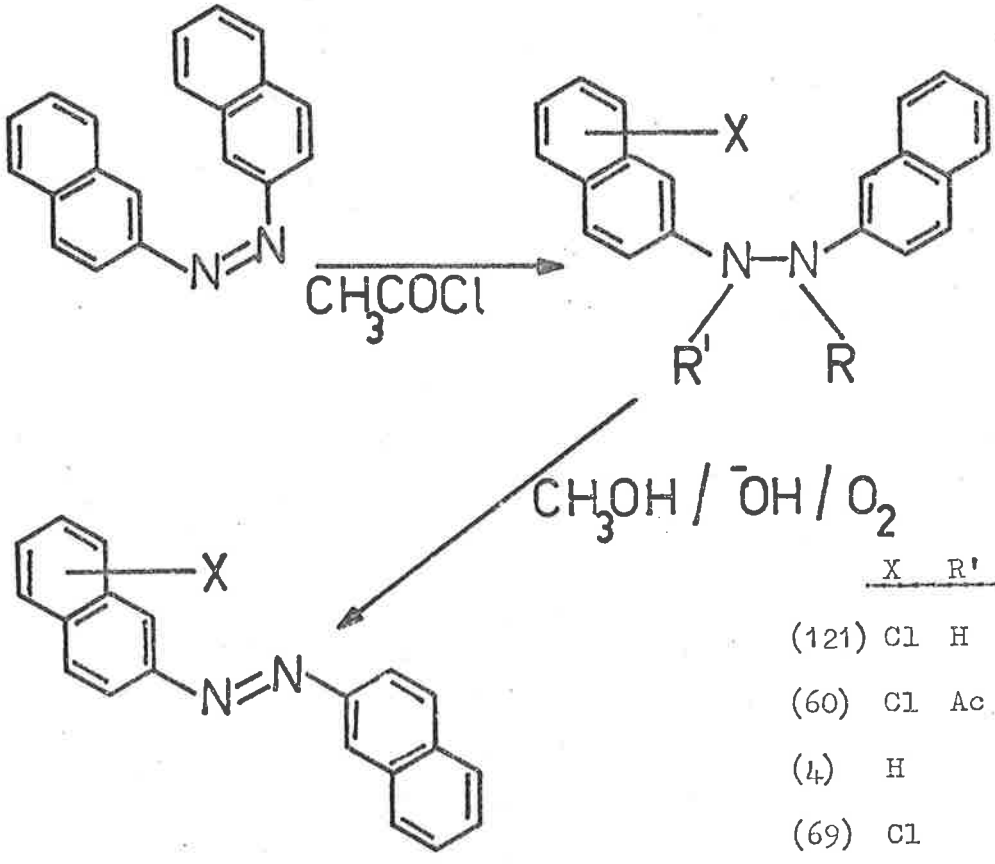
and characterized. For reasons similar to those outlined in Part II.1 it is thought that these products were formed by rearrangement of the mono-acetylated hydrazonaphthalenes under the acidic conditions of the dark reaction.

3. cis-2,2'-Azonaphthalene.

cis-2,2'-Azonaphthalene (7) and excess acetyl chloride were mixed and well stirred for one minute before water was added to destroy all excess acetyl chloride. The crude material obtained from the dichloromethane extract of the reaction mixture showed strong bands at 3200-3350 cm^{-1} (N-H stretching absorptions) and 1675-1710 cm^{-1} (broad, carbonyl absorptions). This mixture was chromatographed on a preparative plate. The only pure compound which was isolated was 2,2'-azonaphthalene. All of the other bands on the plate were shown by thin-layer chromatography to be mixtures. These were therefore combined and subjected to alkaline hydrolysis, followed by aerial oxidation. The material contained in the dichloromethane extract of the hydrolysis product was partially separated into its components by preparative plate chromatography. Two partly resolved bands were collected and rechromatographed. Complete separation of the two compounds could not be achieved. The recombined mixture was examined by gas chromatography. Two peaks (integrated area c. 1:1) were resolved and were shown to have identical retention times to authentic samples of 2,2'-azonaphthalene (4) and x-chloro-2,2'-azonaphthalene (69). The latter compound (69) had previously been isolated from the mixture obtained by hydrolysis-oxidation of the photoreaction product.

The mixture obtained from the dark reaction probably contained a mixture of the corresponding N-acetyl and/or N,N'-diacetylhydrazo-

naphthalenes. This was assumed on the basis of the infrared spectrum of the crude mixture and by analogy with the corresponding reactions involving cis-1-phenyl- and cis-2-phenylazonaphthalene (see Parts II.1 and II.2). The dark reaction had evidently yielded an N-acetyl and/or N,N'-diacetylhydrazo compound, which underwent dechlorination in the alkaline hydrolysis medium, and an N-acetyl- and/or N,N'-diacetyl-x-chlorohydrazonaphthalene, which did not lose a chloro group under the same conditions.



	X	R'	R
(121)	Cl	H	Ac
(60)	Cl	Ac	Ac
(4)	H		
(69)	Cl		

The results from the dark reaction-hydrolysis sequence suggest that cis-2,2'-azonaphthalene is the active species in the photoreaction of trans-2,2'-azonaphthalene in acetyl chloride.

4. cis-1,2'-Azonaphthalene with Acetyl Chloride.

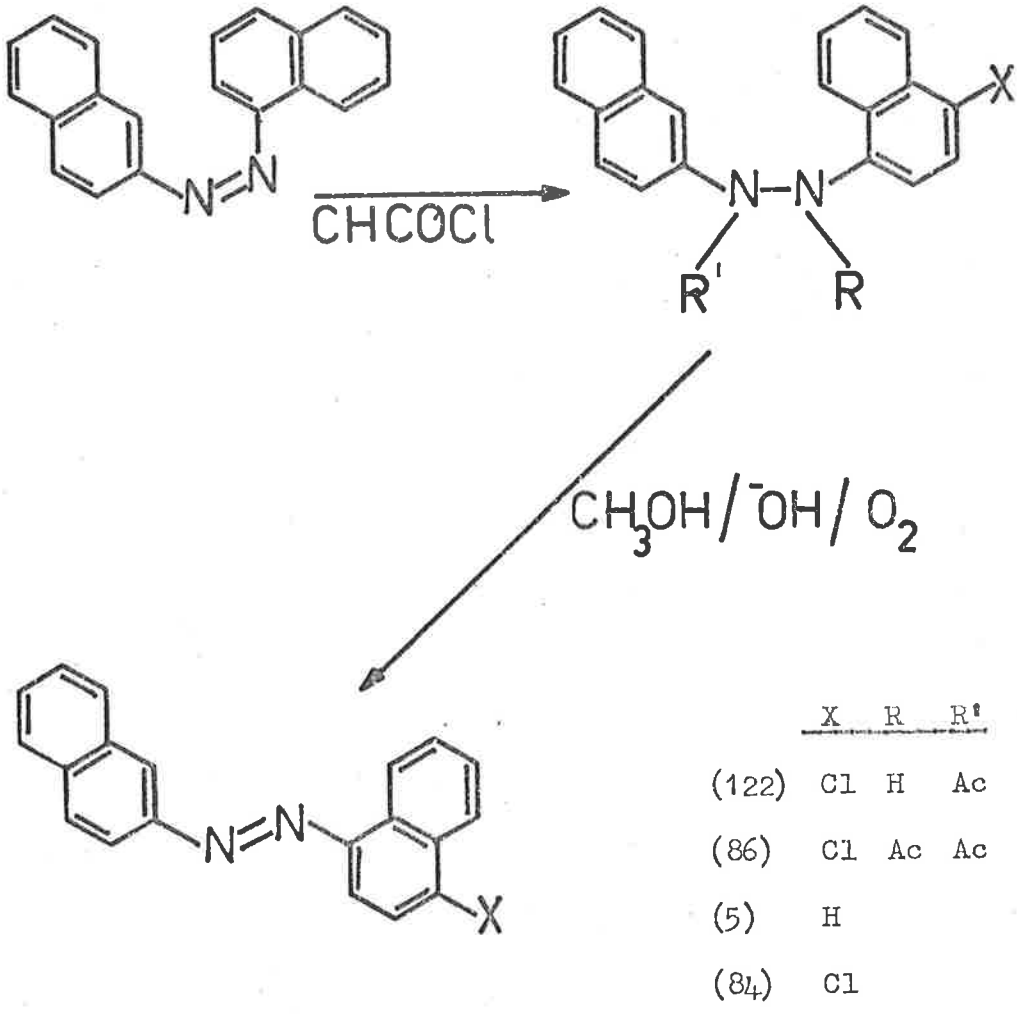
The mixture obtained after treating cis-1,2'-azonaphthalene (8) with acetyl chloride was subjected to preparative plate chromatography. The band of highest R_f afforded trans-1,2'-azonaphthalene (5). Only partial resolution of the material which remained on the plate had been achieved. Accordingly these bands were collected, the silica adsorbent was extracted, and the combined extracts were evaporated to dryness. The infrared spectrum of this mixture showed complex N-H stretching absorptions at 3300-3200 cm^{-1} and broad carbonyl absorptions at 1710-1690 and 1670 cm^{-1}. This mixture was then heated in ethanolic potassium hydroxide solution; and the solution so formed was subjected to aerial oxidation.

The product was chromatographed on a preparative plate and two incompletely resolved orange bands were collected. Thin-layer chromatography indicated that the same two compounds were present in both fractions. The two fractions were therefore recombined and analysed by gas chromatography. The two major components of the mixture were identified as 1,2'-azonaphthalene (5) and 4-chloro-1,2'-azonaph-

thalene (84). Two minor peaks in the chromatogram could not be identified.

The adsorbent contained in the base line of the preparative plate was extracted with chloroform. The oily residue which was formed upon evaporation of the solvent possessed an infrared spectrum which closely resembled that of a fully characterized sample of 4-chloro-N,N'-diacetyl-1,2'-diamino-1',2-binaphthyl (80). Thin-layer chromatography indicated that the material was a mixture of several compounds, but these could not be isolated.

The infrared spectrum of the chromatographed dark-reaction product showed bands which were characteristic of N,N'-diacetylhydrazo (C=O, 1710-1690 cm^{-1}), N-acetylhydrazo (C=O, c. 1695 cm^{-1}; N-H, c. 3250 cm^{-1}), and N,N'-diacetyldiaminobinaphthyl compounds (C=O, 1675 cm^{-1}; N-H, c. 3300 cm^{-1}). This indicated that the mixture contained all three types of compounds. The formation of the azo compounds (5) and (84) in the hydrolysis reaction suggested that equivalent quantities of the chloro N,N'-diacetyl and/or N-acetyl hydrazo compounds were formed in the dark reaction. A proportion of the N-acetyl compounds evidently rearranged to yield the binaphthyl compounds. As was the case for the photoreaction of trans-1,2'-azonaphthalene in acetyl chloride (see Part I.4), the exact position of the chloro group in the acetylated hydrazonaphthalene undergoing dechlorination is unknown.



	X	R	R'
(122)	Cl	H	Ac
(86)	Cl	Ac	Ac
(5)	H		
(84)	Cl		

From the experimental evidence it appears that the dark reaction of cis-1,2'-azonaphthalene with acetyl chloride leads to almost the same mixture of products as that formed in the corresponding photoreaction of the trans-isomer in acetyl chloride. The additional

compounds which were not formed in appreciable quantities in the photoreaction were the N-acetylhydrazonaphthalenes.

5. cis-1,1'-Azonaphthalene.

The product obtained from the reaction of cis-1,1'-azonaphthalene (6) with acetyl chloride (in the absence of light) was a blue-black viscous oil. The infrared spectrum of this material showed strong N-H stretching absorptions at 3290 cm^{-1} and carbonyl absorptions at 1700 and 1680 cm^{-1}.

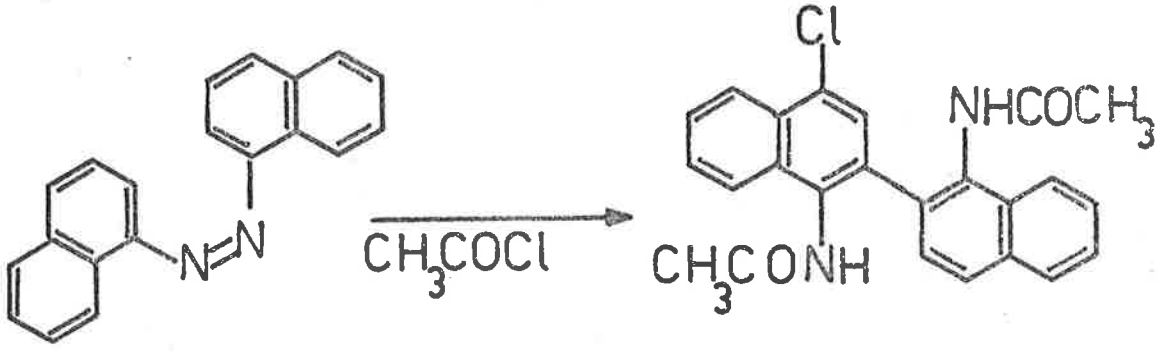
The crude mixture was chromatographed on a column of silica. trans-1,1'-Azonaphthalene (3) was the first compound eluted from the column. It was identified by direct comparison with an authentic sample.

A second fraction afforded a pale purple oil, the infrared of which showed strong carbonyl absorptions at 1715 and 1700 cm^{-1} and no bands in the region 3000-3500 cm^{-1}. On the basis of the spectrum it was concluded that one or more N,N'-diacetylhydrazonaphthalenes had been formed. However, treatment of this mixture with ethanolic potassium hydroxide and chromatography of the product so formed yielded no azonaphthalenes. The infrared spectrum of the material extracted from the adsorbent on the plate was essentially the same as that of the oil before hydrolysis-oxidation. This fraction evidently did not

contain acetylated hydrazonaphthalenes; and the structure of the product, which was apparently unreactive under alkaline conditions, is not known.

A third fraction was collected; and after removal of the solvent followed by recrystallization of the residue 4-chloro-N,N'-diacetyl-1,1'-diamino-2,2'-binaphthyl (94) was obtained. The structure of this compound was confirmed by direct comparison with an authentic sample.

From the results described above it was concluded that cis-1,1'-azonaphthalene yielded mainly binaphthyl compounds when treated with acetyl chloride. None of the N,N'-diacetylhydrazo compounds were formed in the reaction.



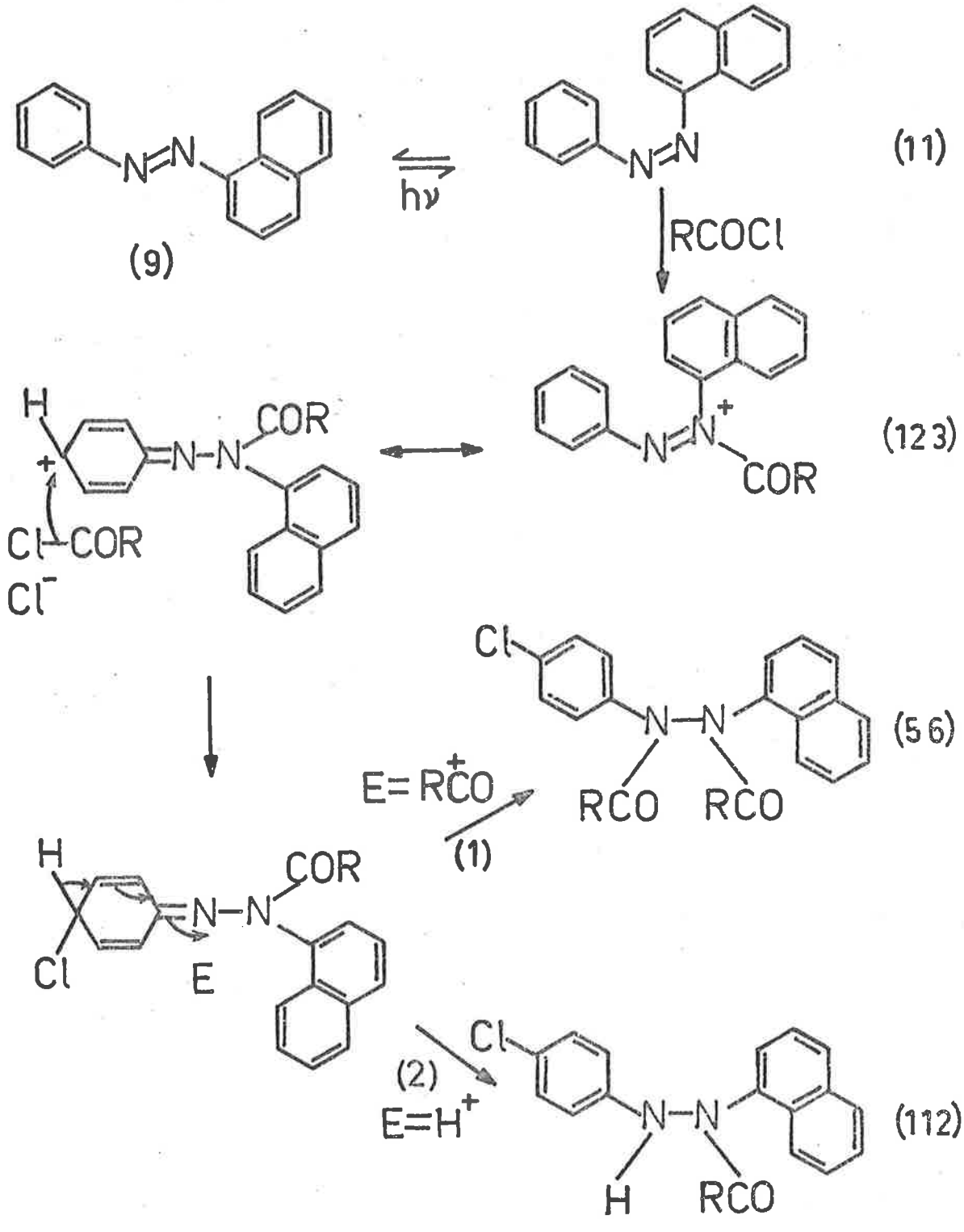
(6) (94)

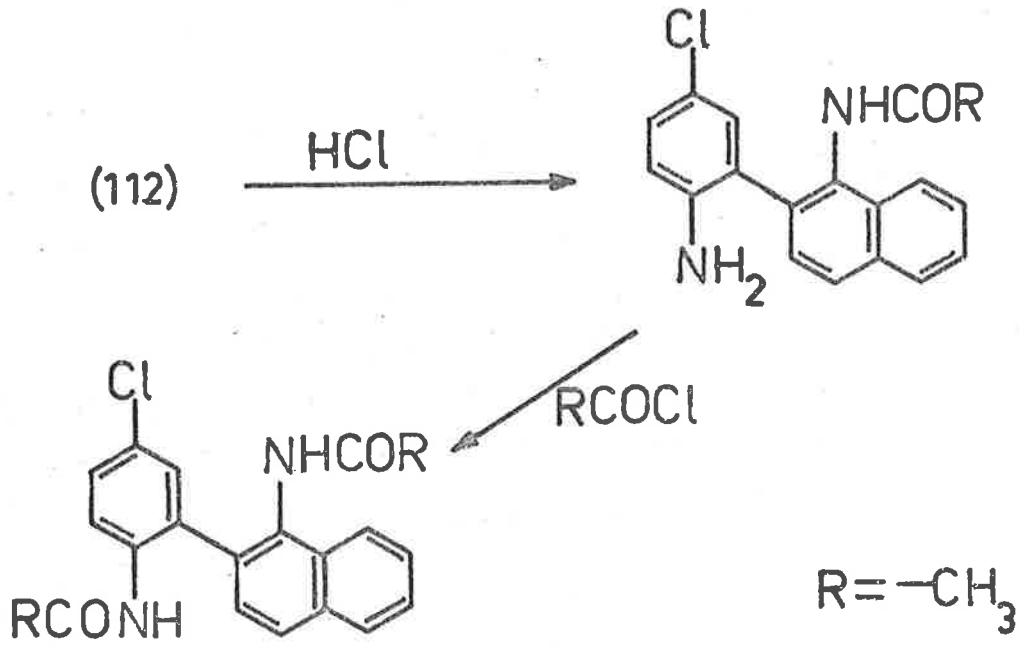
The major product formed in this dark reaction was the same as that isolated from the photoreaction involving the trans-isomer. Hence the participation of the cis-isomer in the photoinduced reaction was established.

6. Mechanisms of the Photochemical Reactions.

The reactions of cis-1-phenylazonaphthalene (11), cis-2-phenylazonaphthalene (12), and cis-2,2'-azonaphthalene (7) with acetyl chloride in the absence of light yielded N,N'-diacetylchlorohydrazonaphthalenes, N-acetylchlorohydrazonaphthalenes, and products arising from rearrangement. Alkaline hydrolysis of the mono- and diacetylated hydrazo compounds yielded azonaphthalenes which were identical to those isolated from the corresponding photochemical reactions of the trans-isomers with acetylchloride. These results indicated that the photo-induced reactions involved initial trans $\rightleftharpoons$ cis isomerization followed by a non-photochemical reaction of the cis-isomer with acetyl chloride. A mechanistic pathway has been proposed by Lewis and Mayfield[103,104] (Scheme III,Introduction) for the photochemical reaction involving trans-azobenzene. This may be reasonably extended to the azonaphthalenes; and a typical mechanistic sequence involving trans-1-phenylazonaphthalene is shown in Scheme X. It was suggested[103,104] on the basis of preferential para-substitution by chlorine that the process was ionic and involved acetylium ions.[101,102] Further work[104] with acid chlorides of widely differing ionizabilities established that the extent of ionization of the acid chloride effected the position of chlorine substitution.

Delocalization of the positive charge in the species (123) can occur to the ortho or para positions of the phenyl ring. This makes it


(9)
hν
(11)
RCOCl
(123)
COR
Cl
COR
Cl⁻
(56)
E= RCO
(1)
RCO
RCO
COR
Cl
E
(2)
E=H⁺
(112)
H
RCO

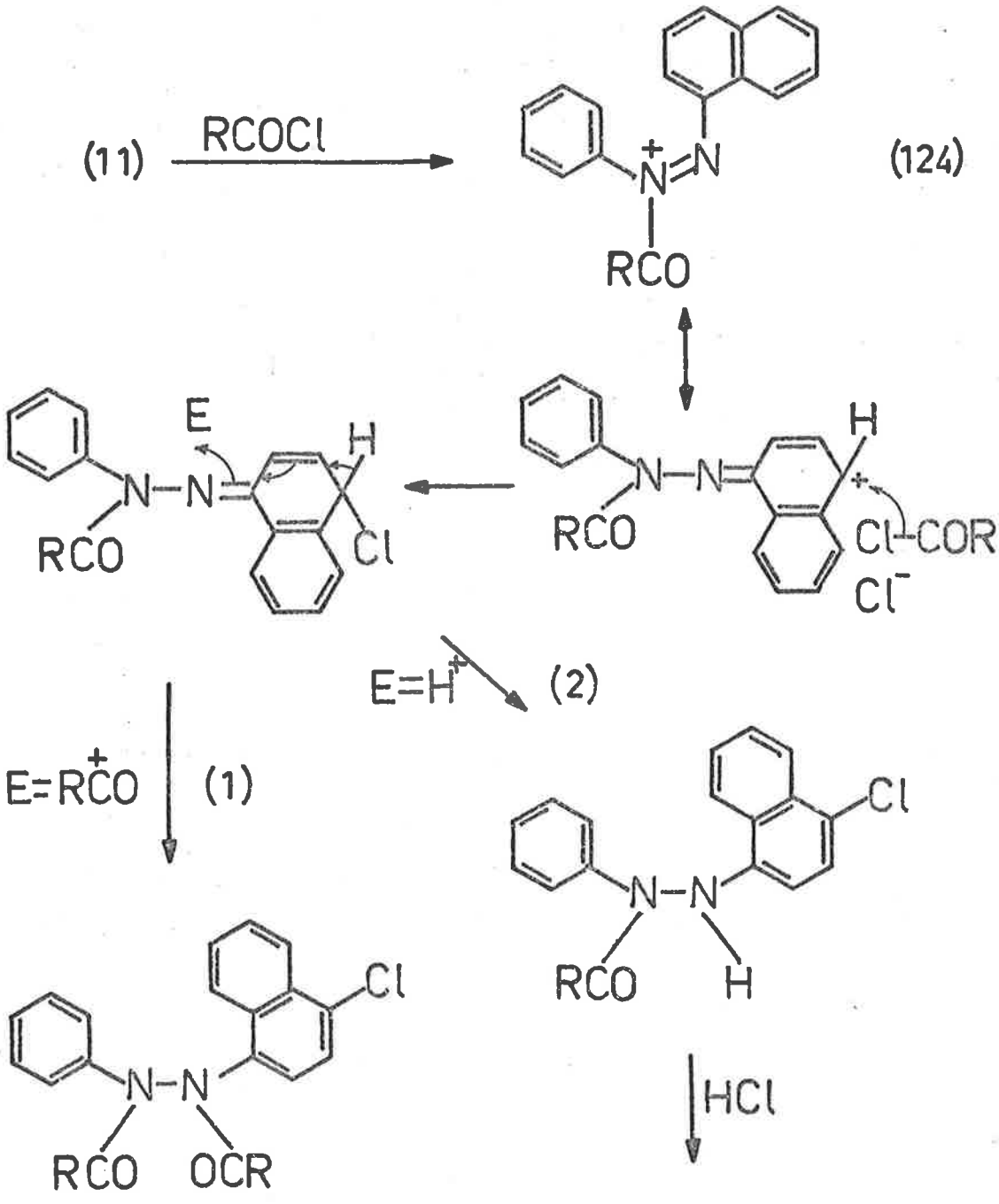


Scheme X.

possible for a mixture of the ortho and para chlorinated N,N'-diacetyl-hydrazonaphthalenes to be formed.

An alternative pathway is shown in Scheme XI where an acetylium ion is first attached to the nitrogen atom adjacent to the benzene ring to form (124).

In both Schemes two reactions (1) and (2) are indicated which lead to the diacetyl and monoacetyl hydrazo compound respectively. Pathway (2) evidently only operates to an appreciable extent when a large concentration of hydrogen chloride is present (viz., in the dark reactions). The alternative pathway (1) leads to the products which are formed in the photoreactions.



Rearrangement Products

Scheme XI.

Similar schemes can be presented to account for the products formed in the photoinduced reactions of the other azonaphthalenes with acetyl chloride.

The products formed in the photochemical reactions of 1-phenylazonaphthalene, of 2-phenylazonaphthalene, and of 2,2'-azonaphthalene with acetyl chloride have been shown to be mixtures of N,N'-diacetylchlorohydrazonaphthalenes. The nature of these products was consistent with the structures predicted on the basis of the results obtained by other workers[101-105] for the photoinduced reaction of azobenzene with acetyl chloride. However, when the photoreactions involving 1,2'-azonaphthalene and 1,1'-azonaphthalene were investigated it was found that markedly different types of compounds had been formed. In addition to the expected N,N'-diacetylhydrazo compound, 4-chloro-N,N'-diacetyl-1,2'-diamino-1',2-binaphthyl (80) was also formed in good yield when 1,2'-azonaphthalene was irradiated in acetyl chloride. Under similar reaction conditions, 1,1'-azonaphthalene yielded 4-chloro-N,N'-diacetyl-1,1'-diamino-2,2'-binaphthyl (94); and none of the diacetylated hydrazo compound was formed. A possible mode of formation of these binaphthyls involves a naphthidine-type rearrangement.

Hofmann[138] in 1863 provided the first report of hydrazobenzene undergoing a benzidine-rearrangement in acidic solution. Since that time much work has been done in an attempt to gain a greater understanding of the mechanism of the reaction. The rearrangement is known to be intramolecular and acid-catalysed but the mechanism is not completely

understood. In addition to the ring-substituted hydrazobenzenes, some N-substituted hydrazo compounds have been shown to rearrange in acidic media. N-Methyl-,[139] N-acetyl-,[140,174,185] and N-phenylhydrazobenzene[141] all rearrange to give typical benzidine-type products. It has also been shown[136,142,143] that N,N'-dimethylhydrazobenzene forms N,N'-dimethylbenzidine when treated with acid. In contrast to this, N,N'-diacetylhydrazobenzene is known[185] not to rearrange at room temperature in strong hydrochloric acid. Heating of the mixture caused partial hydrolysis to the mono-acetyl compound which then underwent rearrangement. From this it was concluded that for rearrangement of an N-acetylated hydrazobenzene to take place, at least one of the -NH- groups in the hydrazo linkage must be unsubstituted.

The naphthidine-rearrangements of the hydrazonaphthalenes have also been examined in detail. Comparative studies[186] have shown that the rates of rearrangement lie in the order:

hydrazonaphthalenes > phenylhydrazonaphthalenes > hydrazobenzenes

As is the case with the hydrazobenzenes, the rearrangements are intramolecular and dependent on acid concentration. The rearrangements of hydrazobenzene[174] and phenylhydrazonaphthalene[186] are second order with respect to the acid concentration, whereas the rearrangements of hydrazonaphthalenes are first order in acid. This dependence on concentration indicates that the rearrangement of the hydrazonaphthalenes

proceeds via a monoprotonated hydrazonaphthalene (Scheme XII). The hydrazonaphthalenes are known to preferentially form "ortho" rearrangement products, e.g. 1,1'-hydrazonaphthalene rearranges to give 1,1'-diamino-2,2'-binaphthyl;[191] and 1,2'-hydrazonaphthalene forms 1,2'-diamino-1',2-binaphthyl.[82,149]

The hydrazonaphthalenes have been shown to undergo "thermal" benzidine-type rearrangements in hydrocarbon solvents[67,134,135,149,187-190] and in the solid state.[149] This indicated that the presence of acid was not an essential factor for rearrangement of these compounds to occur. Sufficient dissolved HCl would probably be present in the photoreaction mixtures to catalyse the rearrangement process.

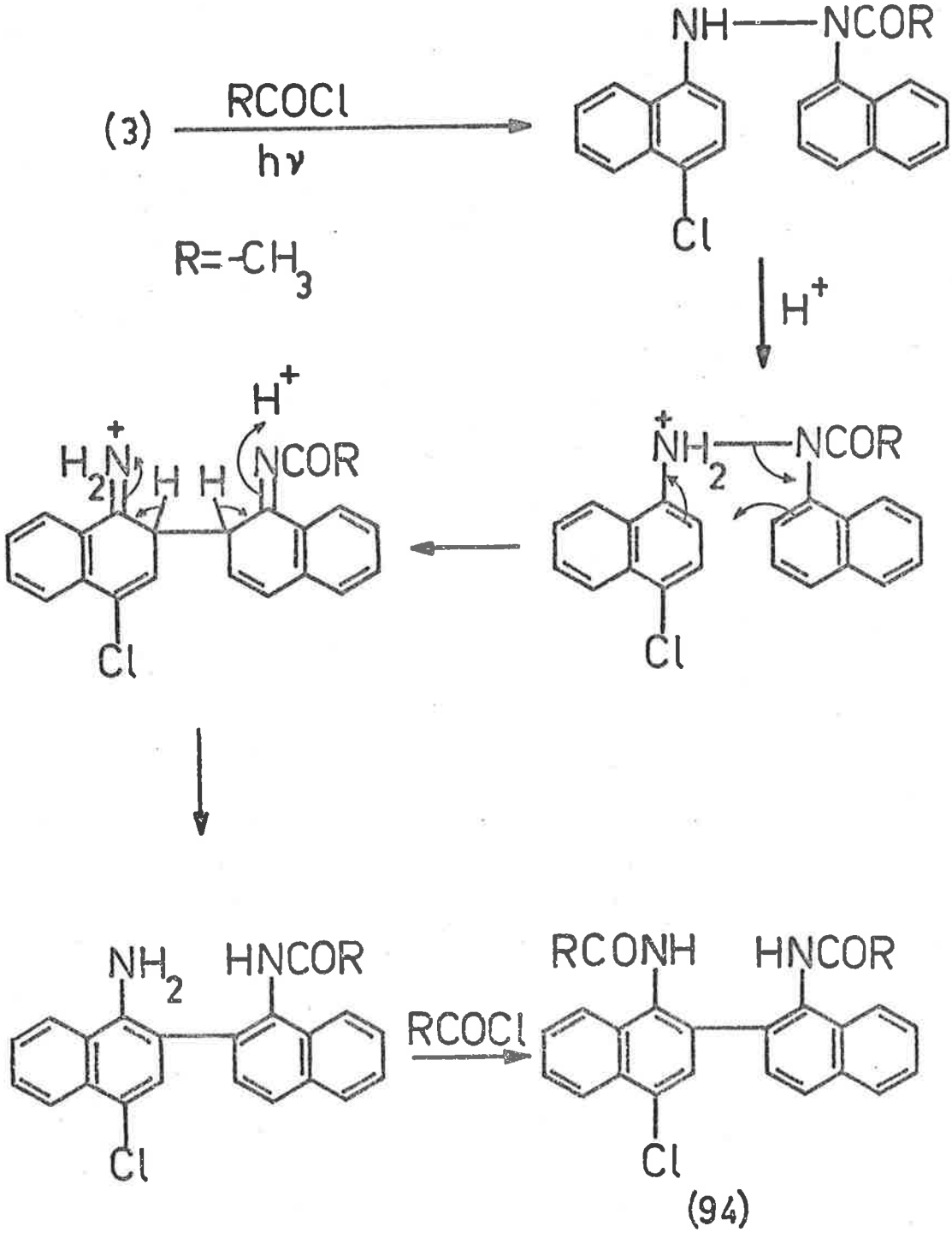
The formation of the binaphthyls in the photoreactions was therefore thought to proceed via the rearrangement of an intermediate chlorohydrazonaphthalene, chloro-N-acetylhydrazonaphthalene, or chloro-N,N'-diacetylhydrazonaphthalene. In an effort to determine which of these compounds was involved, several N,N'-diacetyl and N-acetyl compounds were heated individually under reflux with acetyl chloride. The N,N'-diacetylhydrazo compounds were recovered unchanged thereby eliminating them as possible precursors of the binaphthyls. The N-acetyl compounds, however, readily formed rearrangement products. Rearrangement of the simple hydrazonaphthalenes also occurred under these conditions, but from mechanistic considerations the N-acetyl compounds were concluded to be the photoproducts which underwent

rearrangement to form the chloro-binaphthyls. Such a reaction is illustrated by Scheme XII.

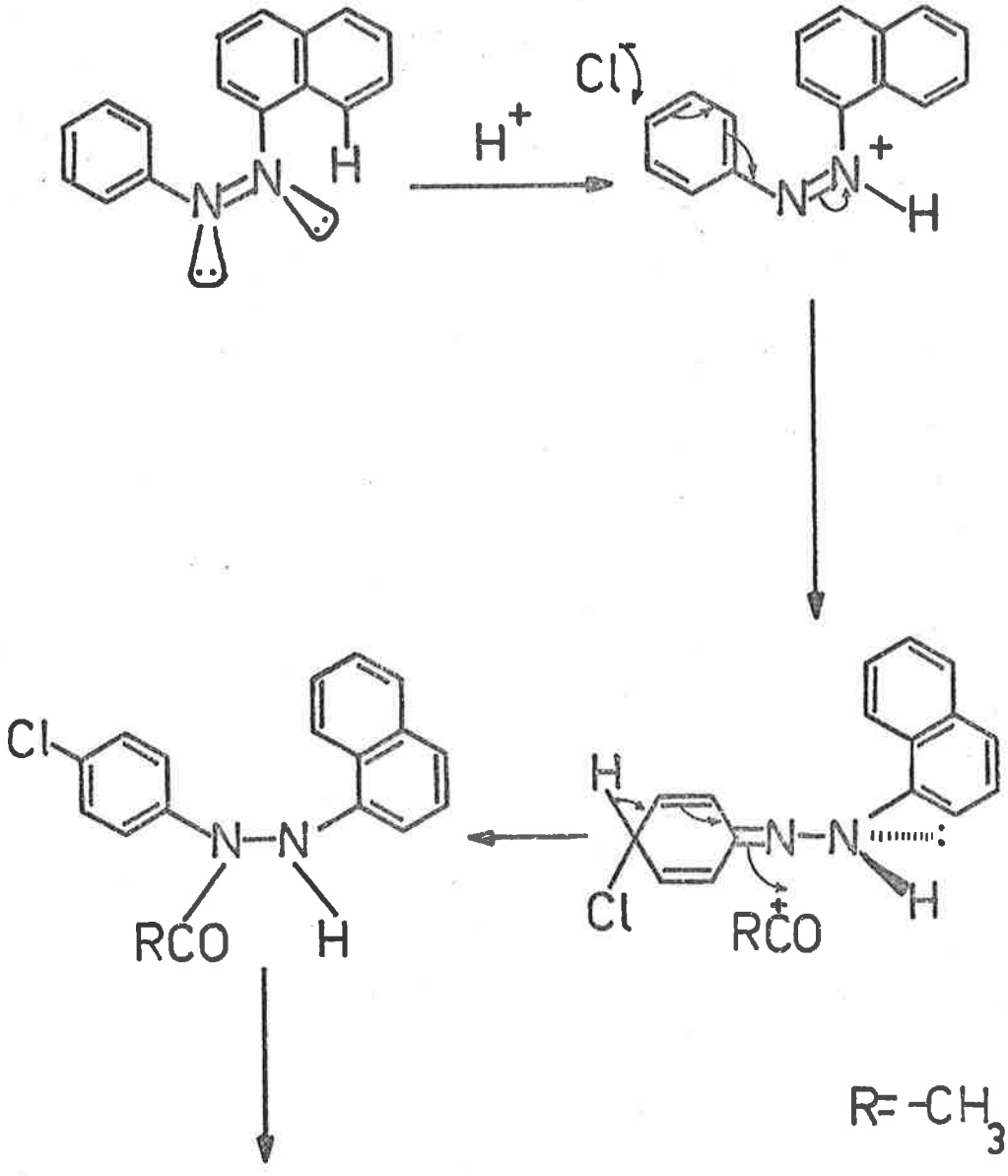
A similar mechanistic pathway can be formulated to account for the formation of 4-chloro-N,N'-diacetyl-1,2'-diamino-1',2-binaphthyl (80) in the photoinduced reaction of trans-1,2'-azonaphthalene with acetyl chloride.

The reasons for the formation of rearrangement products in the photoreactions of 1,2'- and 1,1'-azonaphthalene are not fully understood. It appears that an α-naphthyl ring is essential for the rearrangement to occur and that the other ring must also be a naphthyl ring. If there are two α-naphthyl rings present (viz. 1,1'-azonaphthalene) then rearrangement occurs exclusively. If α- and β-naphthyl rings are in the molecule (viz. 1,2'-azonaphthalene) then a mixture of rearrangement products and "normal" N,N'-diacetylhydrazonaphthalenes are formed. Two postulated mechanisms will now be presented. One of these only partially explains the formation of the products, but the other mechanism gives a plausible explanation of the reaction pathways involved.

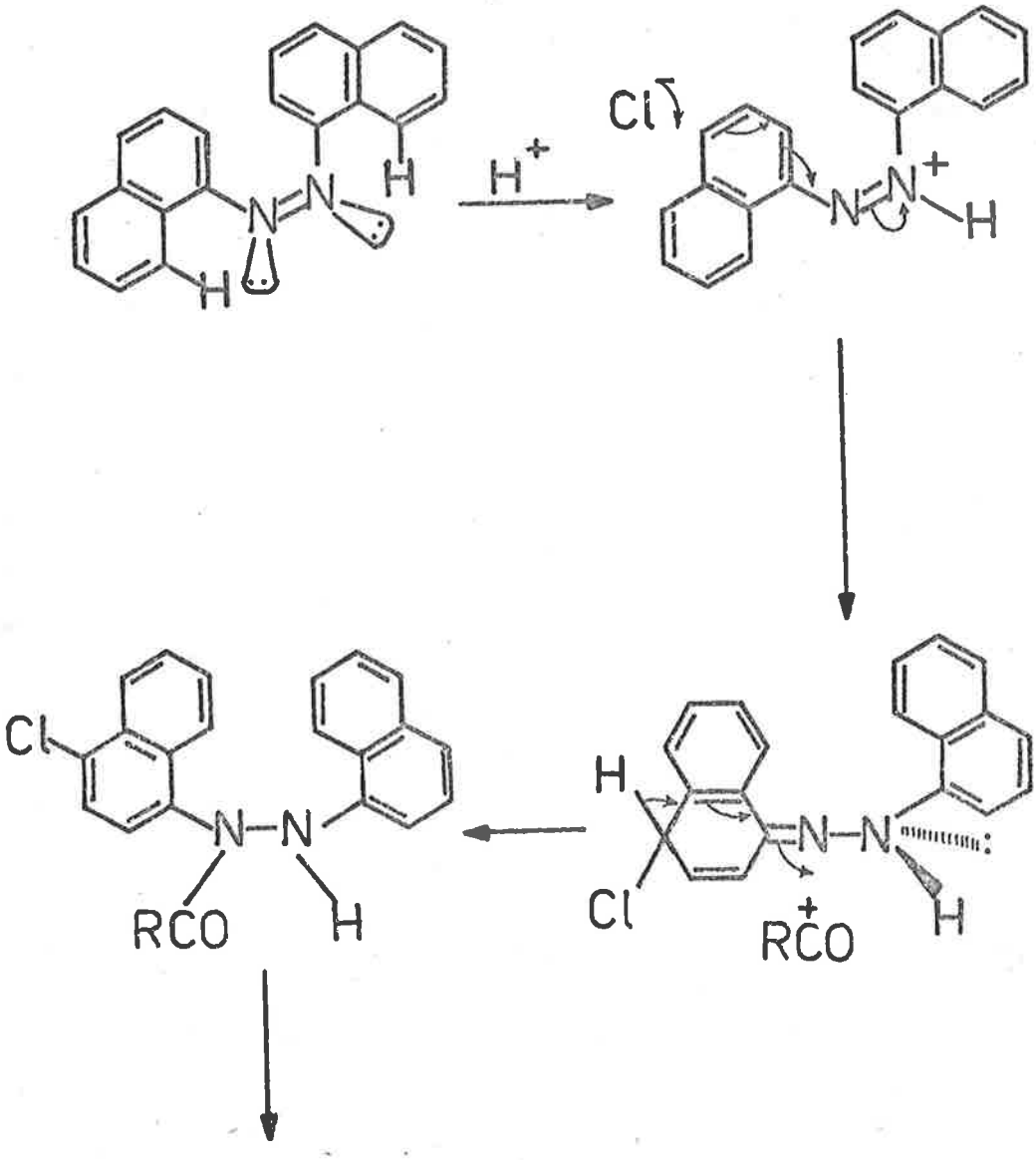
The first mechanism requires that initial acylation at the nitrogen atom adjacent to the α-naphthyl ring is sterically hindered by the peri-hydrogen atom. Protonation would therefore occur at this atom in preference to acetylation (see Schemes XIII, XIV). The monoacetylated compounds so formed could then undergo a benzidine-type rearrangement. This would explain the formation of 4-chloro-N,N'-


(3)
RCOCl
hν
R=-CH3
NH—NCOR
Cl
H+
NH2
NCOR
Cl
H+
H2N
H
H
NCOR
Cl
NH2
HNCOR
Cl
RCOCl
RCONH
HNCOR
Cl
(94)

Scheme XII.

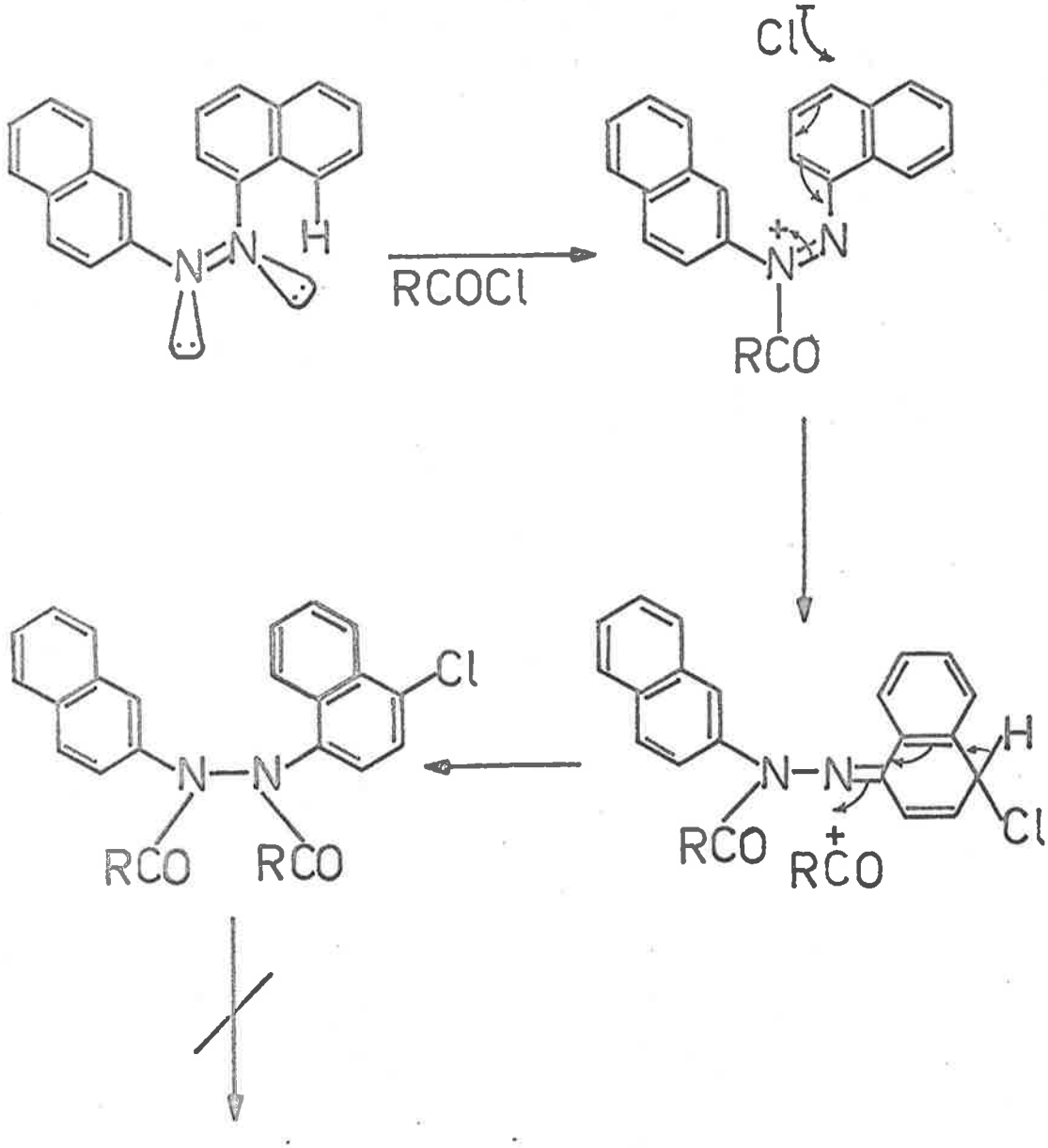


Scheme XIII.



Rearrangement Products

Scheme XIV.

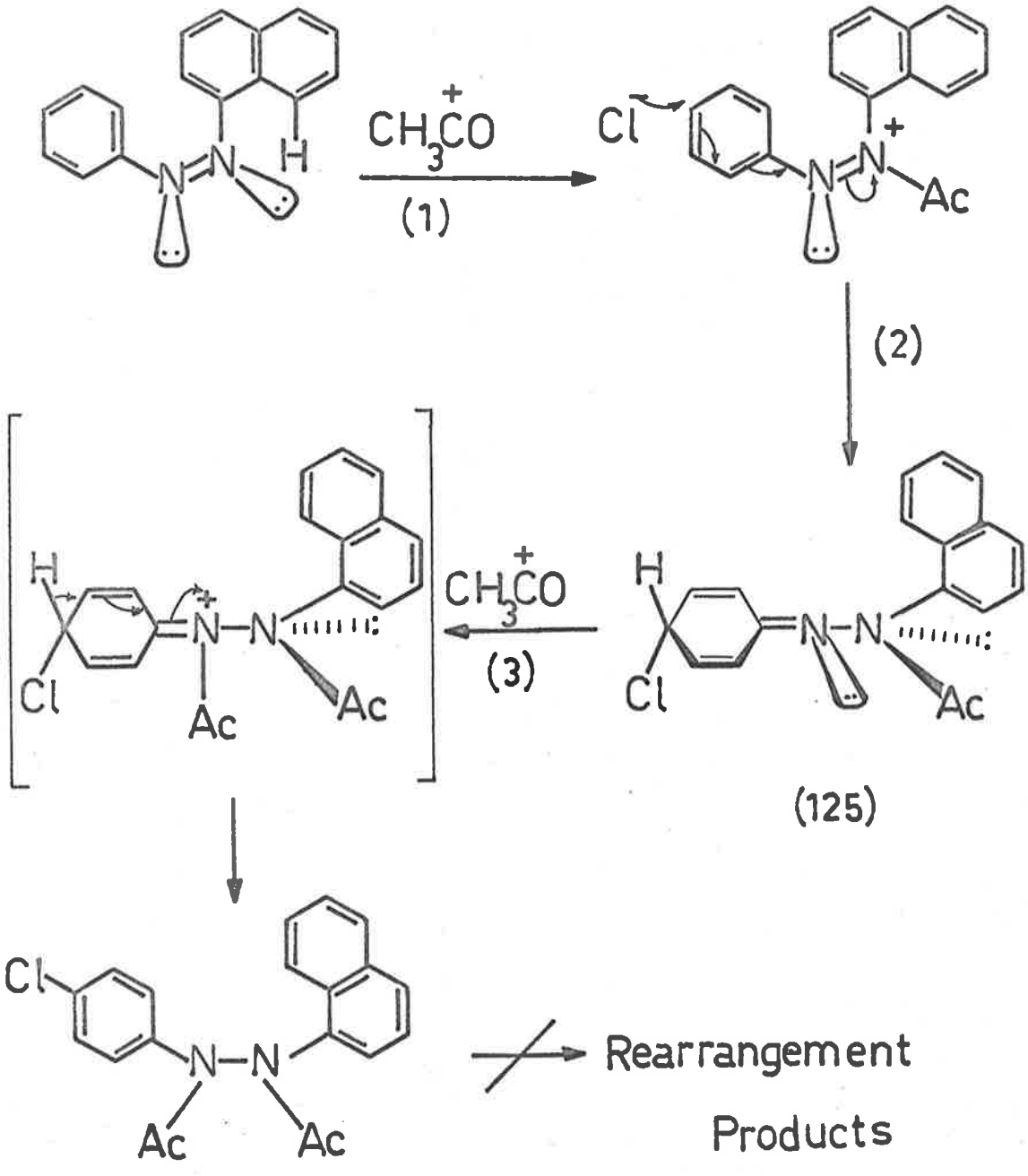


Scheme XV.

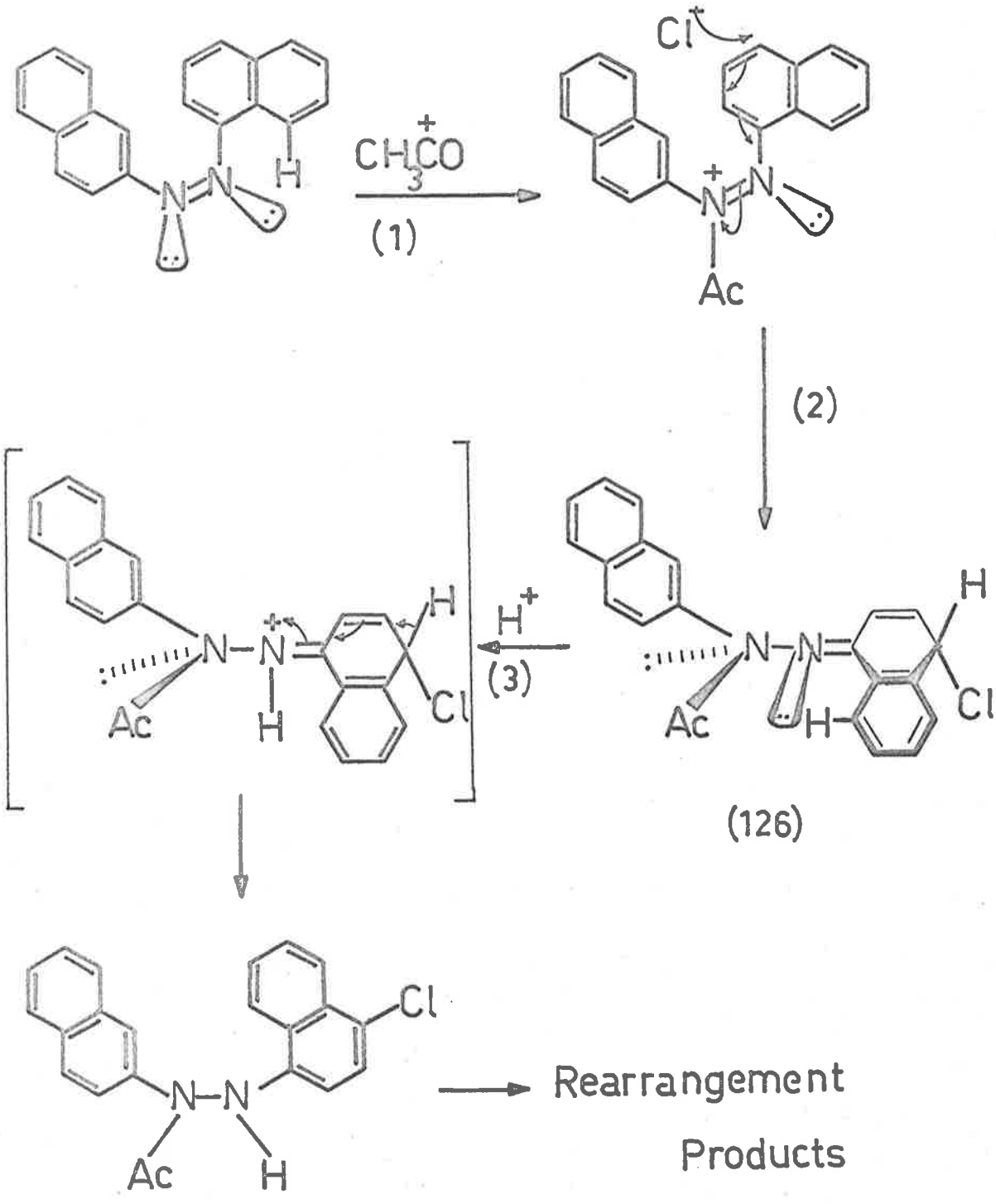
diacetyl-1,1'-diamino-2,2'-binaphthyl (94) from the photoreaction of 1,1'-azonaphthalene with acetyl chloride. However such a mechanism is not in agreement with the results obtained from the photoinduced reactions of 1-phenylazonaphthalene and 1,2'-azonaphthalene with acetyl chloride. The naphthidine-rearrangement product (80) formed in the 1,2'-azonaphthalene reaction has a chloro group in the 4-position of the α-naphthyl ring. The ionic mechanism proposed by Lewis and Mayfield[103,104] to account for the photoreaction of azobenzene with acetyl chloride requires the initial addition of an acetylium ion to one of the nitrogen atoms, followed by halogen substitution in the aromatic ring furthest from that atom. The formation of compound (80) according to such a mechanism would require acetylation at the nitrogen atom adjacent to the β-naphthyl ring. This is contrary to the requirements of the proposed mechanism (Scheme XIII) which requires acetylation at the other nitrogen atom if rearrangement is to occur. The N,N'-diacetyl-x-chloro-1,2'-hydrazonaphthalene (86), which was formed in the same reaction, probably contained some compound which was halogenated in the β-naphthyl ring. If the mechanism of Lewis and Mayfield[103,104] is again applied (Scheme XV), then for halogenation to take place in the β-naphthyl ring acetylation should first occur at the nitrogen atom adjacent to the α-naphthyl ring. From Scheme XIV this would be expected to lead to a rearranged product and not an N,N'-diacetylhydrazo compound. A similar argument can be used to show why such a mechanism cannot apply to the 1-phenylazonaphthalene reaction. If the above

described argument is correct then steric hindrance in the initial acetylation step does not appear to be a factor responsible for the formation of the observed naphthidine-rearrangement products.

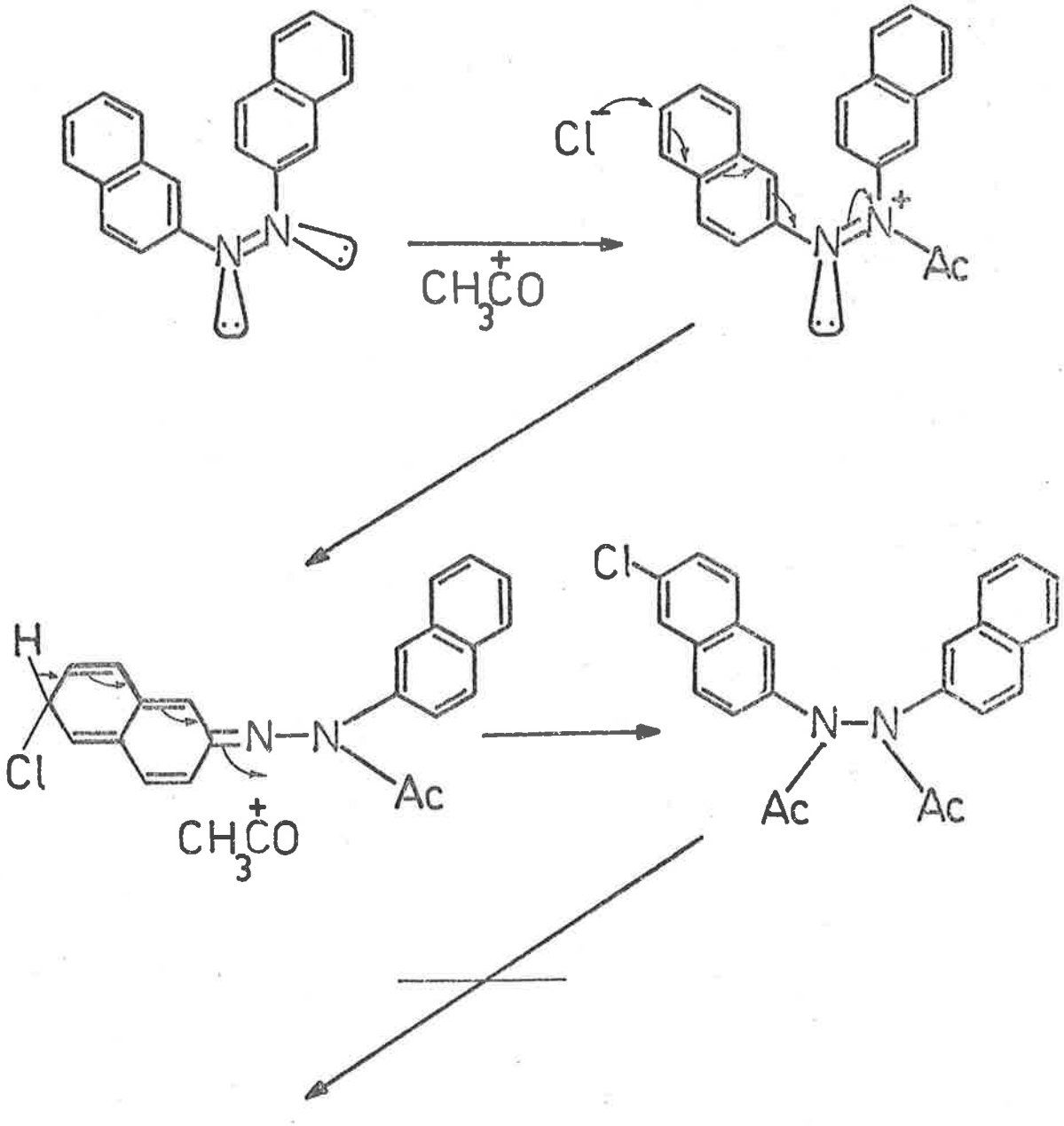
The second proposed mechanism gives a reasonable explanation for the observed photoproducts. Steric hindrance to the addition of the second acetyl group leads to mono-acetylation and subsequent rearrangement. The orbital lobe containing the lone-pair electrons on the nitrogen atom adjacent to the α-naphthyl ring would be in the same plane as the ring. In the preferred configuration shown in (126), Scheme XVII, considerable hindrance to the approach of a large group (viz., $CH_3{}^+CO$) to these electrons would be offered by the peri hydrogen atom. Such an effect would not exist where a phenyl or β-naphthyl ring was adjacent to the second nitrogen atom to be acetylated (Schemes XVI, XVIII). Hence no mono-acetylhydrazo compound would be formed in these reactions which could yield rearrangement products.


CH3CO+
(1)
Cl
Ac
(2)
H
Cl
N–N
Ac
CH3CO+
(3)
(125)
Cl
Ac
Ac
Rearrangement
Products

Scheme XVI.



Scheme XVII.

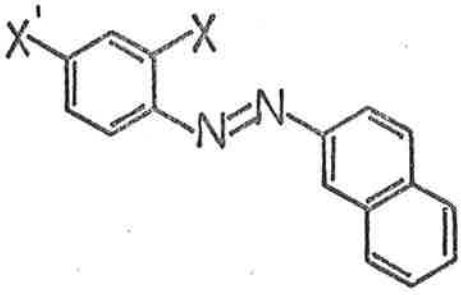


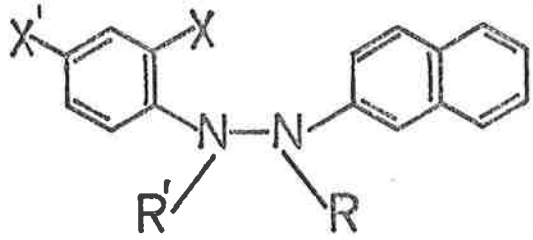
Rearrangement Products

Scheme XVIII.

III PHOTOCHEMICAL REACTIONS IN OXALYL CHLORIDE AND MALONYL DICHLORIDE.

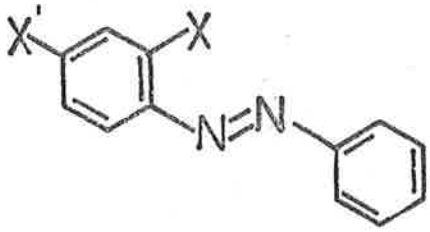
2-Phenylazonaphthalenes (10) and azobenzene (1)[101,102] have been shown to undergo a photoinduced reaction with acetyl chloride to give 2-(N,N'-diacetyl-4'-chlorophenylhydrazo)naphthalene (37) and 4-chloro-N,N'-diacetyl-hydrazobenzene (29) respectively. The proposed ionic mechanisms for these reactions have already been described (Scheme VIII and Scheme III).

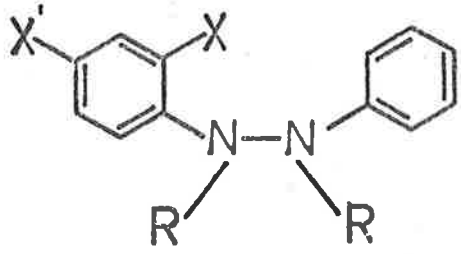




	X	X'
(10)	H	H
(33)	H	Cl
(34)	Cl	H

	R'	R	X	X'
(37)	Ac	Ac	H	Cl
(38)	Ac	Ac	Cl	H
(117)	H	Ac	H	Cl
(118)	H	Ac	Cl	H

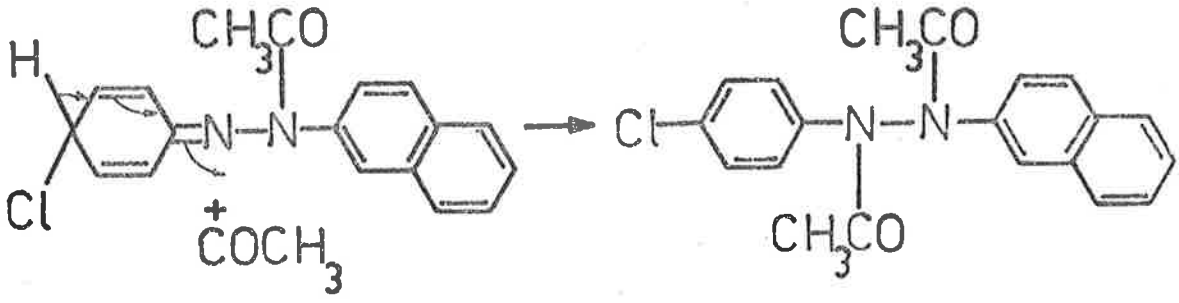




	X	X'
(1)	H	H
(30)	H	Cl
(127)	Cl	H

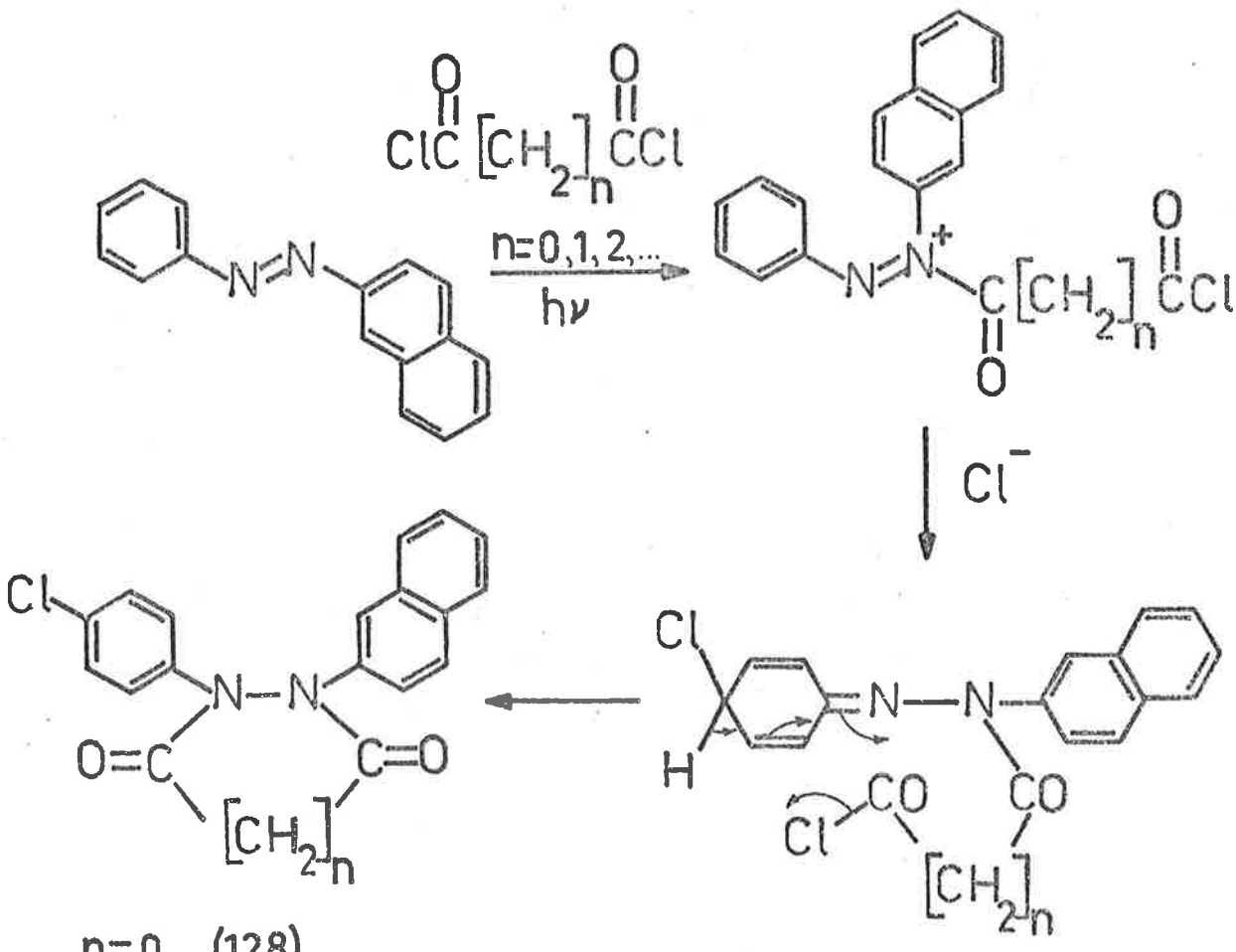
	R	X	X'
(29)	Ac	H	Cl
(31)	Ac	Cl	H

The proposed mechanism in each case involves the addition of a second acetylium ion to a postulated mono-acetylated intermediate (e.g. 190) to give the final diacetylated hydrazo compound (e.g. 37).



(190) (37)

It was thought possible that if the acid chloride contained two active centres (e.g. oxalyl, malonyl, or succinyl chloride) then this step could be achieved by an intramolecular reaction leading to the formation of heterocyclic compounds containing two nitrogen atoms (e.g. Scheme XIX). The photoreactions of 2-phenylazonaphthalene and azobenzene with oxalyl chloride and malonyl dichloride were investigated to determine whether such products could be formed.



Scheme XIX.

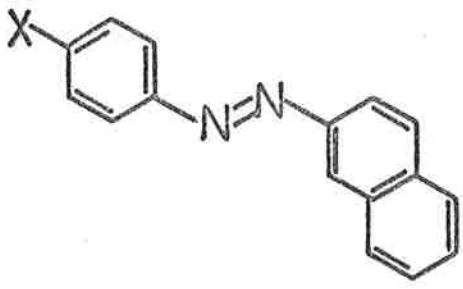
PHOTOCHEMICAL REACTIONS IN OXALYL CHLORIDE.

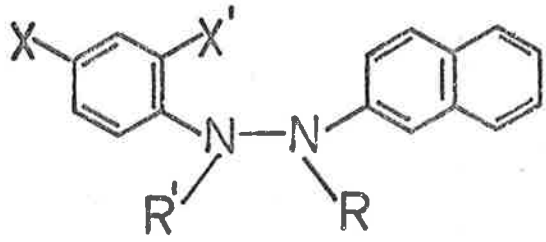
1. trans-2-Phenylazonaphthalene.

2-Phenylazonaphthalene was irradiated in oxalyl chloride until the reaction was complete, as shown by ultraviolet-visible absorption spectroscopy.

A crystalline photo-product precipitated directly from the reaction mixture; and this was collected by filtration. Attempts to purify this material by recrystallization from various solvents were not successful. The crystalline solid was found to react rapidly with moist air to form a red-brown gum with liberation of hydrogen chloride gas. An infrared spectrum of the crude photo-product indicated the presence of a secondary amino group and two carbonyl groups in the compound. When a sample of this material was subjected to alkaline hydrolysis and aerial oxidation in ethanolic potassium hydroxide a mixture of azo compounds was obtained. The final mixture was resolved into 2-(4'-chlorophenylazo)naphthalene (33) (8%) and 2-phenylazonaphthalene (10) (94%) by a combination of column chromatography and recrystallization.

The results described suggested that the photo-product was a mixture of 2-(N-oxalyl-4'-chlorophenylhydrazo)naphthalene (131) and N-oxalyl-2-phenylhydrazonaphthalene (132). The possible presence of the corresponding N,N'-dioxalylated compounds, (133) and (134), could not be completely discounted.





(10) X = H

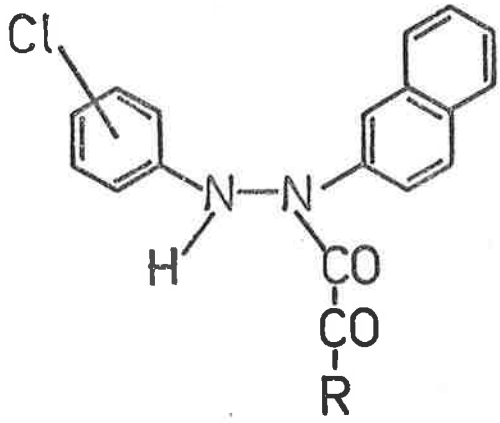
(33) X = Cl

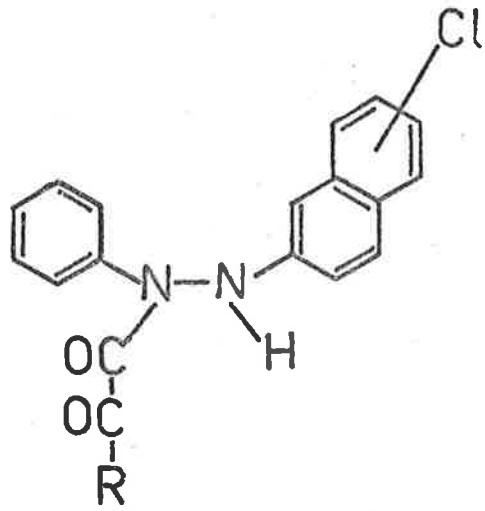
Ox ≡ -COCOCl

	R	R'	X	X'
(131)	Ox	H	Cl	H
(132)	Ox	H	H	H
(133)	Ox	Ox	H	H
(134)	Ox	Ox	Cl	H
(145)	Ox	Ox	H	Cl
(146)	Ox	H	H	Cl

Treatment of the photo-product with hot ethanol yielded a single compound which was subsequently identified as the ethyl ester of x-chloro-N-oxalyl-2-phenylhydrazonaphthalene, (135) or (137). The structure (135) would result from chlorination in the phenyl ring (e.g. Scheme XXII) and structure (137) from substitution in the naphthalene ring (e.g. Scheme XXIII) during the photoreaction.

In view of the elementary analysis and infrared and mass spectra, (135) and (137) are possible structures for the ester . Hydrolysis and oxidation in alkaline media afforded 2-phenylazonaphthalene





(135) R = -OEt

(136) R = -OMe

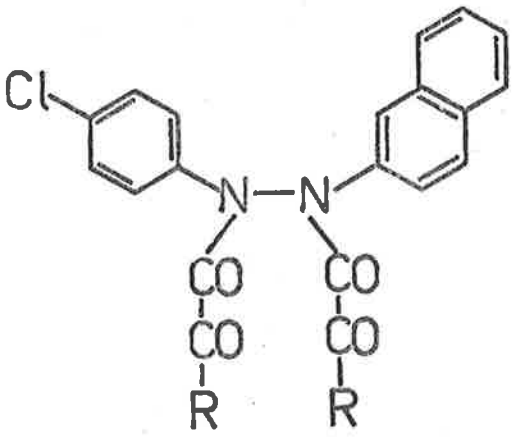
(137) R = -OEt

(138) R = -OMe

(10) (88%) and a trace of 2-(4'-chlorophenylazo)naphthalene (33). The latter compound could be detected by gas chromatography only.

The precursor of (33) is probably the mono-oxalyl compound (131). However, the possibility of the diester of 2-(N,N'-dioxalyl-4'-chlorophenylhydrazo)naphthalene,(139), being present and yielding (33) upon hydrolysis cannot be overlooked.

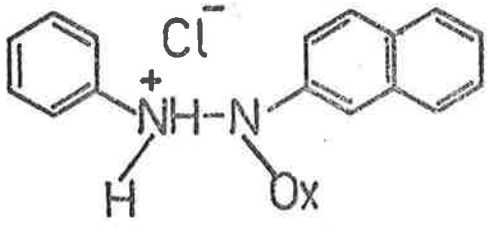
The most likely compound from which 2-phenylazonaphthalene could be obtained is the ester of N-oxalyl-2-phenylhydrazonaphthalene (132). However the analytical data and the mass spectrum indicated the presence of one chloro group in the molecule.



(139) R= $-OC_2H_5$

(140) R= $-OCH_3$

Two alternative explanations can be given to account for these conflicting facts. The first and less likely, is that chlorine is present in ionic form as in (141). The halogen in this compound would be readily removed in the alkaline hydrolysis reaction. Treatment of such a compound with methanolic or aqueous silver nitrate solution would be expected to give a dense white precipitate of silver chloride; such a result was not obtained.



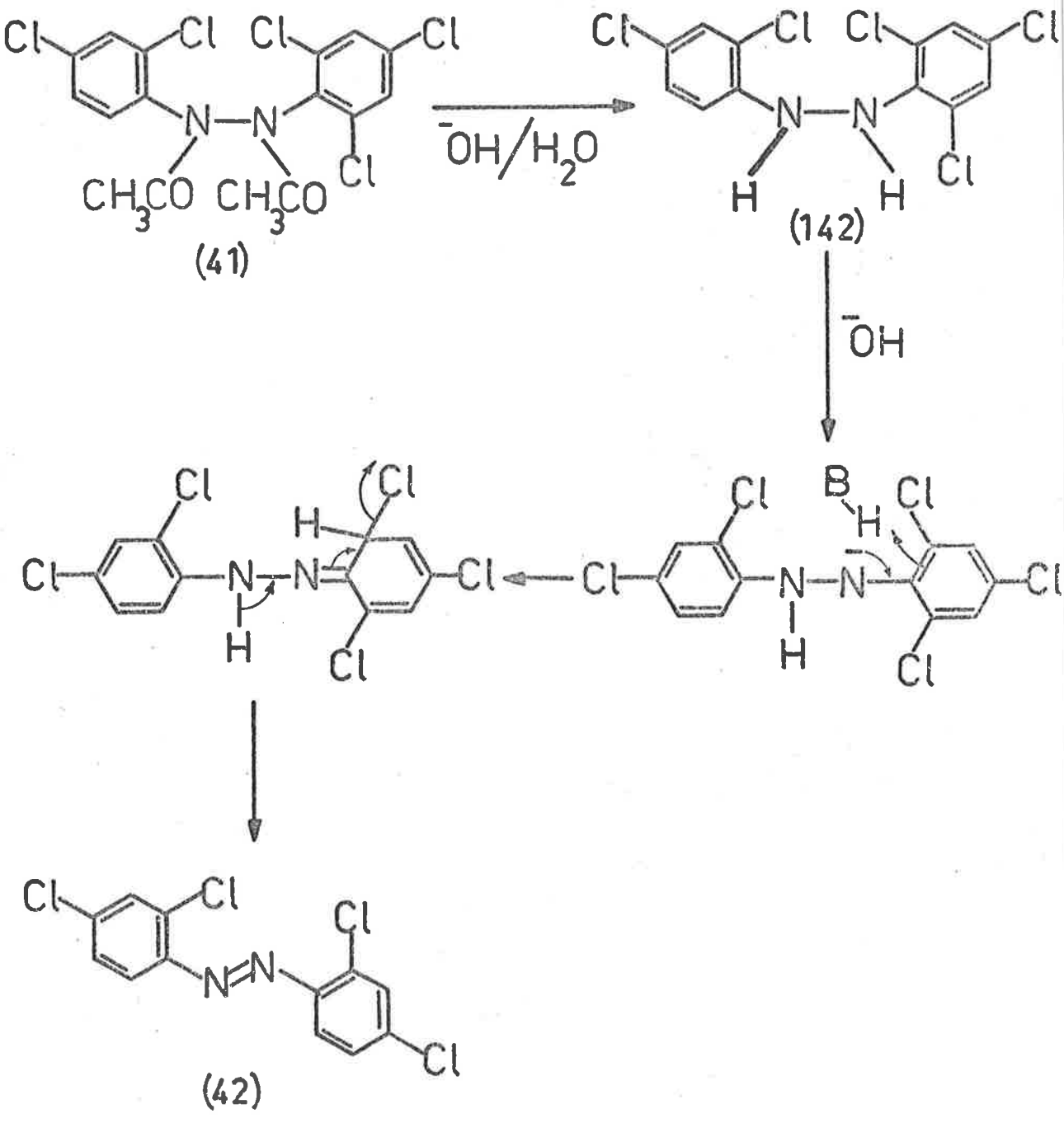
(141)

Radical addition to the azo linkage would be required to form the mono-oxalyl compound, and this would not be a favourable process under the conditions of the irradiation.

The second alternative involves the removal of the chloro group from the phenyl or naphthyl ring in the hydrolysis-oxidation reaction. This type of reaction has been observed by Mayfield[179] who deacetylated N,N'-diacetyl-2,4,6,2',4'-pentachloroazobenzene (41) under alkaline conditions and detected by gas chromatography an appreciable quantity of 2,4,2',4'-tetrachloroazobenzene (42) in the final product. A mechanistic pathway for this reaction was postulated (Scheme XX).

The oxidation of hydrazobenzene in basic media has been shown to proceed via the dianion formed when both hydrazo protons are removed.[178] In the above case removal of the proton from the nitrogen adjacent to the trisubstituted ring was thought to be aided by the three electron-withdrawing chloro groups. A cage effect was suggested to operate leading to a preferential loss of an ortho chloro group. However, the intermediacy of (142) was not proven by separate treatment of this compound under the same conditions.

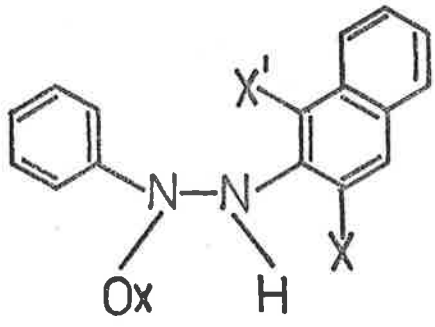
Previous work (see Part I) has shown that this type of dechlorination reaction occurs whenever the N,N'-diacetylated photo-products derived from phenylazonaphthalenes and azonaphthalenes are hydrolysed. Separate examination of the N-acetyl- and N,N'-diacetyl- derivatives of 2-(4'-chlorophenylhydrazo)naphthalene and 2-(2'-chlorophenylhydrazo)-naphthalene under similar conditions (see Part I.7) did not yield



Scheme XX.

dechlorinated products. A similar result was obtained with the parent chloro-2-phenylhydrazonaphthalenes. This suggested that the photoproduct undergoing dechlorination was chlorinated in the naphthyl ring, but this has not been confirmed using authentic samples of such compounds.

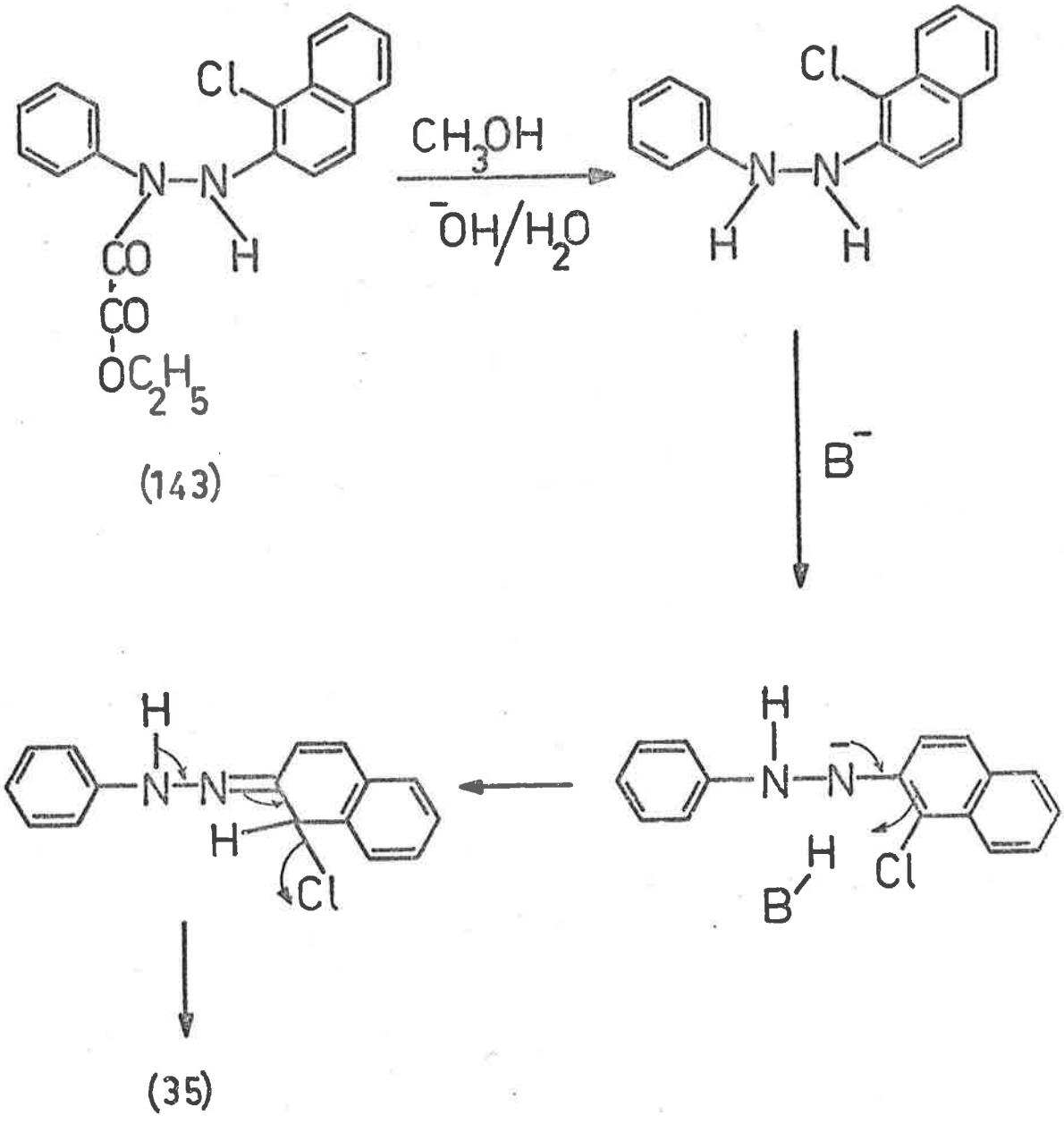
It is tentatively proposed that the major compound formed in the photoreaction of oxalyl chloride with 2-phenylazonaphthalene is substituted in the naphthyl ring. Mechanistically the four possible positions of substitution in that nucleus are the 1-, 3-, 6-, and 8-positions, the 1- and 3-positions being the more likely and leading to compounds (143) and (144).



	X	X'
(143)	H	Cl
(144)	Cl	H

On the assumption that the chloro group is in the 1-position the following mechanism is proposed (Scheme XXI) for the formation of the dechlorinated product.

A cage effect need not be operating and the chloro group could be lost from a position which is not ortho to the nitrogen atom. A related reaction, which indicates the presence of such an effect, is



Scheme XXI.

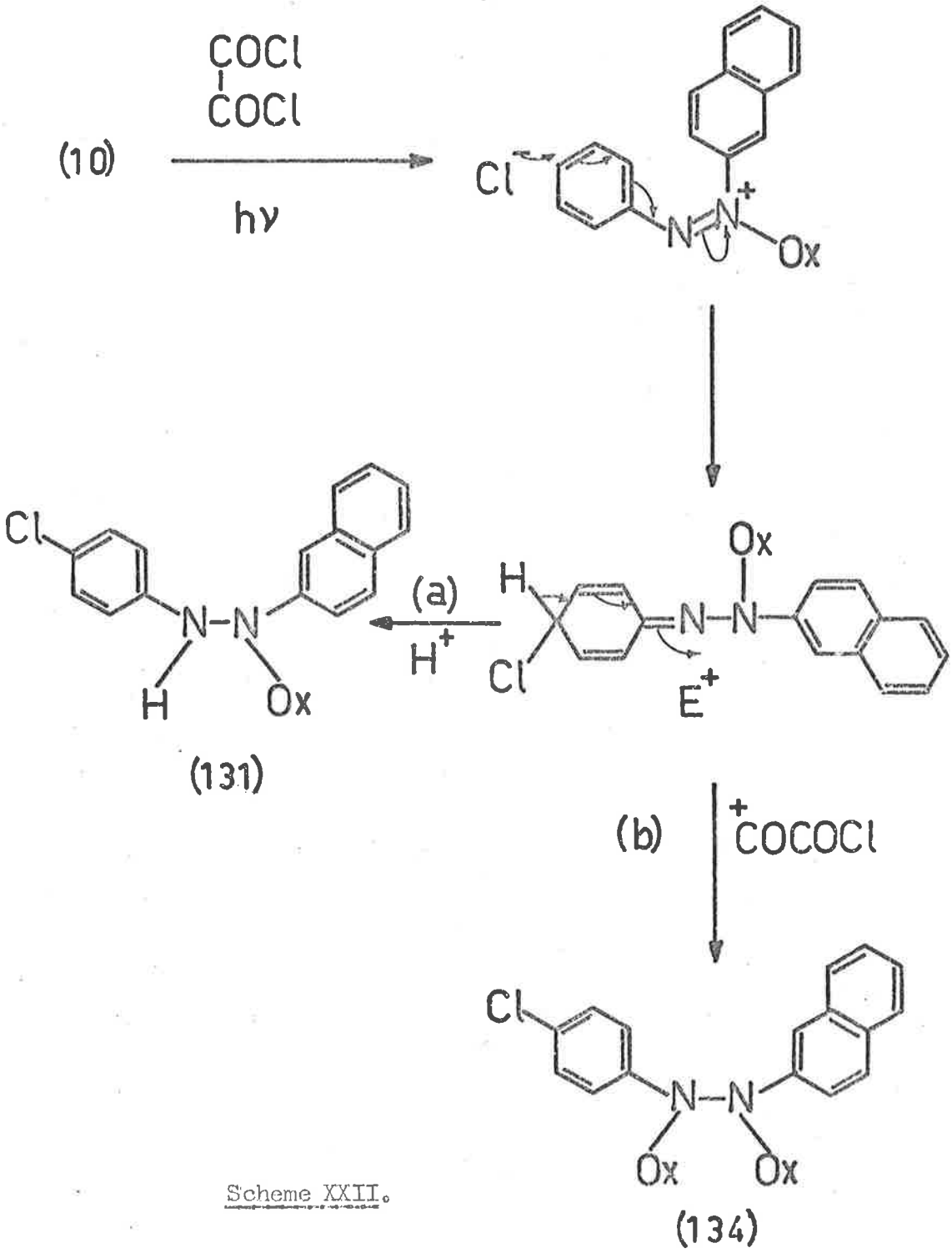
the hydrolysis-oxidation of the photo-product from the reaction of 2,2'-azonaphthalene with acetyl chloride (see Part I.3). Here a similar mixture was obtained comprising 2,2'-azonaphthalene and x-chloro-2,2'-azonaphthalene. The position of the halogeno group in the latter product has not been conclusively proven, but the available evidence indicated that it was in the 6- or 8-position. This suggested that the non-chlorinated product was formed by the dechlorination of a 1- and/or 3-substituted photo-product, and that the 6- or 8-position was not involved. This implies indirectly that a cage effect does operate in these reactions leading to "ortho" dechlorination.

The excess oxalyl chloride was removed from the filtrate obtained from filtration of the original photoreaction mixture. The infrared spectrum was similar to that of the crystalline photo-product. The crude material could not be separated into its components and was thereafter subjected to alkaline hydrolysis. Column chromatography and crystallization of the product yielded 2-phenylazonaphthalene (10). Comparative gas chromatography showed the mother liquor to consist mainly of 2-(4'-chlorophenylazo)naphthalene (33), together with traces of 2-phenylazonaphthalene (10), 2-(2'-chlorophenylazo)naphthalene (34) and a fourth unidentified compound. The isolation of (33) and (34) in this reaction implied that compounds such as (131) and (146) were present in the photoreaction mixture. The dioxalyl compounds,(134) and(145), could also have been present.

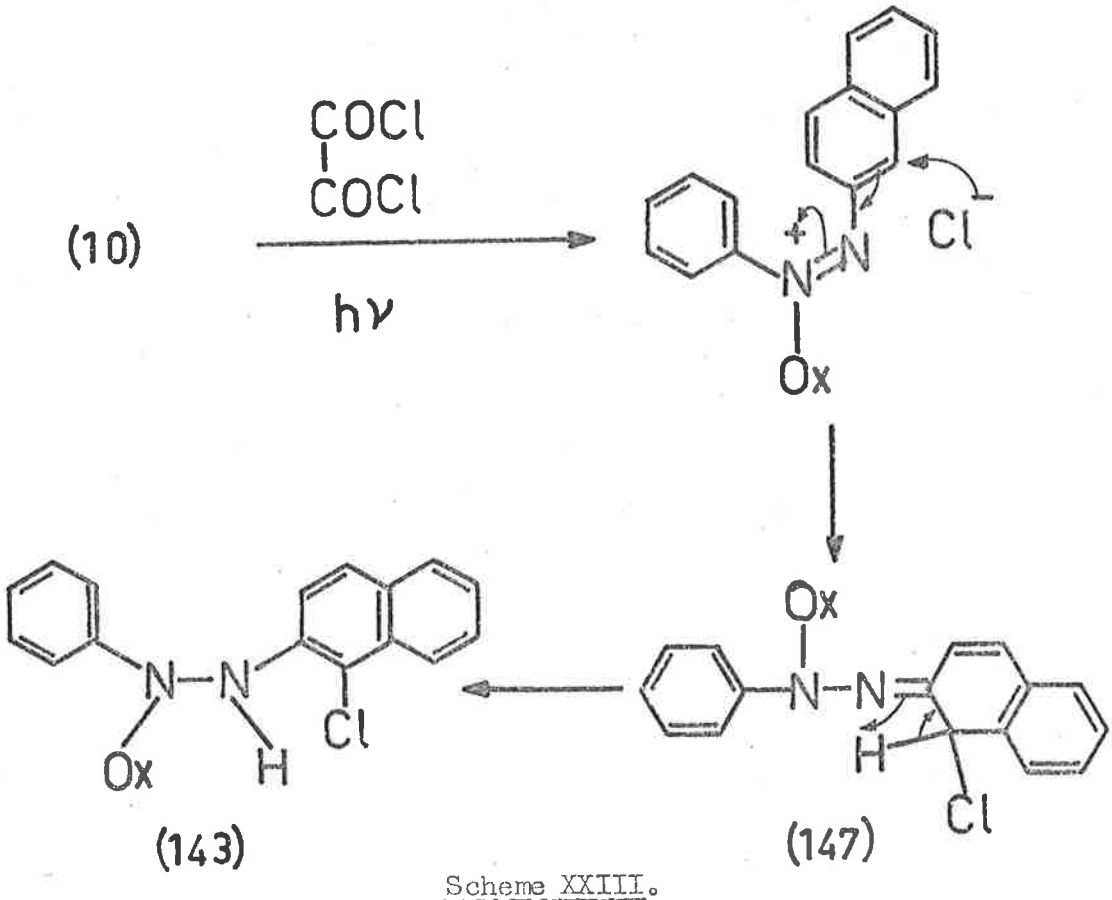
One reason for the apparent exclusive formation of mono-oxalyl product could be the steric bulk of the oxalyl group. If the addition of the second oxalylium ion is sterically unfavourable then a proton which is less bulky could be added in its stead (see Scheme XXIIa). However, molecular models of the proposed intermediates do not indicate that this factor would be important enough to cause what is essentially exclusive mono-oxalylation.

A second explanation of the observed result involves an intramolecular proton transfer from an ortho position in one of the two aromatic rings to the nitrogen atom adjacent to that ring. The example chosen in Scheme XXIII shows a proton shift from the 1-position of the naphthyl ring via the intermediate (147). Such a transfer in preference to direct addition of an oxalyl species would lead to the mono-oxalyl compound (143). This latter pathway which involves "ortho" chlorination would lead to mono-oxalyl compounds whereas substitution in any position not "ortho" to the nitrogen atoms would lead to dioxalated products because intramolecular proton-transfer would be impossible. This would mean that any 2-(4'-chlorophenylazo)naphthalene (33) isolated from the hydrolysis reactions was derived from 2-(N,N'-dioxalyl-4'-chlorophenylhydrazo)naphthalene (134) and not the corresponding N-oxalyl compound (131).

Both of these arguments are unproven and further work is required to elucidate the mechanism of this reaction.


COCl
COCl
(10)
hν
Cl
N
N+
Ox
Cl
N-N
H
Ox
(131)
(a)
H+
H
Cl
Ox
N-N
E+
(b)
+COCOCl
Cl
N-N
Ox
Ox
(134)

Scheme XXII.



Scheme XXIII.

Treatment of the original crystalline photo-product with boiling methanol yielded the methyl ester of x-chloro-N-oxalyl-2-phenylhydrazo-naphthalene (136, 138). The structure of this compound was deduced from infrared and mass spectral data combined with elemental analysis. When subjected to alkaline hydrolysis-oxidation this compound yielded identical products (10, 33) to those isolated from the hydrolysis of the ethyl ester.

None of the predicted product (128) resulting from ring formation

was detected in the reaction mixture. This was attributed to the chain length in the acid chloride not being long enough to bridge the two nitrogen atoms and thereby undergo the intramolecular reaction that would have led to ring closure.

Compounds (10), (33), and (34) were identified by direct comparison with authentic samples. 2-(4'-Chlorophenylazo)naphthalene (33), 2-(2'-chlorophenylazo)naphthalene (34), and 2-phenylazonaphthalene (10) were available from earlier work (see Experimental I).

Dark Reaction of 2-Phenylazonaphthalene in Oxalyl Chloride.

2-Phenylazonaphthalene was heated under reflux with oxalyl chloride for 30 days in the complete absence of light. The excess acid chloride was removed; and chromatography of the residue yielded unchanged 2-phenylazonaphthalene (94% recovery). The previously isolated photo-products could not be detected in the material that remained. Photoactivation is evidently required for the reaction to occur.

2. trans-Azobenzene.

This reaction had been performed by other workers,[104] but no attempt was made to isolate and characterize the individual photo-products.

A solution of azobenzene (1) in oxalyl chloride was irradiated until the solution was completely decolourized. The crude product remaining after removal of the excess oxalyl chloride slowly hardened

over a period of several days to form a pale brown glass. This material reacted with moist air with liberation of hydrogen chloride gas. The infrared spectrum of the crude mixture indicated the presence of a secondary amino group and of several carbonyl groups. The mass spectrum showed a fragment at m/e 399. The crude product was subjected to hydrolysis and aerial oxidation in aqueous methanolic potassium hydroxide. The final product was examined by gas chromatography and this revealed a mixture (4-chloroazobenzene (30) and 2-chloroazobenzene (127) in 60% and 30% overall yields respectively) of azo compounds.

The purification of the mixture was attempted by fractional distillation under reduced pressure; but the individual components could not be isolated.

Attempts to separate the product of the photoreaction into its components by column chromatography (alumina or silica) yielded colcured oils with infrared spectra that were different from that of the non-chromatographed material. These products from chromatography were possibly mixtures of the acids obtained from the reaction of the oxalyl chloride groups in the photo-products with water to give the corresponding acids, (153) and (155). Analytical data obtained for these products did not yield any usable information regarding their structures. When treated with ethanolic potassium hydroxide the mixture from both columns yielded 2-chloro- and 4-chloroazobenzene (total yield 90%) in the ratio of 1:2 (gas chromatography). This was further evidence that the column materials were effecting only the reactive acid chloride

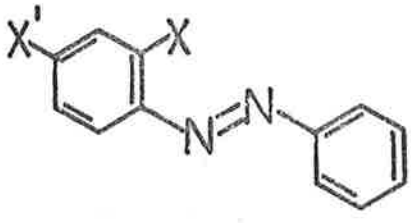
group in the molecule.

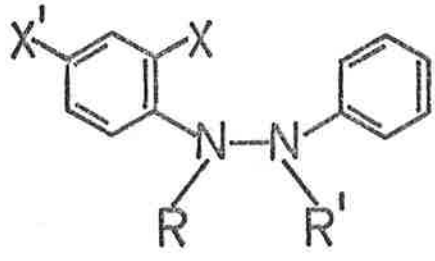
The conversion of the photo-product into its stable ethyl ester was attempted by heating it with ethanol under reflux. Removal of the solvent yielded a pale yellow oil. The infrared spectrum of this mixture was essentially the same as those of the material isolated from the alumina and silica columns. The mass spectrum showed no fragments containing more than one chloro group and a probable molecular ion appeared at m/e 419. On the basis of the spectral data it appeared that the esterification had been successful. However, the individual compounds in the mixture could not be separated and the crude product was treated with ethanolic potassium hydroxide. Examination of the final product by gas chromatography revealed the presence of 2-chloroazobenzene (127) and 4-chloroazobenzene (30) in the molar ratio of 1:2.

The photo-product was treated with boiling water so as to hydrolyse all active acid chloride groups in the molecule. The aqueous mixture was extracted with chloroform; and removal of the solvent from this solution yielded an oily residue. The infrared spectrum of this material was identical with those of the products isolated from the columns. Information derived from the infrared and mass spectra indicated that the hydrolysis had occurred. All attempts to crystallize the mixture failed and separation by column chromatography into its individual components was unsuccessful. The crude mixture was subjected to alkaline hydrolysis-oxidation, and analytical gas chromatography was used to show that the ratio of 2-chloro- and 4-chloroazobenzene in the final product

was 1:2 (combined yield 75%).

Since 2-chloroazobenzene (127) and 4-chloroazobenzene (30) were isolated from the hydrolysed photochemical reaction mixture it was concluded that the corresponding 2-chloro- and 4-chloro-N-oxalyl-hydrazobenzenes (151 and 149) and 2-chloro- and 4-chloro-N,N'-dioxalyl-hydrazobenzenes (150 and 148) were probably formed as photo-products. The presence of the N-oxalyl products was suggested by the strong infra-red absorption at3300 cm^{-1} attributed to a secondary amino group. The appearance of a molecular ion at m/e 399 in the mass spectrum indicated that some of the N,N'-dioxalyl product was formed. However, attempts to separate the N,N'-dioxalyl isomers (148) and (150) from the N-oxalyl isomers (149) and (151) were unsuccessful and an accurate estimate of the relative proportions of each cannot be given.

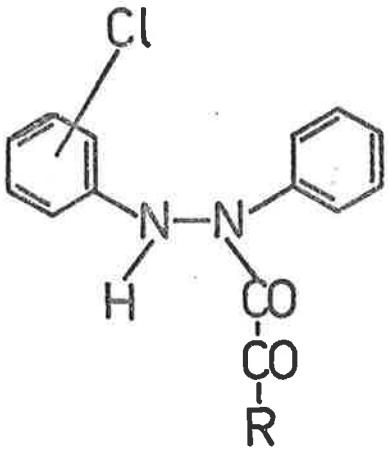


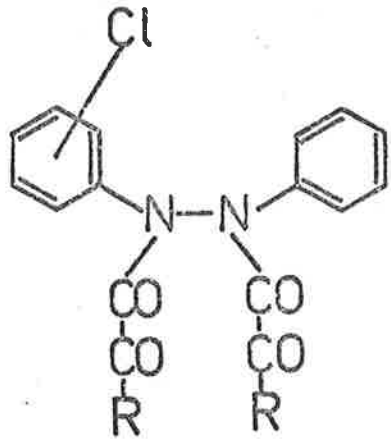


	X'	X
(30)	Cl	H
(127)	H	Cl
(1)	H	H

	R	R'	X	X'
(148)	Ox	Ox	H	Cl
(149)	H	Ox	H	Cl
(150)	Ox	Ox	Cl	H
(151)	H	Ox	Cl	H

When the photo-product was treated with ethanol or with water a mixture of the respective ethyl esters (152, 154) and acids (153, 155) was evidently formed from the N-oxalyl and N,N'-dioxalyl compounds. The extent to which decarboxylation may have occurred is not known.





	R		R
(152)	-OEt	(154)	OEt
(153)	-OH	(155)	OH

Attempts to isolate a cyclised product such as (128) from the photoreaction mixture met with no success. The formation of this compound did not appear to have occurred.

PHOTOCHEMICAL REACTIONS IN MALONYL DICHLORIDE.

3. trans-2-Phenylazonaphthalene.

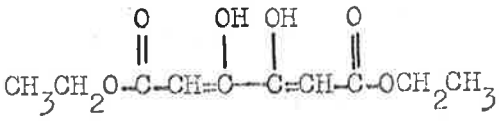
The photoinduced reaction of 2-phenylazonaphthalene (10) with malonyl dichloride yielded a crystalline photo-product (156) which was removed directly from the reaction mixture by filtration. This material rapidly decomposed when exposed to moisture, forming a resinous material and gaseous hydrogen chloride. Attempts to purify this compound sufficiently for analysis were unsuccessful because of its instability.

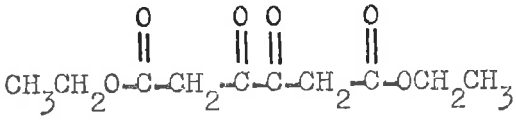
When the compound (156) was treated with ethanolic potassium hydroxide no phenylazonaphthalenes appeared to be formed.

The photo-product (156) reacted vigorously with ethanol at room temperature, hydrogen chloride being evolved. The solid precipitated from the final reaction mixture, was purified by multiple recrystallization or by sublimation. The analysis figures for the material (157) obtained by either method were consistent with the general formula of $C_8H_7O_5Cl$.

The infrared spectrum of (157) showed the presence of two carbonyl groups and at least one enolic hydroxy group in the molecule. The formation of a deep purple colour, when the compound (157) was treated with ferric chloride solution, confirmed the presence of an enolic grouping.

Examination of the n.m.r. spectrum (see Table V) led to the conclusion that the compound (157) was the enol tautomer (158) of hexanedioic acid-3,4-dioxo-diethyl ester (159).

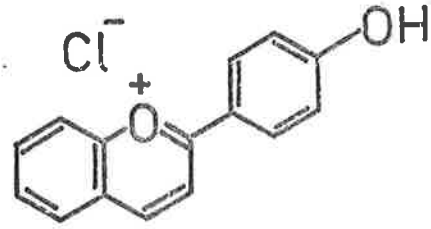
(158) 

(159) 

The signals in the spectrum were in agreement with the expected proton-resonances for the structure (158). The integrated peak areas were all in the exact ratios that would be expected for (158), which is a known compound.[180] The compound has been shown[180] to exist in the keto form under similar acidic conditions to those used to prepare compound (157). The melting point of (158) was 78°. However, a structure such as (158) did not explain the presence of a chloro group in the molecule or a molecular weight of 228 (two units less than required for (158)) suggested by the mass spectrum and the analytical data.

From the non-appearance of chlorine in the supposed molecular ion at m/e 228 in the mass spectrum, it was concluded that the chloro group was one of the first fragments removed from the parent molecule. A fragment at m/e 36 which contained one chlorine atom was assigned to the loss of HCl from the parent species. This may have been to some extent a thermal reaction and not exclusively due to loss of HCl on electron impact.[181] A doubly charged parent ion occurred in the spectra at m/e 114. This type of behaviour in the mass spectrometer has been observed for flavylium salts; and in particular the chlorides.[181]

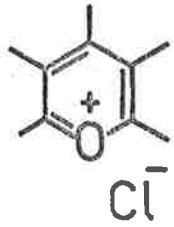
These compounds (e.g. 160) were found to initially lose HCl to give a molecular ion at m/e M-36. A doubly charged ion always appeared at m/e $\frac{M-36}{2}$. This was attributed to the high degree of charge delocalization in the flavylium ions making these ions fairly stable in the mass spectrometer.



(160)

The relative intensity of the (M-36) peak in the spectra of flavylium salts was much greater than that of the supposed (M-36) peak of the product (157). This suggested that the $(M-36)^{+\cdot}$ ion of (157) was less stable than the $(M-36)^{+\cdot}$ fragments of flavylium salts. This could be attributed to a smaller degree of charge delocalization in the $(M-36)^{+\cdot}$ from (157). Structure (157) being a flavylium salt (161) could account for the observed mass spectrum.

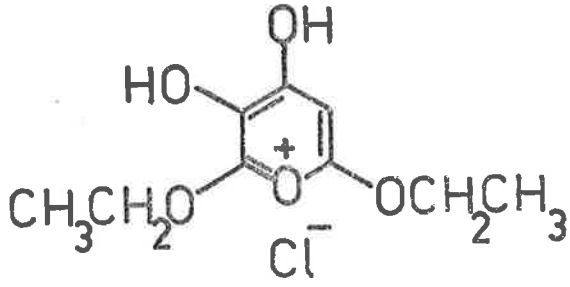
Treatment of the compound (157) with ethanolic or aqueous silver nitrate solution gave a white precipitate of silver chloride. This was further evidence that the chlorine in the molecule was present as a chloride ion or as a very easily removable bonded atom.



(161)

The ultraviolet spectrum showed strong absorptions in the regions of 214 and 306 mμ. An aromatic compound, such as a pyrylium salt, would be more likely to give such a spectrum than a non-aromatic open chain compound.

A structure that could possibly account for the mass spectrum is (162). However, this structure does not fit the n.m.r., infrared,



(162)

and elemental analysis data and therefore is purely conjectural.

Further work is required to determine the exact nature of this product and to account for the apparently conflicting sets of data.

The photo-product (156) or the compound (157) was heated under reflux with ethanol. The ethanol was removed and the liquid residue

TABLE V.

Compound 157; Solvent $CDCl_3$.

Signal	Chemical Shift p.p.m.	Proton Count	J Hz	Assignment
triplet	1.35	6	6.5	$-CH_3$
quartet	4.42	4	6.5	$-CH_2-$
singlet	6.20	2	-	$=C(H)-$
singlet	14.1	2	-	$=C(OH)-$

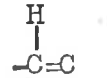
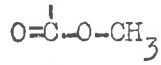
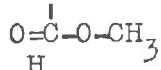
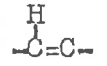
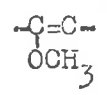
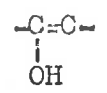
Compound 163; Solvent $CDCl_3$

triplet	1.27	3	7.6	$-CH_3$
triplet	1.30	3	7.0	$-CH_3$
triplet	1.43	3	7.2	$-CH_3$
singlet	3.72	2	-	$-CH_2-$
singlet	4.72	1	-	$=CH-$
quartet	4.19	4	7.0	$2x-O-CH_2-$
quartet	4.25	2	7.0	$-O-CH_2-$
singlet	14.0	1	-	$=C(OH)-$

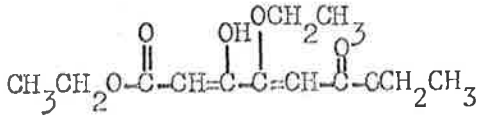
Compound 169; Solvent $CDCl_3$

singlet	3.90	6	-	$-CH_3$
singlet	6.18	2	-	$=CH-$
singlet	13.9	2	-	$=C(OH)-$

Compound 170; Solvent $CDCl_3$

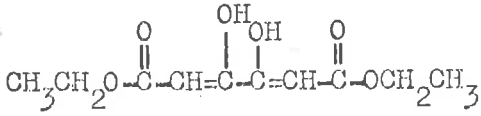
singlet	3.63	1	-	
singlet	3.70	3	-	
singlet	3.74	3	-	
singlet	3.80	1	-	
singlet	3.85	1	-	
singlet	13.2	1	-	

was fractionally distilled to give a colourless liquid. This compound (163) contained no chloro group and the mass spectrum suggested a molecular weight of 256. A structure (164) for this product (163) was proposed based on the mass and n.m.r. spectral data.



(164)

The elemental analysis figures, however, indicated a possible formula of $C_{10}H_{14}O_6$. The agreement between the found and calculated figures was not exact; and these values may have been in error. A structure (165) can be drawn that agrees with the analytical data.



(165)

The structure (164) could have been a contaminant in (165) thus causing inaccurate data to be obtained from the mass and n.m.r. spectra.

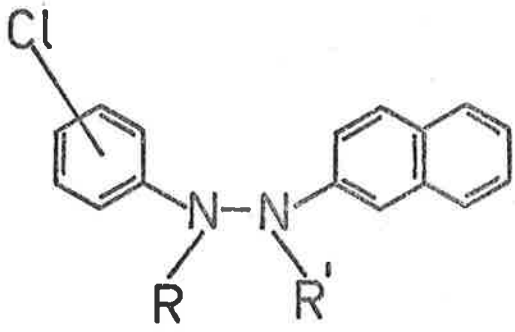
If the crystalline compound (157) was a pyrylium salt this reaction could be explained in terms of the loss of aromatic stability of the ring upon removal of the chloride ion from the molecule. This would result in the formation of a comparatively unstable ring such as (166) which could then be readily opened by the attack of an ethanol molecule.

(166)

The conversion of the solid product (157) to the liquid compound (163) was followed spectrometrically at room temperature. The absorption in the ultraviolet region at 306 mμ, which is characteristic of (157), gradually diminished as a corresponding increase in the intensity of the absorption at 246 mμ occurred due to (163) being formed. The shift in absorption suggested that a less conjugated eneone (open-chain) was being formed.

The liquid collected from the photoreaction was subjected to

alkaline hydrolysis; and the mixture obtained was chromatographed. No 2-phenylazonaphthalene (10) was recovered and the chlorophenylazonaphthalenes were also absent. This indicated that all of the azo compound had reacted during the irradiation, and that none of the N,N'-dimalonyl (167) and N-malonyl phenylhydrazonaphthalenes (168) had been formed.



Ma ≡ $-COCH_2COCl$

	R	R'
(167)	Ma	Ma
(168)	H	Ma

The photoreaction was also carried out with benzene as an inert solvent. Removal of the solvent and treatment of the solid photoproduct with ethanol, gave a compound which was identical to the product, (157), obtained from the photoreaction in which benzene was not used. Unsuccessful attempts were made to isolate by chromatography the compounds contained in the non-crystalline photoreaction product. None of the predicted heterocyclic compound (128) was detected in the mixture.

Proof that the azo compound needed to be present for the reaction

to proceed was provided by a separate reaction. The pure malonyl dichloride was irradiated under the same conditions as were used when 2-phenylazonaphthalene was present. None of the previously isolated photo-product was formed.

A solution of 2-phenylazonaphthalene in malonyl dichloride was kept in the dark under a nitrogen atmosphere for seven days. Virtually all of the azonaphthalene was recovered unchanged, and none of compound (157) was detected in the alcoholic reaction mixture. From this result it was concluded that the observed reaction was photo-induced, and not simply a non-photochemical process.

4. trans-Azobenzene.

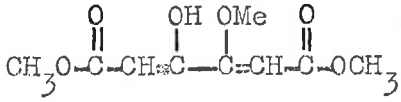
The novel photoreaction that occurred when 2-phenylazonaphthalene (10) was irradiated in malonyl dichloride led us to determine whether this reaction was general for all aromatic compounds or only applied to (10).

Azobenzene (1) was treated with malonyl dichloride in the same fashion as described for the 2-phenylazonaphthalene reaction. Again the photo-product was deposited as a solid mass in the reaction vessel, and this was collected and treated with cold ethanol. The material isolated was identical with that isolated in the previous reaction in which azobenzene was not used.

The photo-product also gave rise to a stable product when treated with cold methanol. The compound (169) so obtained was identical struc-

turally with (157) except that in place of ethoxy groups there were methoxy groups. A similar situation existed where the n.m.r. and mass spectral data, and the analytical data all appeared to contradict each other.

Treatment of the product from the photoreaction with boiling methanol and fractional distillation of the product yielded a colourless liquid (170). Analytical data and the mass, n.m.r. (see Table V), infrared, and ultraviolet spectra suggested a structure (171) for (170).

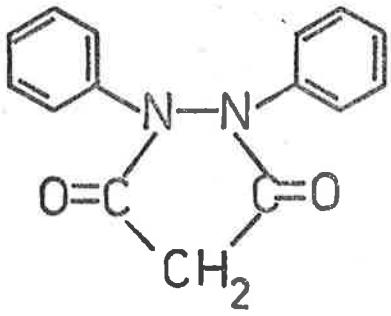


(171)

The mode of formation of this compound is not known and further information concerning the exact form of its precursor (156) is required.

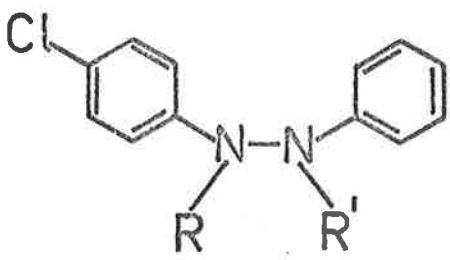
The filtrate obtained after removal of the solid photo-product from the photoreaction mixture was treated with methanol to destroy all of the remaining malonyl dichloride. The mixture was extracted and attempts were made by column chromatography to detect the presence of a heterocyclic compound (m), which could be formed by the addition of one molecule of the acid chloride across the azo linkage. None of the required product was obtained.

The crude photoreaction mixture was subjected to alkaline hydrolysis followed by aerial oxidation of the product. Column chromatography yielded only one recognizable product, namely 4-chloroazobenzene (30) in 3% overall yield. This indicated that 4-chloro-N-



(m)

malonyl-hydrazobenzene (172) and/or 4-chloro-N,N'-dimalonyl-hydrazobenzene (173) were formed in the photoinduced reaction; but in very low yield.



	R'	R
(172)	Ma	H
(173)	Ma	Ma

Ma ≡ $-CO.CH_2.CO.Cl$

A separate reaction on a larger scale was carried out in an effort to determine whether a definite relationship existed between the amount of azobenzene (1) used and the quantity of ethanolysis product (157) isolated. Using 50 ml of malonyl dichloride it was found that, even

though the reaction proceeded in the presence of small quantities of azo compound, approximately 3 g of this material was required before solid photo-product (156) was deposited from the reaction mixture. This implied that the azobenzene was not acting purely as a catalyst. The molar ratio of (1):(157) was found to be 1:4. The ratio of 1:4 was assumed to be the same as the molar ratio for (1):(156).

The part that azobenzene and 2-phenylazonaphthalene play in this photochemical reaction is still unknown. It is significant that none of the unchanged azo compound is ever recovered. Additional work is needed to determine the mechanism of this reaction.

The chain lengths of the two acid chlorides so far used could have been too short for an intramolecular reaction to take place, which would lead to a heterocyclic compound being formed. Further studies with longer chain-length acid chlorides (e.g. succinyl chloride) might indicate whether or not such a reaction is possible.

IV. REACTIONS WITH OTHER ACYL HALIDES.

Lewis and Mayfield[101,102] have shown that irradiation of azobenzene in acetyl chloride and subsequent hydrolysis-oxidation of the photo-products gives a mixture of 4-chloroazobenzene (30) and 2-chloroazobenzene (127). It was shown in separate experiments employing different acid chlorides that the relative extents of ortho and para halogenation were associated with the ionizability of the acyl halide. Inhibition of ionization of the acid chloride in the photoreaction mixture was found to increase the ortho/para [(127)/(30)] product ratio. This was further demonstrated by including benzene or cyclohexane as an inert diluting solvent; a marked increase in the ortho/para product ratio was observed in each case.

Irradiation of several trans-azonaphthalenes in acetyl chloride followed by alkaline hydrolysis-oxidation of the photoreaction product has already been shown to yield mixtures of chlorinated and non-chlorinated azonaphthalenes.

In order to examine the effect of several acid chlorides on the final composition of the photo-product, the trans-azonaphthalenes were irradiated in the presence of various acyl and aroyl chlorides. On some occasions benzene was used as a diluting solvent to decrease the polarity of the medium. Aliquots of the reaction solutions were examined spectroscopically to ensure that no unchanged azonaphthalene remained. The isolation of individual photo-products was in each case found to be

impracticable; and the crude photoreaction mixtures were therefore subjected to alkaline hydrolysis and subsequent aerial oxidation. The final reaction mixtures were examined by analytical gas chromatography. In this way the ratio of azonaphthalenes in the mixture was determined.

In all of the photoreactions the solutions irradiated were equimolar with respect to the trans-azo naphthalene. These solutions were irradiated for the periods indicated.

1. Hydrolysis Product Ratios.

The rate at which the photoreactions proceeded varied widely with the acid chloride used. Reactions with trimethylacetyl chloride were particularly slow and this was probably due to the unreactive nature of the acid chloride. In the photoreaction involving 1,2'-azonaphthalene the reaction proceeded at approximately the same rate as for the acetyl chloride reaction (see Table IX). The quantity of azo compound isolated from this reaction sequence was small and the apparently increased rate of reaction may be due to a different type of reaction occurring viz. naphthidine-type rearrangement products being formed in preference to N,N'-diacylhydrazonaphthalenes.

The unreactive nature of trimethylacetyl chloride could be due to both the steric and electronic effects of the methyl groups.

Results in Tables VI, VII, VIII, and IX show that the composition of the final photo-product varies markedly with the nature of the substituent attached to the acid chloride. It can be assumed that the

Acid Chlorides as Solvent Reactants

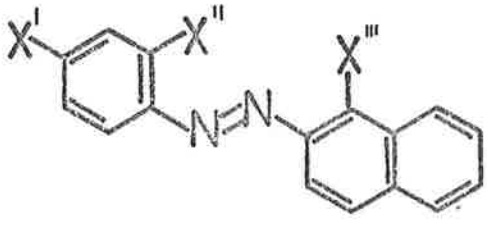
(115 ml of acid chloride with 250 mg of trans-azonaphthalene)

TABLE VI. Photoreactions Involving 2-Phenylazonaphthalene : Yields and Ratio of 2-Phenylazonaphthalene (10), 2-(4'-Chlorophenylazo)naphthalene (33) and 2-(2'-Chlorophenylazo)naphthalene (34).

Acid Chloride	Irradiation Period min.	Combined Yield mg.	Product Ratio (10) : (33) : (34)
Acetyl	40	187	183 : 34 : 1
Propionyl	50	177	68 : 40 : 1
Dimethylacetyl	50	144	20 : 15 : 1
Trimethylacetyl	4 days	50	1 : 11 : 2.5
Monochloroacetyl	45	-*	-
Dichloroacetyl	50	-*	-
Trichloroacetyl	70	≠ -*	-
Benzoyl	70	42	35 : 1 : 40
Oxalyl	65	190 mg	10 : 1

* No azo compounds were obtained from these reactions.

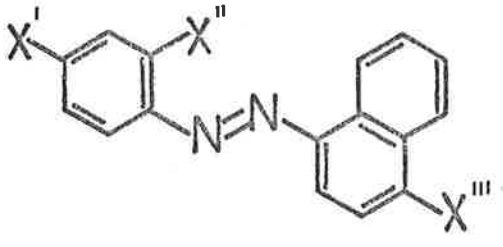
≠ See section IV.2.



	X'	X''	X'''
(10)	H	H	H
(33)	Cl	H	H
(34)	H	Cl	H
(35)	H	H	Cl

TABLE VII. Photoreactions Involving 1-Phenylazonaphthalene : Yields and Ratio of 1-Phenylazonaphthalene (9), 1-(2'-Chlorophenylazo)naphthalene (53), and 1-(4'-Chlorophenylazo)naphthalene (52).

Acid Chloride	Irradiation Period min.	Combined Yield mg.	Product Ratio (9) : (52) : (53)
Acetyl	10	122	36 : 20 : 1
Propionyl	20	177	6 : 1 : -
Dimethylacetyl	20	167	13 : 1 : -
Trimethylacetyl	60	160	440 : 40 : 1
Trichloroacetyl	35	40	128 : 39 : 1
Benzoyl	20	40	103 : 1 : -

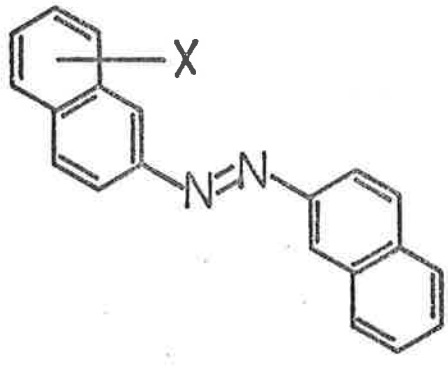


	X'	X''	X'''
(9)	H	H	H
(52)	Cl	H	H
(53)	H	Cl	H
(55)	H	H	Cl

TABLE VIII. Photoreactions Involving 2,2'-Azonaphthalene : Yields and Ratio of 2,2'-Azonaphthalene (4) and x-Chloro-2,2'-azonaphthalene (69).

Acid Chloride	Irradiation Period min.	Combined Yield mg.	Product Ratio (4) : (69)
Acetyl	30	159	2 : 1
Propionyl	35	139	(4) sole product
Dimethylacetyl	70	37	"
Trimethylacetyl	17 hr	67	"
Monochloroacetyl	90	-*	-
Dichloroacetyl	100	-*	-
Trichloroacetyl	110	-*	-
Benzoyl	52	28	1 : 11

* No azo compounds were obtained from these reactions.

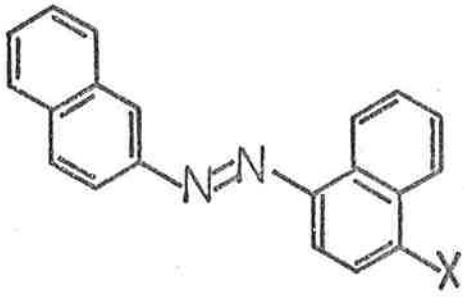


	X
(4)	H
(69)	Cl

TABLE IX. Photoreactions Involving 1,2'-Azonaphthalene : Yields and Ratio of 1,2'-Azonaphthalene (5) and 4-Chloro-1,2'-azonaphthalene (84).

Acid Chloride	Irradiation Period min.	Combined Yield mg	Product Ratio (5) : (84)
Acetyl	30	52	4.9 : 1
Propionyl	30	30	(5) sole product
Dimethylacetyl	35	20	"
Trimethylacetyl	30	2	"
Monochloroacetyl	130	-*	-
Dichloroacetyl	50	-*	-
Trichloroacetyl	70	-*	-
Benzoyl	25	10	(5) sole product

* No azo compounds were obtained from these reactions.



	X
(5)	H
(84)	Cl

ratios of the azonaphthalenes formed by hydrolysis-oxidation of the photoreaction mixtures compare favourably with those of the corresponding acylated hydrazonaphthalenes in the photo-product. This assumption could be false in several respects. In the hydrolysis step it is possible that preferential rearrangement rather than oxidation of the intermediate hydrazonaphthalene occurs. In addition, other reactions during the photoreaction may selectively remove compounds halogenated in specific positions. As a consequence the values obtained may not reflect the extent to which certain positions in the molecule are favoured for chlorination. The extensive formation of non-chlorinated azonaphthalenes also poses a problem, as the precursors of these compounds have not been identified. The extent to which phenyl and naphthyl rings compete for the chloro group (as the acid chloride is varied) is another unknown factor.

From the results in Tables VII, VIII, and IX it is not possible to find a definite pattern of variation relating the product ratio to the nature of the acid chloride. Further information regarding the structure of the compound(s) which yield the non-halogenated azonaphthalenes upon hydrolysis may help to solve this problem. The lack of formation of azo compound upon hydrolysis-oxidation of the photoproducts formed in chloroacetyl chloride solutions cannot be satisfactorily explained. It may be due to exclusive formation of rearrangement products (viz. acylated diaminophenylnaphthyls and binaphthyls) in the

photoinduced reaction. Results of investigations into this problem are discussed in IV.2.

The results listed in Table VI and section IV.2 concerning the photoreactions of 2-phenylazonaphthalene can be partly accounted for in terms of the nature of the substituent attached to the acid chloride. Strongly electron-attracting substituents appear to yield a greater proportion of "ortho" substituted products. For example, trichloroacetyl chloride affords much more 1-chloro-2-phenylazonaphthalene than does acetyl chloride. This argument would explain the observed variation in yields of 2-phenylazonaphthalene if this was formed by dehalogenation of "ortho" substituted photo-products. However this precursor has not been identified and the explanation, while convenient, has no proven basis.

Lewis et al.[104] suggested that two competing mechanisms could operate in the photoreaction of azobenzene with acid chlorides. Where the ionization of the acid chloride was restricted, an intramolecular reaction was considered to operate which would result in almost exclusive ortho substitution. If the ionization of the acid chloride was not limited then para chlorination predominated.

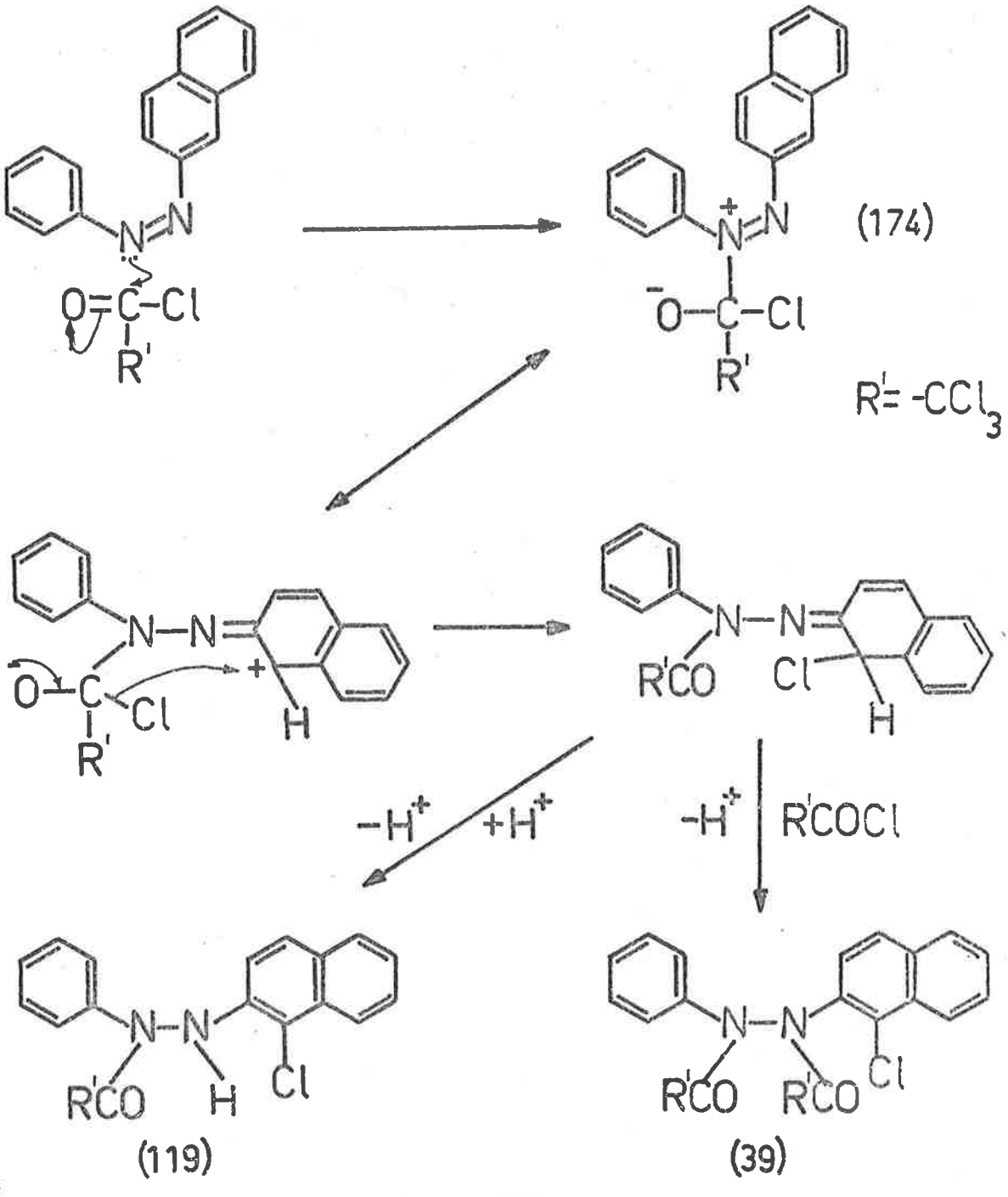
Trichloroacetyl chloride would be expected to ionize much less readily than acetyl chloride. Hence using the argument advanced by Lewis et al.[104] the mechanistic pathway shown in Scheme XXIV would predominate in the reaction involving trichloroacetyl chloride. The pathway outlined in Scheme XXV would be the preferred one for the reaction involving

acetyl chloride.

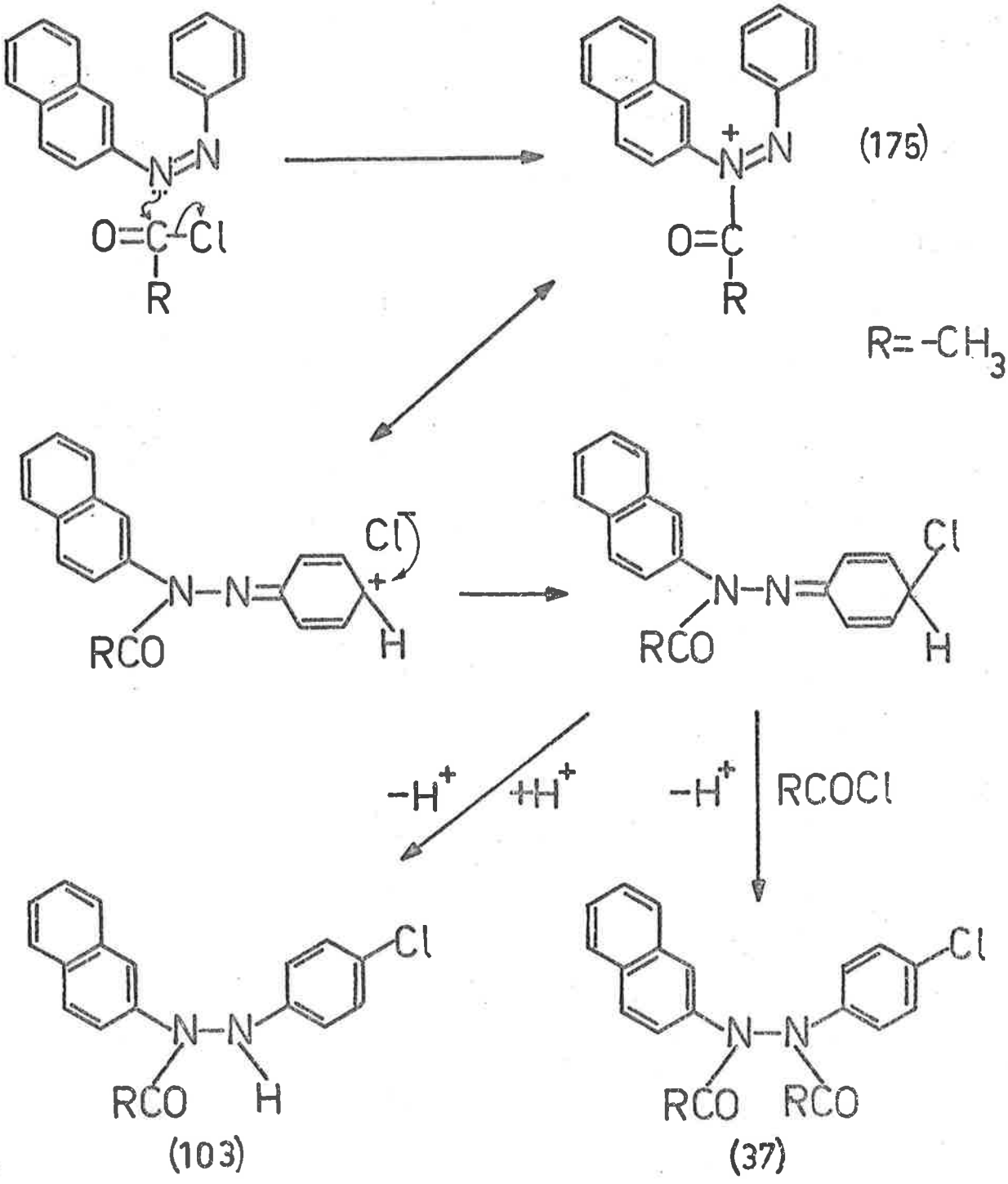
Cations (174) and (175) are probably formed in a bimolecular reaction between the acid chloride and the cis azo compound. The slow rate of photochemical reaction of the trimethylacetyl and p-methoxybenzoyl chlorides with azobenzene was suggested by Mayfield[192] to be evidence for this type of formation. Long irradiation times were generally required for the photoreactions of azonaphthalenes with trimethylacetyl chloride.

Dilution of the photochemical medium with an inert non-polar solvent (e.g. benzene, cyclohexane) would be expected to suppress ionization of the acid chlorides. Lewis et al.[104] have reported that this increases the proportion of ortho chlorination in the photoreactions between acid chlorides and azobenzene. Only a limited number of photoreactions between azonaphthalenes and acid chlorides in the presence of benzene have been examined.

Irradiation of trans-2-phenylazonaphthalene in trichloroacetyl chloride/benzene solution and alkaline hydrolysis of the photo-product yielded only 2-(2'-chlorophenylazo)naphthalene (34) and 1-chloro-2-phenylazonaphthalene (35), [(34) : (35) = 1:4]. In contrast with the reaction where benzene was not present, no 2-(4'-chlorophenylazo)-naphthalene was formed. A similar sequence using acetyl chloride/benzene as the photoreaction medium resulted in a three-fold increase in the quantity of 2-(2'-chlorophenylazo)naphthalene formed, compared with the values obtained when pure acetyl chloride was used.



Scheme XXIV.



Scheme XXV.

A similar sequence of reactions involving trans-1,2'-azonaphthalene increased the 1,2'-azonaphthalene : 4-chloro-1,2'-azonaphthalene product ratio from 4.9:1 when no benzene was present to 13:1 when benzene was employed.

It is obvious then that diluting solvents have an effect upon the nature of the products formed in such photoreactions involving azonaphthalenes, although the results are not easy to rationalise.

2. Photo-products.

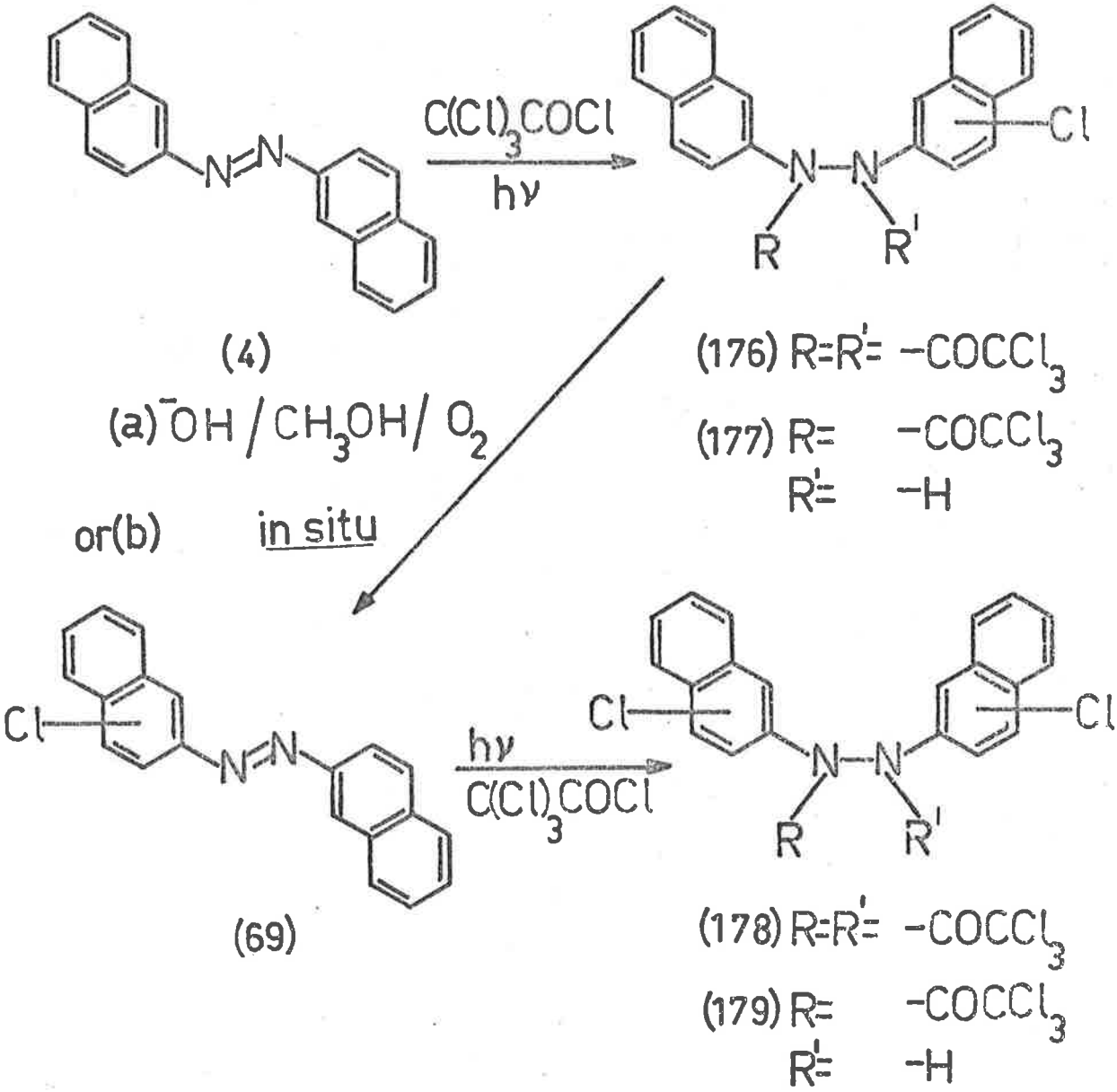
As described in the previous section, the photoreactions of trans-azonaphthalenes with mono-, di-, and trichloroacetyl chlorides and subsequent alkaline hydrolysis-oxidation of the photo-products afforded no azo compounds. From these observations it was concluded that neither N,N'-diacyl nor N-acylhydrazonaphthalenes were formed in the photoreaction. An alternative explanation was that rearrangement of the compounds to the corresponding binaphthyls and phenyl naphthyls occurred during the hydrolysis-oxidation sequence. Attempts were therefore made to separate the mixtures of compounds obtained from the photoreactions of several azonaphthalenes with trichloroacetyl chloride.

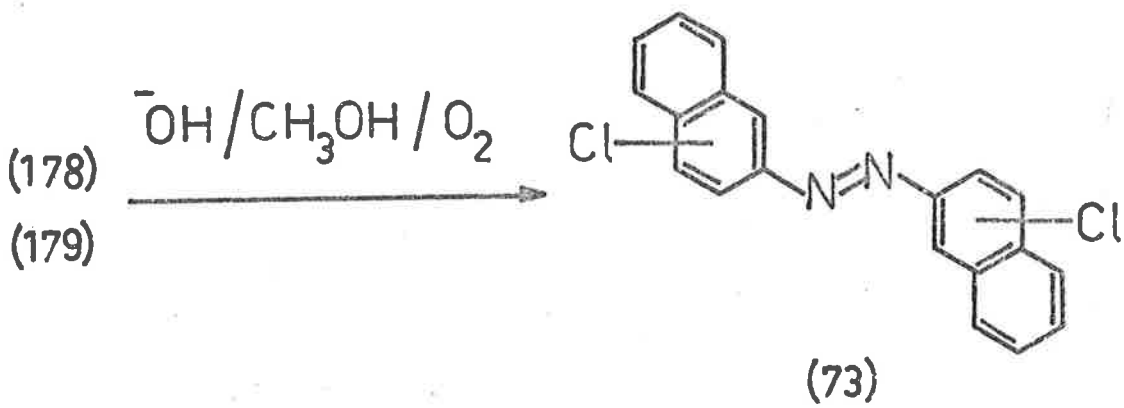
Irradiation of trans-2,2'-azonaphthalene in trichloroacetyl chloride under an atmosphere of nitrogen resulted in rapid decolouration of the solution. The photo-product was obtained as a green-black gum. The infrared spectrum of this mixture exhibited a broad band in the N-H

stretching region (c. 3300 cm^{-1}) and strong bands in the C=O stretching region (1760 and 1720 cm^{-1}). Isolation of individual compounds from the photoreaction mixture by column chromatography was unsuccessful. Alkaline hydrolysis and oxidation of the recovered material gave a product which was examined chromatographically. Two major fractions were isolated from the column.

The first fraction comprised a red-orange solid, which after recrystallization yielded a dichloroazonaphthalene in 15% overall yield. The structure of this compound was deduced from spectral and analytical data. The compound was shown to be identical (mixed m.p. and infrared spectrum) to the product (73) isolated from the photoreaction of x-chloro-2,2'-azonaphthalene (69) with acetyl chloride followed by hydrolysis-oxidation of the photo-product. Mass spectroscopic examination of the mother liquors from the above-mentioned recrystallization revealed that a mixture of monochloro and dichloroazo compounds was present.

From these results it was concluded that monoacylated and/or diacylated hydrazonaphthalenes containing one and two chloro groups had been formed in the photoreaction. In addition two photochemical sequences were evidently involved, (4)⟶(69) and (69)⟶(73). An initial reaction involving unsubstituted 2,2'-azonaphthalene [(4)⟶(176), (177)] would yield an N-acylated or N,N'-diacylatedhydrazo compound containing one chloro group. This material upon hydrolysis-


C(Cl)3COCl
hν
Cl
N
N
R
R'
(4)
(a) ⁻OH / CH3OH / O2
or(b) in situ
(176) R=R'= -COCCl3
(177) R= -COCCl3
R'= -H
Cl
hν
C(Cl)3COCl
(69)
(178) R=R'= -COCCl3
(179) R= -COCCl3
R'= -H



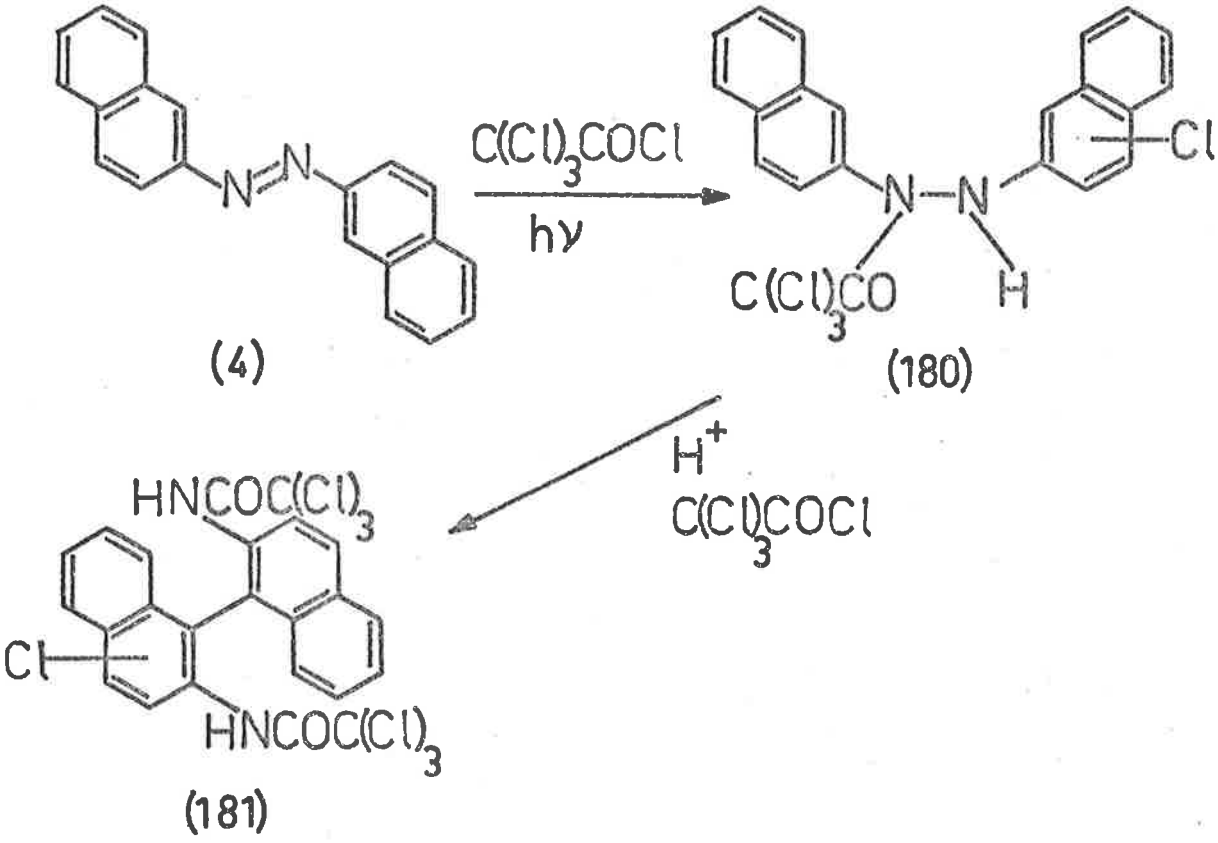
(73)

oxidation would provide the mono-chloroazonaphthalene detected in the hydrolysis product. In addition it may be inferred from the presence of a dichloroazonaphthalene in the hydrolysis mixture that a dichloro-N,N'-diacyl (or N-acyl) hydrazonaphthalene had been formed photochemically. A possible reaction pathway leading to this product would involve the oxidative de-acetylation of the monochloro-N,N'-diacyl photoproduct to the corresponding chloro azo compound. This in turn would then be converted in a further photochemical reaction into a dichloro compound i.e. (69)⟶(178), (179). The base responsible for the oxidative de-acetylation *in situ* could be the *trans*-2,2'-azonaphthalene or the more basic *cis*-2,2'-azonaphthalene. The ease of de-acetylation

of these N,N'-ditrichloroacetylhydrazo compounds was further demonstrated when chloro-2-phenylazonaphthalenes were obtained in good yield by the column chromatography (alumina or silica) of chloro-N,N'-ditrichloroacetylphenylhydrazonaphthalenes.

The second fraction eluted from the column gave a dark brown gum. Strong absorptions in the N-H stretching region (3450 and 3360 cm^{-1}) and the C=O stretching region (1720 and 1695 cm^{-1}) were apparent in the infrared spectrum. From the spectral data and the apparent unreactivity of this mixture under alkaline conditions it was concluded that the compounds in this fraction arose from naphthidine-type rearrangement of the photo-products to the corresponding acylated diamino binaphthyls [e.g. (180)⟶(181)]. However, attempts to isolate and characterise individual members of the mixture by chemical and physical means were unsuccessful. Possibly the low yield of diacylated and monoacylated hydrazo compounds from the photoreaction is due to a relatively easy formation of binaphthyls from preferentially formed monoacylhydrazo compounds. How this can be related to the structure of the acid chloride used is not clear. Further investigations which relate the ease of acid-catalysed rearrangements of monoacylated hydrazonaphthalenes to the nature of the acyl group are obviously required.

trans-2-Phenylazonaphthalene was irradiated in the presence of trichloroacetyl chloride. The crude photo-product was examined by infrared spectroscopy and exhibited a broad band in the N-H stretching



region (c. 3260 cm^{-1}) and two broad bands in the C=O stretching region (1750, 1705 cm^{-1}). From these observations it appeared that quantities of di- and monoacylated hydrazo compounds were formed in the photoreaction, together with naphthidine-type rearrangement products (acylated diaminophenylnaphthyls). The ultraviolet spectrum indicated that no azo compounds were present in the final mixture. Attempts were made to separate the mixture of compounds obtained from the photoreaction. Chromatography on a column of silica yielded three main fractions.

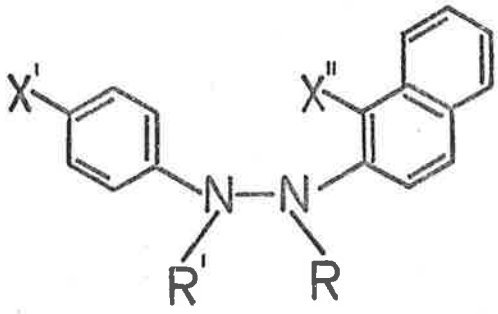
The first band eluted from the column afforded orange crystals of 2-(4'-chlorophenylazo)naphthalene (33) in 2% yield. The identity of this material was confirmed by direct comparison (mixed m.p. and infrared spectra) with an authentic sample.

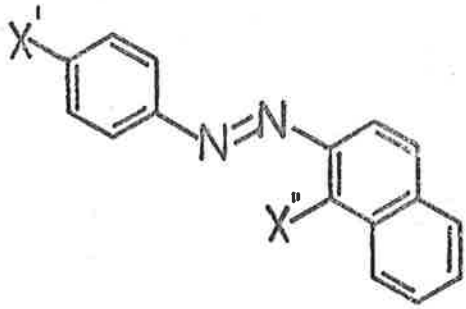
Upon removal of the solvent the second fraction yielded a considerable amount of non-crystalline material. The infrared spectrum indicated that this oil consisted of di- and monoacylated hydrazo compounds in addition to naphthidine-rearrangement products. Further chromatography on alumina gave a 12% yield of 1-chloro-2-phenylazonaphthalene (35). The remaining material eluted from the alumina yielded non-crystalline mixtures of compounds of unknown structures. This product exhibited no absorption in the C=O stretching region.

The final fraction comprised a black-brown gum, the infrared spectrum of which showed bands inter alia at 3350 cm^{-1} (N-H) and 1720 cm^{-1} (C=O). Column chromatography (alumina) gave a small quantity of 1-chloro-2-phenylazonaphthalene. The remaining material on the alumina column was collected and subjected to alkaline hydrolysis-oxidation. Preparative plate chromatography of the product yielded minor amounts of 2-(4'-chlorophenylazo)naphthalene (33) and 1-chloro-2-phenylazonaphthalene (35) (0.5% and 1% overall yields respectively).

It is reasonable to assume on the basis of the quantities of (33) and (35) isolated (2.5% and 16% total overall yields respectively) that at least equivalent amounts of the corresponding mono- and/or diacyl hydrazo compounds [(185), (183), and/or (184), (182)] were present

in the photo-product. It is interesting to note that no non-halogenated azonaphthalene was isolated from the hydrolysis products. From the



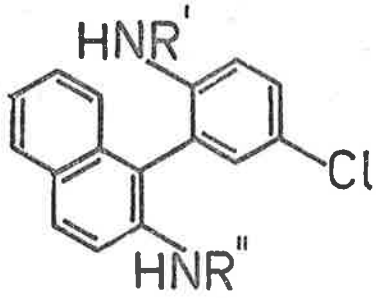


	X'	X''	R	R'
(182)	H	Cl	$-COC(Cl)_3$	$-COC(Cl)_3$
(183)	H	Cl	-H	$-COC(Cl)_3$
(184)	Cl	H	$-COC(Cl)_3$	$-COC(Cl)_3$
(185)	Cl	H	$-COC(Cl)_3$	-H

	X'	X''
(33)	Cl	H
(35)	H	Cl

spectral data available it was concluded that an appreciable amount of rearrangement products [e.g. (186) and (187)] was also formed during the course of the photoreaction.

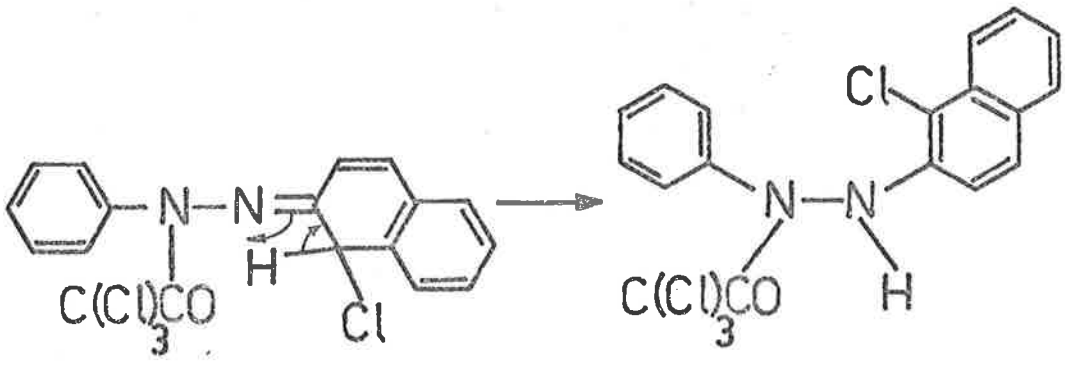
The formation of monoacylated hydrazo compounds in the foregoing photoreaction could involve a process similar to that already suggested for formation of N-acetylated compounds in the dark reactions of azonaphthalenes with acetyl chloride. In such cases it was suggested that protons were able to compete favourably with the acid chloride in



	R'	R"
(186)	H	$-COC(Cl)_3$
(187)	$-COC(Cl)_3$	$-COC(Cl)_3$

attacking the nitrogen atom adjacent to the chlorinated aromatic ring.

Alternatively these products could be formed by the concerted intramolecular process shown in Scheme XXV. This would be expected to lead mainly to mono-acyl ortho-chlorinated photo-products. Such substitution should be favoured when the acid chloride is not readily ionized [e.g. $C(Cl)_3COCl$, $C_6H_5.COCl$].

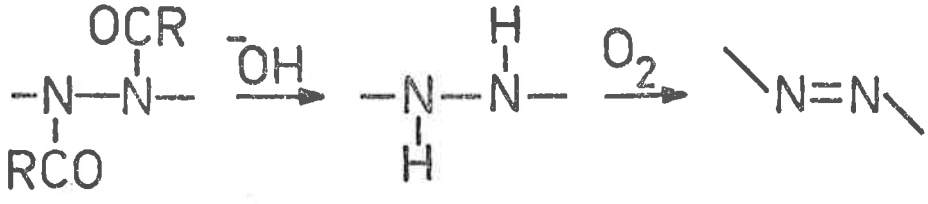


Scheme XXV

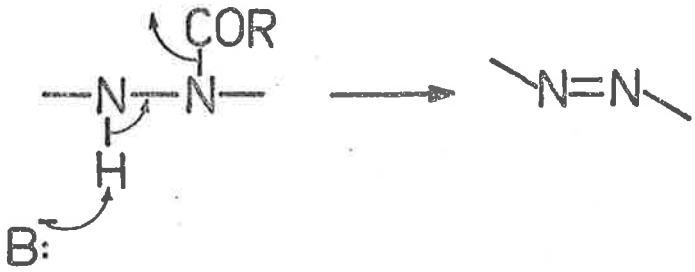
The preferred formation of 1-chloro-2-phenylazonaphthalene supports the suggestion that the position of substitution is associated with the ionizability of the acid chloride.

The ready hydrolysis of the N-acyl and N,N'-diacyl photo-products on an alumina column (and to a lesser extent on a silica column) provided a simple one-step procedure for isolating the chlorinated azonaphthalenes. The hydrolysis product could be seen to form rapidly on the column (marked colour change). Mayfield[197] reported a similar decomposition of N'-benzoyl-2-chlorohydrazobenzene and N'-3,5-dinitrobenzoyl-2-chlorohydrazobenzene to 2-chloroazobenzene. The 4-chloro isomers and the N,N'-diacyl compounds were found to be stable under the same conditions. From Mayfield's[197] results and those relating to the azonaphthalene reactions, it appears that the presence of a strongly electron-attracting group [$-C(Cl)_3$, $-C_6H_4NO_2$, $-C_6H_5$] in the acyl group is necessary for the decomposition to occur. It appears that a mono-acylated compound is involved and not the diacylated material.

The basic hydrolysis of N,N'-diacyl hydrazo compounds normally yields the hydrazo compounds, which can then be oxidised by air to the azo compounds.



However such a mechanism does not explain the ready hydrolysis of the above-mentioned acylated hydrazo compounds. The presence of a strongly electron-withdrawing species in the acyl group would be expected to increase the stability of the compounds in basic media because of a partial reversal of the normal polarization of the C=O bond. A possible explanation of the ease of hydrolysis of such compounds involves the hydrolysis of the mono-acylated compound directly to the azo compound.



This suggested reaction pathway needs to be tested by examination of such hydrolyses under completely oxygen-free conditions.

The effect of employing benzene as an inert diluting solvent was then investigated. trans-2-Phenylazonaphthalene (250 mg) was irradiated in a benzene-trichloroacetylchloride solution. The photoreaction was found to proceed at a much slower rate than when benzene was not present.

The photo-product was subjected to column chromatography. The various fractions so obtained were examined by differing combinations of alkaline hydrolysis-oxidation, preparative plate chromatography, and gas-liquid chromatography. Only a small quantity of azo compound was isolated from the hydrolysis products (17 mg total weight) and this was

shown to be composed of 2-(2'-chlorophenylazo)naphthalene (34), 2-phenylazonaphthalene (10), and 1-chloro-2-phenylazonaphthalene (35) [(34) : (10) = 1 : 4] by gas-liquid chromatography. It is reasonable to assume that at least equivalent quantities of the corresponding N-acyl and/or N,N'-diacyl compounds were formed in the photoinduced reaction.

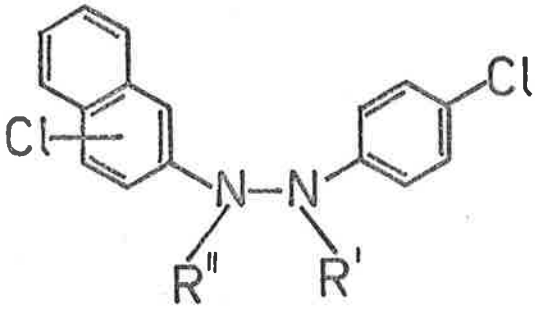
No 2-(4'-chlorophenylazo)naphthalene (33) was detected in the hydrolysis mixture. These results seem to confirm the argument (see section IV.1) that conditions which limit ionization of the acid chlorides should favour the formation of "ortho"-chlorinated products (see Scheme XXIV, IV.1). However, because of the low yield of azo compound obtained, the possibility cannot be ignored that "para"-chlorinated photo-products are formed and are subsequently converted into compounds which do not yield azonaphthalenes upon hydrolysis.

The photoinduced reaction of trans-2-(4'-chlorophenylazo)-naphthalene with trichloroacetyl chloride was also investigated. From the infrared spectrum of the crude photo-product it appeared that the mixture contained a considerable amount of N-acyl and N,N'-diacyl-hydrazo compounds.

Chromatography of the crude mixture afforded a small quantity of a yellow-orange solid which was shown by gas-liquid chromatography to consist of two compounds. Neither of the peaks in the gas chromatogram had a retention time which corresponded to that of an authentic

sample of 2-(4'-chlorophenylazo)naphthalene. The mass spectrum of the mixture showed a molecular ion at m/e 300, which is the expected value for a dichlorinated azonaphthalene. The remainder of the photo-product could not be resolved into its components. It was therefore subjected to hydrolysis-oxidation and subsequent chromatography. Only one band separated from the main body of the product and this was shown by thin-layer chromatography and mass spectroscopy to contain a mixture of 2-(4'-chlorophenylazo)naphthalene and two or more dichloro azo compounds. Physical separation of these compounds on a preparative scale was not achieved.

If the assumption is correct, that all of the photochemically formed N-acyl and N,N'-diacyl hydrazo compounds are converted into azo compounds upon alkaline hydrolysis, then only a very small quantity of products (188) and (189) were formed in the photoreaction. Attempts to characterise the remainder of the photo-product were unsuccessful.



	R'	R''
(188)	$-COC(Cl)_3$	-H
(189)	$-COC(Cl)_3$	$-COC(Cl)_3$

The investigations of the photoreactions of trans-azonaphthalenes with trichloroacetyl chloride did not result in a full description of the nature of the photo-products. Varying amounts of mono- and diacylhydrazo compounds are evidently formed. The yields of these can apparently be increased by increasing the concentration of the azo compound irradiated, but they remain virtually unchanged when benzene is used as a diluting solvent or when a chloro group is originally present in the 4-position of the phenyl ring. The formation of naphthidine-rearrangement products is suggested by the spectral data; but this has not been conclusively proven. These photoreactions require further study.

EXPERIMENTAL

GENERAL:

The photochemical reactions were carried out by exposing solutions of the reactants either to direct sunlight or to the emission from a 125W Philips high pressure mercury quartz lamp. If solar irradiation was used then the solution was sealed in a Pyrex flat-bottomed "culture flask" (31 x 23 x 6.5 cm) under an atmosphere of nitrogen. When a quartz lamp was used the reaction mixture was irradiated in a water-cooled Pyrex glass apparatus which incorporated a nitrogen inlet and a Teflon-coated magnetic stirring bar.

The aqueous ethanolic or methanolic potassium hydroxide used for hydrolysis was composed of a 20% (W:V) solution of potassium hydroxide in 10% (V:V) aqueous alcohol unless otherwise stated.

The packing material for column chromatography was either Spence alumina or B.D.H. Sorbsil silica gel. The acid washed neutral alumina used was activated by heating in a kiln at 300° for 24 hr. All substances chromatographed on alumina or silica columns were adsorbed on Merck kieselguhr before being applied to the top of the column. This allowed easy application to columns of tar-like mixtures and of materials only slightly soluble in solvents of low chromatographic polarity.

The separating medium for preparative plate chromatography consisted of 1:1 (W:W) mixture of Merck HF_{254} and Kieselgel G in a layer 2 mm deep over the surface of a 12" x 12" flat glass plate. The prepared

plates were heated at 120° for a period of 24 hr before use.

The solvents used for chromatography and recrystallization were distilled and dried before use. Petroleum had b.p. 50-65°, and light petroleum had b.p. 30-40°.

For the qualitative separation of components in a mixture by gas chromatography, a Perkin-Elmer 800 gas chromatograph was used. A Perkin-Elmer printing integrator was employed for quantitative gas chromatography. The columns used were as indicated in the Experimental section.

The acid chlorides available from commercial sources were purified by distillation before use. All acid chlorides used were freshly distilled in an atmosphere of nitrogen just before use.

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

Ultraviolet-visible spectra were determined accurately with a Unicam SP800A or a Unicam SP700 spectrophotometer. An Optica CF_4 recording spectrophotometer was used for following reactions spectrophotometrically. Infrared spectra were determined with a Perkin-Elmer 237 spectrophotometer or a Unicam SP200 infrared spectrophotometer.

Nuclear magnetic resonance spectra (n.m.r.) were recorded with a Varian T-60 spectrometer operating at 60 Mc/sec, with tetramethylsilane as the internal standard.

Mass spectra were carried out by Mr. T. Blumenthal with a Hitachi Perkin-Elmer RMU6D spectrometer operating at 70eV.

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

WORK DESCRIBED IN PART I.

Materials and Reference Compounds:

1-Phenylazonaphthalene (9).

This was prepared by condensing 1-naphthylamine with nitrobenzene in the presence of sodium hydroxide.[115] The dark brown oil obtained following extraction with dichloromethane was chromatographed in chloroform-petroleum (5% V:V) on alumina. Recrystallization of the product from petroleum gave 1-phenylazonaphthalene as red-orange plates, m.p. 68-69° (lit.[115] 69°).

2-Phenylazonaphthalene (10).

This compound was prepared in large quantities by condensing nitrobenzene with 2-naphthylamine in the presence of powdered sodium hydroxide at 180°.[115] After purification by chromatography (alumina-petroleum) and recrystallization from ethanol it had m.p. 83-84° (lit.[115] 84°).

2,2'-Azonaphthalene (4).

This compound was prepared by the action of sodium sulphite and sodium acetate on diazotized 2-naphthylamine according to the method of Cohen and Oesper.[169] The crude product was subjected to column chromatography (alumina-petroleum/dichloromethane) and the 2,2'-azonaphthalene isolated from the column was recrystallized from chloroform to give tan coloured plates, m.p. 207-208° (lit.[169] 208°).

1,1'-Azonaphthalene (3).

1-Naphthylamine was diazotized and treated with sodium sulphite and sodium acetate exactly as described above. The 1,1'-azonaphthalene isolated from the column was recrystallized from methanol and formed scarlet needles, m.p. 189-190° (lit.[169] 190°).

1,2'-Azonaphthalene (5).

4-Amino-1,2'-azonaphthalene was diazotized in ethanol containing sulphuric acid, and the mixture was boiled.[150] The crude product was extracted with dichloromethane and chromatographed on alumina, the column being developed with petroleum containing a gradually increasing proportion of dichloromethane. Sharp separation of the product was achieved, and after evaporation of the solvent and recrystallization from methanol the 1,2'-azonaphthalene had m.p. 144-145° (lit.[150] 145°).

Chloroazonaphthalenes.

These were available (see Experimental Part V) from work done in conjunction with the studies of the photoreactions of azonaphthalenes with acetyl chloride. In that work the following compounds were synthesized and have been used to identify and characterize products from the photoreactions: 2-(4'-chlorophenylazo)naphthalene (33); 2-(2'-chlorophenylazo)naphthalene (34); 1-chloro-2-phenylazonaphthalene (35); 1-(4'-chlorophenylazo)naphthalene (52); 1-(2'-chlorophenylazo)naphthalene (53); and 4-chloro-1,1'-azonaphthalene (96).

Gas Chromatography.

A Perkin-Elmer 800 gas chromatograph was used with a 5 ft by 1/8 in aluminium/5% SE-52 column (silicon gum rubber), nitrogen being used as the carrier gas (flow rate c. 30 ml/min). The column temperature for mixtures of phenylazonaphthalenes was 248-250°, and for azonaphthalenes the temperature was 280-282°. The samples of pure phenylazonaphthalenes (substituted and non-substituted), azonaphthalenes (chlorinated and non-chlorinated) and of mixed products (as used for peak identification and analysis) were injected as 4% solutions in acetone (2-10 mμ per injection). The chromatography was carried out on a qualitative basis, no attempt being made at this stage to determine the exact quantities of each compound present in a mixture. The retention times observed for the reference compounds were those listed in Experimental IV.

PHOTOCHEMICAL TRANSFORMATIONS.

1. Photoreaction of 2-Phenylazonaphthalene with Acetyl Chloride.

2-Phenylazonaphthalene (7 g) was dissolved in acetyl chloride (300 ml) and the mixture was irradiated (3 hr) with a high pressure mercury lamp in a water-cooled photochemical reactor. Alternatively, the solution was placed in a sealed Pyrex "culture flask" (31 x 23 x 6.5 cm) and exposed to direct sunlight for a period of 6 hr. In both cases, the initially deep red-orange solution gradually faded in colour as the reaction proceeded, and at the end of the irradiation period the mixture was a pale yellow-brown.

After the removal of the excess acetyl chloride by distillation under reduced pressure, the residual yellow-brown oil was dissolved in dichloromethane, washed (saturated $NaHCO_3$ solution followed by water) and the solution dried (Na_2SO_4). Ether was added to the green-brown glass that remained after evaporation of the solvent, and the solution so formed was left to stand overnight at room temperature. The solid product (6.3 g) that crystallized from the ether solution, was collected by filtration and recrystallized several times from dichloromethane-ether (5% V:V) to yield x-chloro-N,N'-diacetyl-2-phenylhydrazonaphthalene (4C) as cream coloured crystals (4.1 g, 51%), m.p.156.5-157.5° (Found: C, 67.6; H, 4.97; Cl, 11.2; N, 7.7; O, 9.1; mol.wt. (mass spectrum 352. $C_{20}H_{17}N_2ClO_2$ requires: C, 68.1; H, 4.82; Cl, 10.1; N, 7.9; O, 9.1%; mol.wt. 352.5). The infrared spectrum (CCl_4) showed strong bands at

3065 (C-H), 3030 (C-H), 1710 (C=O), 1695 (C=O), 1490, 1425, 1370, 1320, 1300, 1260, 1240, 690, 670, and 624 cm^{-1}. The n.m.r. spectrum showed a sharp singlet at δ2.0 ppm (6 protons), attributed to the acetyl groups, and a complex signal at δ7.4-8.3 ppm that was attributed to the aromatic ring protons.

The mother liquors were recombined, and after removal of the solvent the oily residue (4.4 g) was subjected to column chromatography (silica). Minor quantities of coloured oils (5-25 mg each) were isolated from several of the first fractions (ether-petroleum 0-100% V:V), but the study of these was not pursued.

Elution with chloroform-ether (3% V:V) gave a fraction which afforded a pale yellow oil (3.9 g) after removal of the solvent. Addition of ether to this material caused it to crystallize, and this solid was collected by filtration and purified by multiple recrystallization from ether. Off-white crystals (2.9 g, 36%) were obtained which had m.p. 156-157°. The infrared spectrum of the compound was identical with that of a sample of the photo-product previously obtained. The melting point was not depressed on admixture with a sample of that compound.

The total yield of this photo-product x-chloro-N,N'-diacetyl-2-phenylhydrazonaphthalene, (40) was 87%.

Alkaline Hydrolysis of the Photo-product.

(a) The purified photo-product (2.9 g), m.p. 156-157°, was dissolved in ethanol (40 ml) and to this was added a solution of potassium hydroxide

(12.5 g) in water (10 ml). This mixture was boiled under reflux for 6 hr, and then air was drawn through the cooled solution for an additional 4 hr. The reaction mixture was diluted with water (250 ml), and the suspension formed was filtered. An orange powder was collected, and after washing with water and drying by suction, this solid (1.9 g) had m.p. 59-70°. Several recrystallizations from ethanol did not improve this melting point. Thin-layer chromatography (silica, ether-petroleum 5% V:V) indicated that at least two azo compounds were present in the mixture. The orange hydrolysis product was chromatographed on a silica column using ether-petroleum as the eluting solvent. The ratio of adsorbent:reaction product was 200:1 (W:W).

The first fraction (ether-petroleum, 5% V:V) was collected, and the solvent was evaporated. A yellow-orange residue remained (1.8 g), and this was recrystallized several times from ethanol until constant melting point was obtained. In this way 2-phenylazonaphthalene (653 mg), m.p. 82.5-83.5° (alone or admixed with an authentic sample) was isolated as red-orange needles.

The second fraction (ether-petroleum 8% V:V) from the column afforded 2-(4'-chlorophenylazo)naphthalene (87 mg). After recrystallization from dichloromethane, this compound formed red-orange needles. (52 mg), m.p. 142-143° (Found: C, 72.1; H, 4.43; N, 10.0; Cl, 13.4; mol.wt. (mass spectrum) 266. $C_{16}H_{11}N_2Cl$ requires: C, 72.0; H, 4.13; N, 10.5; Cl, 13.3%; mol.wt. 266.5). When admixed with an authentic sample, the melting point of the product was unchanged. The infrared and ultra-

violet spectra were identical with those of an authentic sample of 2-(4'-chlorophenylazo)naphthalene.

The mother liquors from the recrystallizations of both fractions, were combined and after the solvent had been removed, the residue (1.2 g) was subjected to column chromatography (silica). Elution with dichloromethane-petroleum (8-11% V:V) caused the separation of two orange bands.

The first band yielded an orange crystalline solid (980 mg) which after recrystallization from petroleum formed orange plates of 2-phenylazonaphthalene (180 mg), m.p. 82-83°.

The solvent was evaporated from the second fraction, and the remaining orange solid (120 mg) was recrystallized from dichloromethane, and yielded long red-orange needles (65 mg), m.p. 142-143°. This was identified as 2-(4'-chlorophenylazo)naphthalene by direct comparison (mixed m.p. and ultraviolet spectrum) with an authentic specimen.

Gas chromatography of the residues from the mother liquors, showed that the major component in these mixtures was 2-phenylazonaphthalene with 2-(4'-chlorophenylazo)naphthalene being the other minor constituent.

(b) The purification of the crude photo-product by recrystallization from ether left a large quantity of impure material in the mother liquors. The ether was evaporated from these solutions, and the oily residues obtained (5.3 g) were combined and subjected to alkaline hydrolysis and

aerial oxidation, as described in the foregoing section (a) for the pure material. The hydrolysis product so obtained (3.7 g) was then chromatographed (silica-dichloromethane/petroleum), and several fractions were isolated.

Removal of the solvent from the first fraction gave 2-phenylazonaphthalene (580 mg), m.p. 70-73° (from ethanol), which was identified by comparison (mixed m.p.) with an authentic sample.

The second major fraction afforded orange crystals (3.2 g), m.p. 110-125°. Multiple recrystallization of this product from dichloromethane or chloroform yielded 2-(4'-chlorophenylazo)naphthalene (1.1 g), m.p. 142-143°. The infrared and ultraviolet spectra of this compound were identical with the corresponding spectra of the authentic sample, and a mixed melting point determination showed no depression.

The mother liquors from the second fraction were recombined and evaporated to dryness. Several recrystallizations from petroleum-dichloromethane (80% V:V) gave further quantities of a mixture (demonstrated by gas chromatography) of 2-phenylazonaphthalene and 2-(4'-chlorophenylazo)naphthalene (1.6 g). The residues obtained from the mother liquors were combined and recrystallized from ethanol-petroleum (10% V:V) until a constant melting point was attained. This procedure yielded 1-chloro-2-phenylazonaphthalene (35) (70 mg), m.p. 110-111° (alone or admixed with an authentic sample). This product was isolated on only one occasion and attempts to duplicate this result were not successful.

Photoreaction of 2-Phenylazonaphthalene in Acetic Anhydride-Hydrochloric Acid.

Hydrochloric acid (18 ml, d 1.18) was added gradually to a well-stirred solution of 2-phenylazonaphthalene (500 mg) in acetic anhydride (100 ml.) and the mixture was then irradiated with a mercury lamp for 2 hrs. The excess solvent reactant was removed in vacuo, and the mixture which remained was extracted with chloroform. The extract was washed several times with water, then with Na_2CO_3 solution, and finally with water. Drying of the solution (Na_2SO_4) was followed by evaporation of the solvent (chloroform) to give a green-brown oil. Ether was added to the residue; and application of the same procedure for isolating the photo-product as described for the previous photoreaction yielded x-chloro-N,N'-diacetyl-2-phenylhydrazonaphthalene as a white crystalline solid (300 mg, 70%), m.p. 156-157°. This was shown by direct comparison (mixed m.p. and infrared spectrum) to be identical to the product obtained from the photoreaction of 2-phenylazonaphthalene with acetyl chloride.

Dark Reaction of 2-Phenylazonaphthalene with Acetyl Chloride.

A solution of 2-phenylazonaphthalene (1 g) in acetyl chloride (50 ml) was kept under an atmosphere of nitrogen, and heated under reflux for 7 days in the total absence of light. The acid chloride was removed by distillation under reduced pressure; and the red-orange oil which remained was subjected to column chromatography (alumina-petroleum). The first fraction afforded 2-phenylazonaphthalene (935 mg), m.p. 82-83°

(from ethanol). Small quantities of coloured oils were isolated from later fractions but the quantities involved were too small to allow identification and characterization.

2. Photoreaction of 1-Phenylazonaphthalene with Acetyl Chloride.

1-Phenylazonaphthalene (2 g) was irradiated in acetyl chloride (100 ml) for 3 hr. The solution was either exposed to sunlight in a sealed vessel (a "culture flask") or irradiated with a high pressure mercury lamp in a photochemical reactor. Sunlight generally gave a cleaner photo-product (less coloured by-products).

The acetyl chloride was then removed from the pale brown reaction mixture by distillation (reduced pressure). The residual orange-brown oil (2.2 g) was dissolved in chloroform, and the solution formed was washed with water and dried ($MgSO_4$). Evaporation of the chloroform (last traces under reduced pressure) left a pale yellow-brown gum (2.1 g). This residue was adsorbed on kieselguhr and chromatographed on a column of alumina (ether-petroleum).

A single broad band was eluted from the column (ether-petroleum 20-40% V:V) which afforded 1.8 g of a pale yellow oil after evaporation of the solvent.

A quantity of dark coloured material remained at the top of the column. Elution with ethanol-ether (1% V:V) gave several fractions, each of which contained a dark brown or scarlet oil. Total yield of these products was 182 mg. The infrared spectra (chloroform) of many of these

fractions showed strong bands at 3300-3400 (N-H) cm^{-1}. Thin-layer chromatography indicated that each of the fractions was itself a mixture. The study of these photo-products was discontinued.

The pale yellow oil obtained from the first broad band was dissolved in ether (30 ml); and the solution was allowed to stand overnight at 0°. The crystals which formed (612 mg) were removed by filtration and subjected to repeated recrystallization from chloroform-ether (3% V:V). In this manner colourless crystals of x-chloro-N,N'-diacetyl-1-phenylhydrazonaphthalene (59) (406 mg, 14%) were obtained which had m.p. 147.5-148.5° (Found: C, 68.2; H, 4.90; N, 7.8; O, 9.0; Cl, 10.1; mol.wt. (mass spectrum) 352. $C_{20}H_{17}N_2O_2Cl$ requires: C, 68.1; H, 4.82; N, 8.0; O, 9.0; Cl, 10.1%; mol.wt. 352.5). The infrared spectrum (chloroform) showed bands inter alia at 3050 (C-H), 1710 (C=O), 1695 (C=O), 1600, 1500, 700, 680, 670 and 655 cm^{-1}. The n.m.r. spectrum (deuterochloroform) showed singlets at δ1.86, 1.92, and 1.97 ppm, assigned to acetyl groups, and a broad complex signal at δ7.4-8.4 ppm, assigned to the aromatic ring protons.

All the mother liquors were combined and the ether-chloroform solvent was removed by distillation, leaving a pale yellow oil (1 g). The infrared spectrum (chloroform) of this oil was identical with that of the crystalline product described above.

Alkaline Hydrolysis of the Photo-products.

(a) The purified crystalline photo-product (700 mg), m.p. 147.5-148.5°, was hydrolysed in boiling aqueous ethanolic potassium hydroxide (5 hr) and oxidised with air. The final mixture was diluted with water and extracted with ether. The separated ethereal solution was dried and evaporated to dryness; and the residue was chromatographed on a column of alumina (ether-petroleum).

The first fraction was eluted with petroleum and afforded a mixture (350 mg) of azo compounds. This material was recrystallized several times from aqueous ethanol to yield orange plates of 1-phenylazonaphthalene (280 mg), m.p. 68-69° (alone or admixed with an authentic sample). The mother liquors were shown by gas chromatography to contain mainly 1-phenylazonaphthalene, together with a small quantity of 1-(4'-chlorophenylazo)naphthalene.

The second fraction was eluted with ether-petroleum (20% V:V), and yielded 1-(4'-chlorophenylazo)naphthalene (29 mg), m.p. 124-126°. This compound was identified by direct comparison (mixed m.p. and ultraviolet spectrum) with an authentic specimen [see part (b)].

(b) The crude oil (1 g) recovered from the mother liquors after crystallization of the photo-product, was treated (4 hr) with boiling aqueous ethanolic potassium hydroxide solution. Air was drawn through the cooled mixture for 2 hr, and the suspension formed was extracted with dichloromethane. The extract was washed and dried (Na_2SO_4).

Evaporation of the solvent left an orange residue. This was chromatographed on alumina using petroleum-ether mixtures as the eluting solvent. Two fractions were visibly separated on the column.

The first fraction was eluted with petroleum; and after removal of the solvent an orange solid (290 mg) remained. This was purified by recrystallizations from dichloromethane and ethanol respectively. In this way 1-phenylazonaphthalene (89 mg), m.p. 68-69°, was obtained as red-orange needles. Using gas chromatography the recombined mother liquors were shown to contain mainly 1-phenylazonaphthalene, together with a small quantity of 1-(4'-chlorophenylazo)naphthalene.

Removal of the solvent from the second fraction (ether-petroleum 30% V:V) yielded a red-orange oil (320 mg). This mixture was recrystallized from ethanol.

The first crop of crystals was removed by filtration and recrystallized from dichloromethane to give long yellow-orange needles of 1-(4'-chlorophenylazo)naphthalene (105 mg), m.p. 126.5-127° (Found: C, 71.8; H, 4.45; mol.wt. (mass spectrum) 266. $C_{16}H_{11}N_2Cl$ requires: C, 72.0; H, 4.12%; mol.wt. 266.5). No depression of melting point occurred when this compound was admixed with an authentic sample; and the infrared spectrum of the hydrolysis product was identical with that of the authentically prepared sample.

Partial evaporation of the solvent from the mother liquor yielded a second crop of crystals (90 mg) which had m.p. 65-70°. This compound

was shown by comparison (mixed m.p. and infrared spectrum) to be 1-phenylazonaphthalene. The solvent was removed from the mother liquor; and the residue was dissolved in acetone (4% W:V) and subjected to gas chromatography. One large peak and three smaller peaks were observed. By comparison with the retention times of authentic samples, three of these peaks were identified as belonging to 1-phenylazonaphthalene (large peak), 1-(4'-chlorophenylazo)naphthalene, and 1-(2'-chlorophenylazo)-naphthalene. The fourth peak could not be identified.

Photoreaction of 1-Phenylazonaphthalene in Acetic Anhydride-Hydrochloric Acid.

1-Phenylazonaphthalene (1 g) was irradiated (2 hr) in a solution containing acetic anhydride (100 ml) and hydrochloric acid (18 ml, d 1.18). The reaction vessel was a photochemical reactor, and the radiation source was a high pressure mercury lamp. The procedure then used for the isolation of the photo-product was essentially identical to that previously described for the photoreaction of 2-phenylazonaphthalene with acetic anhydride-hydrochloric acid. The crude solid photo-product so obtained was purified by recrystallization from chloroform-ether (5% V:V). It formed colourless crystals of x-chloro-N,N'-diacetyl-2-phenylhydrazo-naphthalene (400 mg, 46%), m.p. 147-148° (alone or admixed with the previously isolated photo-product). The infrared spectrum of this compound was identical with that of the product isolated from the photoreaction of 1-phenylazonaphthalene with acetyl chloride.

Dark Reaction of 1-Phenylazonaphthalene with Acetyl Chloride.

A solution of 1-phenylazonaphthalene (1.3 g) in acetyl chloride (150 ml) was heated under reflux for 12 hr in a blackened reaction vessel. The acetyl chloride was then removed by distillation (under reduced pressure) and the residual red-orange oil was chromatographed on an alumina column in petroleum. The first fraction contained 1-phenylazonaphthalene (1.1 g), m.p. 68-69°. Further elution with chloroform-petroleum (10% V:V) afforded several brown-black oils (total yield 105 mg), the quantities of each being too small for further study.

3. Photoreaction of 2,2'-Azonaphthalene with Acetyl Chloride (I).

2,2'-Azonaphthalene (820 mg) was dissolved in warm acetyl chloride (400 ml). The solution was cooled, transferred to a "culture flask" and exposed to sunlight for 1 hr. Removal of the acid chloride by distillation under reduced pressure yielded a pale brown, viscous, oily residue (1.25 g). This material was dissolved in ether, and the solution was then washed (water) and dried (Na_2SO_4). The ether solution was evaporated to dryness and the residue (1.1 g) chromatographed on a column of alumina (petroleum-ether).

The major fraction was eluted with ether-petroleum (50-60% V:V). This fraction yielded a pale yellow glass (950 mg), which was dissolved in boiling ether. Hexane was then added until the solution acquired a slightly milky appearance. The material so precipitated was redissolved by the addition of the minimum amount of ether, and the resulting solution

was left to stand overnight at 0°. The crystals deposited were removed by filtration and recrystallized several more times by similar treatment. In this way x-chloro-N,N'-diacetyl-2,2'-hydrazonaphthalene (60) (240 mg, 21%) was obtained as colourless crystals which had m.p. 166.5-168°. (Found: C, 71.4; H, 5.1; N, 6.9; Cl, 8.6; O, 8.0; mol.wt. (mass spectrum) 402. $C_{24}H_{19}N_2ClO_2$ requires: C, 71.6; H, 4.7; N, 7.0; Cl, 8.7; O, 8.0%; mol.wt. 402.5). The infrared spectrum (chloroform) showed bands inter alia at 3065 (C-H), 1715 (C=O), 1690 (C=O), 1365, 1300, 680, and 670 cm^{-1}.

The n.m.r. spectrum (deuterochloroform) showed a singlet at δ2.0 ppm (6 protons), assigned to the acetyl groups, and a broad multiplet at δ8.3-7.4 ppm (13 protons) assigned to the aromatic ring protons.

Alkaline Hydrolysis of the Photo-product.

The crystalline photo-product (265 mg), m.p. 166.5-168°, was dissolved in aqueous ethanolic potassium hydroxide (50 ml); and the solution was boiled under reflux for 6 hrs. Air was bubbled into the cooled solution for a further 1 hr. The mixture was finally diluted with water and extracted with ether. The separated ether layer was dried (Na_2SO_4) and evaporated to dryness; and the residue was subjected to column chromatography (alumina-petroleum/chloroform).

The first fraction (petroleum) yielded an orange solid (180 mg, m.p. 135-185°) which after several recrystallizations from ethanol gave 2,2'-azonaphthalene (120 mg), m.p. 208-209°. The compound was identified

by direct comparison (mixed m.p. and the infrared spectrum) with an authentic sample. The solvent was removed from the combined mother liquors; and the residual mixture was shown by gas chromatography to consist mainly of 2,2'-azonaphthalene. A small quantity of a second compound was also present. The retention time for this peak was the same as that obtained for a sample of x-chloro-2,2'-azonaphthalene (m.p. 167-168°) isolated from the hydrolysis of the crude reaction mixture.

Further elution with chloroform resulted in a second fraction. This afforded a scarlet solid (8 mg), the study of which was not pursued.

Photoreaction of 2,2'-Azonaphthalene and Acetyl Chloride (II).

2,2'-Azonaphthalene (10 g) was partly dissolved in acetyl chloride (1600 ml), and the suspension was exposed to sunlight in a sealed, flat-bottomed flask for 2.5 hrs. The acid chloride was then removed from the pale brown solution (last traces under reduced pressure), and the pale brown glass (15 g) which remained was chromatographed on a column of silica (petroleum-chloroform).

The first fraction (chloroform-petroleum 30-40% V:V) afforded unchanged 2,2'-azonaphthalene (80 mg).

Elution with chloroform-petroleum (60-80% V:V) gave a second fraction, which after removal of the solvent yielded a scarlet solid (105 mg).

A third broad band was eluted from the column with chloroform. Evaporation of the solvent from this fraction yielded a pale brown oil

(14.2 g), which gradually set to a clear glass. This fraction was collected in several parts, but as the infrared spectra of the mixtures isolated from each were identical, they were all combined as one product.

Addition of ether to the glass caused it to crystallize. A small sample of this solid was purified by recrystallization from ether-hexane and was shown to be identical (mixed m.p. and the infrared spectrum) with the compound x-chloro-N,N'-diacetyl-2,2'-hydrazonaphthalene isolated previously.

Except for the sample removed for characterization purposes (see above), all of the crude photo-product (13.5 g) was treated (2 hrs) with boiling aqueous ethanolic potassium hydroxide solution (100 ml). A deep orange colour rapidly developed as the reaction proceeded, and this intensified when air was drawn through the cooled reaction mixture for 1 hr. Water (500 ml) was added to the red-brown suspension; and the precipitated solid was collected by filtration. After being washed and dried, this orange-brown solid (9.5 g) was chromatographed on an alumina column in chloroform-petroleum mixtures as the eluting solvent.

A single broad orange band was eluted from the column (chloroform-petroleum 30% V:V). This fraction yielded a yellow-orange crystalline solid (7.6 g). The solid was recrystallized from acetone. The first crop of crystals was removed by filtration (5.6 g) and recrystallized several times from acetone to give long orange needles of x-chloro-2,2'-azonaphthalene (69) (3.8 g, 36%), m.p. 167.5-169° (Found: C, 76.2; H, 4.21; N, 8.7; Cl, 11.2; mol.wt. (mass spectrum) 316. $C_{20}H_{13}N_2Cl$ requires

C, 75.9; H, 4.11; N, 8.9; Cl, 11.2%; mol.wt. 316.5).

The mother liquors were recombined; and part of the solvent was removed by evaporation. From the remaining solution a second crop of crystals was obtained (600 mg), which consisted of a mixture of the above described chloroazonaphthalene and 2,2'-azonaphthalene. This procedure was repeated several times, each time on the mother liquor obtained from the previous step. By this procedure a mother liquor was finally isolated which yielded 2,2'-azonaphthalene (520 mg), m.p. 208-209° (alone or admixed with an authentic sample) as yellow-orange plates.

Dark Reaction of 2,2'-Azonaphthalene with Acetyl Chloride.

A pale orange solution of 2,2'-azonaphthalene (1 g) in acetyl chloride (50 ml) was heated under reflux (12 hrs) in apparatus which had been blackened to prevent light from reaching the mixture. After the acid chloride had been removed by distillation, the residual material was chromatographed on an alumina column (chloroform-petroleum 25% V:V). The single fraction eluted from the column gave 2,2'-azonaphthalene (946 mg), m.p. 206-208°, after the solvent had been removed.

4. Photoreaction of x-Chloro-2,2'-azonaphthalene (69) with Acetyl Chloride.

An acetyl chloride solution (800 ml) of x-chloro-2,2'-azonaphthalene (1.9 g), m.p. 267.5-269°, was exposed to sunlight in a sealed Pyrex flask for 5 hrs. The excess acetyl chloride was removed from the pale

brown solution under reduced pressure; and the yellow-brown residue (2.9 g) was subjected to column chromatography (silica-petroleum/chloroform).

Elution with chloroform-petroleum (5-50% V:V) gave fractions which afforded small quantities of coloured oils (total yield 165 mg).

The main fraction (chloroform-petroleum, 70-80% V:V) afforded a pale orange glass (2.4 g). This was dissolved in the minimum quantity of ether; and the solution was left in a cold-room overnight (0°). The off-white crystals which separated were filtered from the solution and recrystallized repeatedly from ether to yield cream coloured crystals of x,y-dichloro-N,N'-diacetyl-2,2'-hydrazonaphthalene (72) (1.6 g, 62%), m.p. 209-216°. The melting point could not be raised by further recrystallizations or by chromatography. The mass spectrum of this product showed a molecular ion at m/e 436 ($C_{24}H_{18}N_2Cl_2O_2$ requires mol.wt. 436). The relative abundance of the isotope peaks in this ion was correct for two chloro groups being present.

The infrared spectrum (carbon tetrachloride) showed strong bands at 1710 (C=O), 1690 (C=O), 1375, and 1305 cm^{-1}. No bands appeared in the region 3100-3500 cm^{-1}. The n.m.r. spectrum (deuterochloroform) showed a sharp singlet at δ2.0 ppm (6 protons), assigned to the acetyl groups, and a broad, complex signal at δ7.3-8.25 ppm (12 protons), assigned to the aromatic ring protons.

Removal of the solvent from the mother liquors left a residual oil (695 mg). The infrared spectra (carbon tetrachloride) of this mixture

and of the white crystalline solid described above were identical.

Hydrolysis of Photo-products.

(a) The crystalline photo-product (500 mg) was hydrolysed in boiling aqueous ethanolic potassium hydroxide solution (6 hrs) and oxidized with air. The reaction mixture was diluted with water; and the precipitated solid was filtered off, washed with water, and dried (Na_2SO_4). This material was chromatographed on a column of alumina (petroleum-dichloromethane).

A single broad band was eluted; and when the solvent was distilled off, a red-orange substance (370 mg) remained. This had m.p. 150-180°. The product was clearly a mixture of two or more compounds but all attempts to separate the compounds chromatographically failed.

The mixture was dissolved in benzene, and the solution was left undisturbed for several days. Long yellow-orange needles (m.p. 240-250°) were formed; and these were collected by filtration and recrystallized from benzene until a constant melting point was obtained. By this procedure x,y-dichloro-2,2'-azonaphthalene (73) was isolated as red-orange needles (77 mg, 20%), m.p. 272-273° (Found: C, 68.5; H, 3.47; N, 7.7; Cl, 20.3; mol.wt. (Mass spectrum) 350. $C_{20}H_{12}N_2Cl_2$ requires: C, 68.6; H, 3.43; N, 8.0; Cl, 20.0%; mol.wt. 350).

The mother liquors were collected, concentrated by partial evaporation of the solvent, and allowed to cool slowly. The crystals which separated were collected. This procedure was repeated with the

mother liquor obtained from that sequence, and the crystals were once again removed by filtration. The sequence was repeated until the crystals isolated from a particular mother liquor melted over a small range. This crop of crystals was purified further by recrystallization from dichloromethane, and from this solution x-chloro-2,2'-azonaphthalene (90 mg), m.p. 166-168° (alone or admixed with an authentic sample), was obtained as red-orange needles.

The combined mother liquors were evaporated to dryness; and the residue was subjected to qualitative gas chromatography. Four peaks (two large and two small) were observed. The large peaks were assigned to x-chloro-2,2'-azonaphthalene and x,y-dichloro-2,2'-azonaphthalene (comparison of retention times). The other two peaks could not be identified.

(b) The oily photo-product (500 mg), which could not be crystallized, was hydrolyzed and subjected to aerial oxidation. The method was essentially the same as that described in part (a).

The red-orange solid isolated from the column (320 mg) was dissolved in hot benzene; and the crystals which separated after several days were removed by filtration. This product was recrystallized from dichloromethane to give x,y-dichloro-2,2'-azonaphthalene as red-orange needles (130 mg, 40%), m.p. 273-274° [alone or admixed with a sample of the previously characterized product from (a)].

Isolation of further material from the mixture of x-chloro- and x,y-dichloro-2,2'-azonaphthalene (gas chromatography) contained in the

mother liquors, was not attempted.

Hydrogenolysis of x,y-Dichloro-2,2'-azonaphthalene.

x,y-Dichloro-2,2'-azonaphthalene (80 mg) was suspended in boiling methanol (15 ml), and three portions of stannous chloride-concentrated hydrochloric acid (50 mg $SnCl_2$ in 0.15 ml HCl) solution were added to this mixture over a period of 45 mins. The mixture was heated under reflux for a further 4 hrs, during which time the solid azo compound slowly dissolved, leaving a clear colourless solution. Approximately 10 ml of the alcohol was removed from the reaction mixture by distillation under reduced pressure. The residual solution was diluted with 50 ml of water, and the mixture was rendered basic with 10% ammonium hydroxide solution. A buff-coloured suspension was thus obtained; and this was extracted with benzene. The extract was washed with water and dried (K_2CO_3). Nearly all the benzene was removed under reduced pressure; and hexane was added to the concentrate. This yielded pale yellow-orange crystals (30 mg), m.p. 90-102°. The crystals rapidly discoloured on exposure to air and light. Recrystallization from hexane gave cream-coloured crystals, m.p. 116-120° (Found: C, 67.6; H, 4.68; mol.wt. (mass spectrum), 177. $C_{10}H_8ClN$ requires: C, 67.6; H, 4.51%; mol.wt. 177.5). The infrared spectrum (carbon tetrachloride) showed bands at 3475 (N-H), 3385 (N-H), 3045 (C-H), 1605, 1540, 1250, 1000, and 975 cm^{-1}.

5. Photoreaction of 1,2'-Azonaphthalene with Acetyl Chloride.

1,2'-Azonaphthalene (10 g) was dissolved in freshly distilled acetyl chloride (1200 ml), and the solution was placed in a sealed glass vessel. The mixture was exposed to direct sunlight for 2 hrs, during which time the initial red-orange colour gradually faded. The solution at this stage was pale brown in colour and colourless crystals were attached to the sides of the vessel. The product was filtered from the solution and found to consist of off-white crystals (A) (3.1 g), m.p. 290-300°. The filtrate was cooled (-15°) and maintained at this temperature for 2 hrs. A cream-coloured suspension was formed. This was filtered off to give a further 300 mg of the product (A) already isolated.

On some occasions, the collected solid rapidly changed to a brown gum while on the filter pad. To prevent this occurring the collected solid was rapidly transferred to a small container of methanol (c. 80 ml) in which it was vigorously agitated for 1 hr. Filtration of the suspension gave the same solid (A) as described above.

The acid chloride was completely removed from the filtrate under reduced pressure. The residue was dissolved in chloroform; and the solution was washed with sodium carbonate solution, then with water, and finally dried (Na_2CO_3). Evaporation of the solution to dryness yielded a pale brown glass (B) (11.8 g), m.p. 70-85°.

Purification of Photo-product (A).

The crystalline product (A) was found to be insoluble in chloroform, dichloromethane, ether, petroleum, ethanol, and methanol. It was

slightly soluble in acetyl chloride. However, it was very soluble in glacial acetic acid and dimethyl sulphoxide, and it could be successfully recrystallized from aqueous acetic acid or small volumes of dimethyl sulphoxide.

The crude product was recrystallized several times from dimethyl sulphoxide to give colourless crystals (2.5 g, 18%), m.p. 331-332° (Found: C, 71.5; H, 5.13; N, 7.7; O, 7.0; Cl, 8.4; mol.wt. (mass spectrum) 402. $C_{24}H_{19}N_2O_2Cl$ requires: C, 71.6; H, 4.73; N, 7.0; O, 8.0; Cl, 8.7%; mol. wt. 402.5). The ultraviolet spectrum (ethanol) showed strong absorptions at λ_{max} 290 and 230 mμ. The infrared spectrum (Nujol) showed bands at 3270 (N-H), 2900 (complex, C-H), 1680 (C=O), 1660, 1600, 1530, 1460, 1380, 1300, 820, and 770 cm^{-1}.

This compound was shown to be 4-chloro-N,N'-diacetyl-1,2'-diamino-1',2-binaphthyl (80) by direct comparison with an authentically prepared sample. Admixture of the photo-product with the authentic specimen caused no depression of the melting point; and the infrared spectra of the two compounds were identical. The bis-salicylidene anils obtained from the diamino binaphthyls (formed by the acid hydrolyses of these compounds) were also found to be identical (mixed m.p. and infrared spectrum).

Alkaline Hydrolysis of (A).

The crystalline photo-product (430 mg) was suspended in ethanol (30 ml), and to this was gradually added a hot solution of potassium

hydroxide (25 g) in water (10 ml). This mixture was heated under reflux in an atmosphere of nitrogen for 1.5 hr. The reaction mixture was cooled, diluted with water (250 ml), and extracted with benzene. The separated benzene layer was washed (water) and dried ($MgSO_4$). The solvent was removed from the solution under reduced pressure, and the residue was dissolved in sodium-dried benzene (50 ml). Dry hydrogen chloride gas was bubbled into this solution and a pale pink suspension was formed. This was filtered, and the collected solid was washed with benzene which had previously been saturated with hydrogen chloride. After being dried (under vacuum) the cream-coloured solid was treated with ammonium hydroxide solution (50%) and the pale grey powder that remained was dried under reduced pressure (5 mm). The yield of product, m.p. 74-86° was 350 mg (95%).

The mass spectrum showed a molecular ion at m/e 318 ($C_{20}H_{15}N_2Cl$ requires M.W. 318.5). The infrared spectrum ($CHCl_3$) had bands at 3450 (N-H), 3360 (N-H), 2990 (C-H), 1620, 1525, and 1390 cm^{-1}.

This compound (a diamino binaphthyl) was not purified further, and was used in impure form to prepare the Schiff's base.

The hydrolysis product was dissolved in methanol (3 ml). To this was added 1 ml of redistilled salicylaldehyde, and the pale yellow solution was heated at 100° in a sealed tube for 30 min. The reaction mixture was cooled and the yellow precipitate was collected by filtration. After repeated recrystallizations from ethanol-chloroform (80% V:V), the product had formed bright yellow needles (220 mg, 37%), m.p. 218-219°, of bis-

salicylidene-4-chloro-1,2'-diamino-1',2-binaphthyl (82). The identity of this compound was proven by direct comparison (mixed m.p. and infrared spectrum) with an authentic sample.

Acid Hydrolysis of (A).

The product from the photoreaction (200 mg) was suspended in 70% sulphuric acid (20 ml), and the mixture was heated at 145-150° for 5 min. The brown-black solution was cooled, poured onto ice (50 g); and the milky suspension so formed was stirred vigorously. The pale grey precipitate was collected by filtration, washed with 30% ammonium hydroxide (to liberate the free base), and the off-white powdery solid which remained was dried. The infrared spectrum (chloroform) showed bands at 3450 (N-H), 3360 (N-H), 1620, 1525, and 1390 cm^{-1}. The mass spectrum showed a molecular ion at m/e 318, and the isotope peaks had the correct relative abundance for one chloro group.

This crude diamino binaphthyl (80 mg, 50%), m.p. 104-111°, was not purified further. It was used in its impure state for the next step.

The above product (80 mg) was dissolved in ethanol (2 ml) and treated with salicylaldehyde at 100°. The procedure thereafter used to isolate and purify the bis-salicylidene anil was essentially the same as that described in the preceding section. The compound was recrystallized (ethanol-chloroform). It formed long yellow needles (60 mg, 50%), m.p. 217-219° (alone or admixed with an authentic sample of bis-salicylidene-4-chloro-1,2'-diamino-1',2-binaphthyl).

Purification of Photo-product (B).

The crude mixture (B), obtained as a pale brown glass from the filtered photoreaction mixture, could not be induced to crystallize even though a wide range of solvents was used. Cooling these solutions to low temperatures (-50°) did not effect crystallization. The infrared spectrum (chloroform) of this product showed bands inter alia at 3270 (N-H), 1710 (C=O), 1690 (C=O), 1680, and 1660 cm^{-1}.

The glass (11.8g) was dissolved in chloroform, preadsorbed on kieselguhr, and chromatographed on an alumina column (chloroform-ether).

Elution with chloroform containing 0-90% ether gave several fractions, which after evaporation of the eluate yielded a range of coloured oils and gums (385 mg total yield).

The major fraction was eluted with methanol-ether (0-5% V:V). This afforded a pale-brown glass (9.4 g).

A portion of this glass (250 mg) was chromatographed on a preparative plate (silica-ethanol/chloroform 2% V:V), and the single pale brown band was collected and extracted (chloroform). The chloroform extract was evaporated to dryness and the pale yellow glass (180 mg) which remained was dissolved in ether. Addition of hexane (or light petroleum) and cooling did not cause crystallization. The solvent was removed from the solution; and the residue was distilled under reduced pressure (200-202°/.05 mm) to yield a pale yellow glass (90 mg), x-chloro-N,N'-diacetyl-1,2'-hydrazonaphthalene (87) (Found: C, 71.9; H, 4.65; N, 6.8; O, 8.0; Cl, 8.6; mol.wt. (mass spectrum) 402.

$C_{24}H_{19}N_2ClO_2$ requires: C, 71.6; H, 4.73; N, 7.0; O, 8.0; Cl, 8.7%; mol.wt. 402.5). The infrared spectrum (chloroform) showed bands at 3020 (C-H), 1710 (C=O), 1695 (C=O), 1380, and 1320 cm^{-1}. The n.m.r. spectrum (deuterochloroform) showed sharp singlets at δ1.83, 1.87, 1.90, and 1.96 ppm, assigned to acetyl protons, and a broad multiplet at δ6.9-8.3 ppm assigned to the aromatic ring protons.

Alkaline Hydrolysis of the Photo-product (B).

The crude off-white glass (B) (5 g) was dissolved in methanol (100 ml); and a solution of potassium hydroxide (10 g) in water (10 ml) was slowly added. The resulting light brown solution was boiled under reflux for 2 hrs, during which time the reaction mixture became a deep orange in colour. Air was bubbled through the mixture for 1 hr, and the brown-orange suspension was then extracted with dichloromethane (100 ml). The extract was adsorbed in kieselguhr and chromatographed on an alumina column (petroleum-benzene).

The first fraction was eluted with benzene-petroleum (25-35% V:V) and afforded 1.7 g of a red-orange crystalline solid.

Three other minor fractions were collected from the column (benzene-petroleum 40-50% V:V), and these yielded two scarlet oils and a dark brown gum (combined yield 85 mg).

The column was finally eluted with methanol-benzene (3-5% V:V), and after removal of the solvent this fraction gave 4-chloro-N,N'-diacetyl-1,2'-diamino-1',2-binaphthyl (2.1 g), m.p. 327-329° (alone or

admixed with an authentic sample). The infrared spectrum (Nujol) was identical with that of a previously characterized specimen.

Thin-layer chromatography (alumina-dichloromethane/petroleum 10% V:V) indicated that the first fraction was comprised of two azo compounds. However, attempts to separate the mixture into its components by column chromatography (alumina, silica) were unsuccessful. Preparative plate chromatography (silica-dichloromethane/petroleum 15% V:V) was used to separate small quantities (100 mg) of the mixture into its constituents. In this way, samples of 1,2'-azonaphthalene, m.p. 143-144°, and 4-chloro-1,2'-azonaphthalene, m.p. 188-190°, were obtained from the hydrolysis product. The compounds were identified by direct comparison (mixed m.p. and infrared spectrum) with authentically prepared samples.

Isolation of the individual components in the mixture was achieved on a larger scale by the use of fractional recrystallization. The product (1.6 g), m.p. 150-175°, obtained from the first fraction, was dissolved in benzene and allowed to stand overnight. The deposited crystals were removed by filtration and recrystallized once more from benzene. This was repeated several times. Long red-orange needles (85 mg), m.p. 188-190°, were obtained. Recrystallization of the product from dichloromethane gave red-orange needles of 4-chloro-1,2'-azonaphthalene, m.p. 189-190.5°. Admixture with an authentic sample caused no depression of the melting point . The respective infrared and ultraviolet spectra of the two samples were identical.

The recombined mother liquors were concentrated by partial

evaporation of the solvent; and after cooling the crystals which formed were filtered off. The crystalline product was retained and the above procedure was repeated on the mother liquor. After several such sequences a crystalline solid was isolated which had a reasonably sharp melting point (139-142°). This particular crop of crystals was recrystallized from ethanol and formed red-orange needles of 1,2'-azonaphthalene (715 mg), m.p. 143-144° (alone or admixed with the authentic compound). The impure crystalline mixtures and the residual material from the mother liquors were combined and subjected to gas chromatography. The major components in the mixture were found to be 1,2'-azonaphthalene and 4-chloro-1,2'-azonaphthalene. A third peak was resolved but this could not be identified.

Dark Reaction of 1,2'-Azonaphthalene with Acetyl Chloride.

An acetyl chloride (100 ml) solution of 1,2'-azonaphthalene (1 g) was heated under reflux (12 hr) in a nitrogen atmosphere. Light was excluded from the reaction mixture during that period. The solvent-reactant was removed (distillation under reduced pressure), and the residual solid was chromatographed on an alumina column. The first fraction eluted from the column (chloroform-petroleum, 20% V:V) afforded unchanged 1,2'-azonaphthalene (952 mg), m.p. 144-145° (unchanged by admixture with an authentic sample).

Further elution of the column with chloroform yielded a dark brown gum (22 mg). Infrared spectroscopy indicated that both 4-chloro-

N,N'-diacetyl-1,2'-hydrazonaphthalene and 4-chloro-N,N'-diacetyl-1,2'-diamino-1',2-binaphthyl were not present in this material.

6. Photoreaction of 1,1'-Azonaphthalene with Acetyl Chloride.

Recrystallized 1,1'-azonaphthalene (10 g), m.p. 190-191°, was dissolved in acetyl chloride (1200 ml) and the red solution was placed in a flat-bottomed "culture flask" and sealed in the flask under an atmosphere of nitrogen. The mixture was exposed to strong sunlight for 2.8 hr. During the irradiation period the red colour of the solution rapidly disappeared and was replaced by a dark brown colour. A grey-black precipitate was formed after an irradiation time of 15 min, and the reaction mixture was shaken every 10 min. to settle any floating material to the bottom of the flask. The ultraviolet spectrum (ethanol) of a sample of the mixture showed that no 1,1'-azonaphthalene remained unreacted after 2.7 hr. The acetyl chloride was distilled from the reaction mixture (reduced pressure 14 mm) until 600-700 ml of the acid chloride had been removed.

The following procedure was the most successful method used to isolate the photo-product.

The residual solution obtained from the distillation was filtered, yielding a dark grey solid (750 mg) and a dark brown filtrate. A further 400 ml of the acetyl chloride was removed from the filtrate by distillation under reduced pressure. To the solution which remained was gradually added water (400 ml). The mixture was vigorously stirred

and cooled (ice-salt bath) during the addition. A pale grey precipitate was formed; and this was collected by filtration and dried (7 g). A further 500 ml of water was added to the filtrate, and the precipitated material was removed by filtration and dried to yield a cream-coloured solid (4.6 g). Neutralization ($NaHCO_3$) of the solution and filtration of the suspension so formed gave an additional 1.1 g of pale pink solid.

The pale grey solid (7 g) was dissolved in boiling acetyl chloride (500 ml), and water was added cautiously to the hot solution until no visible reaction occurred on addition of more water. The mixture was allowed to cool to room temperature and a navy blue solid was removed by filtration (220 mg). The pale purple filtrate was agitated and excess water (c. 150 ml) was added in 25 ml portions. A faint purple solid separated from the solution, and this was filtered off, washed with sodium carbonate solution and water, and then dried (5.9 g).

The treatment outlined in the preceding paragraph was repeated with the product collected. This yielded a pink-white solid (4.6 g).

The combined yield of this off-white solid was 10 g (89% yield based on a formula of $C_{24}H_{19}N_2ClO_2$, M.W. 402.5). Further purification by recrystallization (methanol) yielded 4-chloro-N,N'-diacetyl-1,1'-diamino-2,2'-binaphthyl (9d) as off-white crystals (4 g, 35%), m.p. 344.5-346° (Found: C, 70.9; H, 4.97; N, 7.1; O, 8.3; Cl, 9.2; mol.wt. (mass spectrum) 402. $C_{24}H_{19}N_2ClO_2$ requires: C, 71.5; H, 4.72; N, 7.0; O, 8.0; Cl, 8.8%; mol.wt. 402.5). The infrared spectrum (chloroform) showed strong bands at 3200 (N-H), 1690 (C=O), 1675, and 1660 cm^{-1}.

The identity of this compound was shown from the bis-salicylidene anil of the diamino binaphthyl that was formed by the hydrolysis of the photo-product. Direct comparison (mixed m.p. and infrared spectrum) of this anil with a sample of authentic bis-salicylidene-4-chloro-1,1'-diamino-2,2'-binaphthyl showed that the two derivatives were identical. An authentically prepared sample (direct acetylation of 4-chloro-1,1'-diamino-2,2'-binaphthyl) of 4-chloro-N,N'-diacetyl-1,1'-diamino-2,2'-binaphthyl was identical (mixed m.p. and infrared) to the photo-product (see Experimental VII for the two authentic samples used for characterization).

Acid Hydrolysis of the Photo-product and Formation of the bis-Salicylidene Anil.

(a) Hydrolysis:

The N,N'-diacetylated binaphthyl (2.1 g, pink-cream solid) was suspended in 70% sulphuric acid (15 ml). The black-green suspension was heated to 145-150° and maintained at that temperature for a period of 5 min. The solution was cooled and poured into cold water (250 ml), the mixture being vigorously stirred during the addition. To the suspension formed was added concentrated ammonium hydroxide solution until the mixture was basic to litmus. The brown precipitate of 4-chloro-1,1'-diamino-2,2'-binaphthyl (93) was collected by filtration, washed with water, and dried by suction.

(b) Formation of bis-salicylidene-4-chloro-1,1'-diamino-2,2'-binaphthyl (95):

The dry hydrolysis product (93) (1.3 g) was dissolved in the minimum volume of ethanol (8 ml) and to this solution was introduced salicylaldehyde (1.5 g). The reaction mixture was heated in a sealed tube at 100° for 25 min. The solution rapidly became red-orange in colour and a bright yellow solid precipitated from the solution. The product was collected by filtration and recrystallized several times from methanol-chloroform (85% V:V) to give bright yellow needles (470 mg, 22%), m.p. 278-279°. Admixture with an authentic sample of the bis-salicylidene anil of 4-chloro-1,1'-diamino- 2,2'-binaphthyl did not depress the melting point. The infrared spectra of the two specimens were identical.

Alkaline Hydrolysis of the Photo-product and Formation of the bis-Salicylidene Anil.

(a) Hydrolysis:

The N,N'-diacetylated binaphthyl (1.5 g) was dissolved in absolute ethanol (200 ml) and potassium hydroxide solution (50 g in 20 ml water) was stirred into the mixture. The solution was boiled under reflux for 10 hrs in a nitrogen atmosphere. Ethanol (150 ml) was removed (by distillation) from the final reaction mixture and water (100 ml) was added to the solution which remained. The suspension was extracted with dichloromethane (150 ml), the extract washed (water), and dried ($CaCl_2$). The dichloromethane solution was evaporated to dryness

leaving an orange-brown oil. This material was dissolved in dry chloroform and dry hydrogen chloride gas was bubbled into the solution. The precipitated solid was collected by filtration, dried by suction, and treated with 20% ammonium hydroxide solution. The cream-pink solid (920 mg)was washed with water and dried. The infrared spectrum (chloroform) of this product showed strong bands at 3425 (N-H), 3350 (N-H), and 1625 cm^{-1}.

(b) Anil formation:

The 4-chloro-1,1'-diamino-2,2'-binaphthyl formed in the foregoing reaction was treated with salicylaldehyde (500 mg) in ethanolic solution (2.5 ml) at 70°. After a period of 0.5 hr the pale yellow solid was collected by filtration and recrystallized (ethanol) to yield bis-salicylidene-4-chloro-1,1'-diamino- 2,2'-binaphthyl (44 mg), m.p. 178-179° (alone or admixed with a previously characterized sample).

Alkaline Hydrolysis-Oxidation of a Crude Photoreaction Mixture.

A solution of 1,1'-azonaphthalene (5 g) in acetyl chloride (200 ml) was exposed to direct sunlight (2 hrs) in a sealed flask. The acetyl chloride was removed (reduced pressure) and the residual gum (7.2 g) was heated under reflux with aqueous ethanolic potassium hydroxide (20% W:V) for 4 hrs. The mixture was cooled, diluted with water, and extracted with dichloromethane. The extract was washed (water), dried (Na_2SO_4), and evaporated to dryness and chromatographed on a

column of alumina (petroleum-chloroform).

A single red-orange band was eluted from the column and removal of the solvent from that fraction afforded a red-orange crystalline solid (107 mg). After several recrystallizations (dichloromethane) this material formed long orange needles of 4-chloro-1,1'-azonaphthalene (96) (22 mg, 0.5%), m.p. 178-179° (alone or admixed with an authentic sample). Thin-layer chromatography (silica) showed that the recombined mother liquors contained the above-mentioned compound and a second azo compound. Preparative plate chromatography (silica, dichloromethane-petroleum 30% V:V) followed by recrystallization of the material isolated from the two separated bands gave 4-chloro-1,1'-azonaphthalene (8 mg, upper band) and 1,1'-azonaphthalene (17 mg, lower band). The nature of the latter compound was shown by comparison (mixed m.p. and ultraviolet spectrum) with an authentic sample.

Further elution of the column yielded viscous oils (4.2 g) which were found to contain several compounds (thin-layer chromatography). These mixtures could not be induced to crystallize; and attempts to isolate the individual components from each mixture were unsuccessful. The infrared spectra (chloroform) of the mixtures showed the presence of amide groups (3200-3300, N-H; 1640-1690, C=O cm^{-1}).

Photoreaction of 1,1'-Azonaphthalene in Degassed Acetyl Chloride in an Atmosphere of Nitrogen.

Acetyl chloride was twice distilled in a stream of dry, oxygen-

free nitrogen at atmospheric pressure and collected in a vessel partly immersed in liquid nitrogen. The solid acid chloride was allowed to warm to room temperature, and a quantity (115 ml) was transferred to a dry flask. A nitrogen atmosphere was maintained at all times.

1,1'-Azonaphthalene was purified by recrystallization (methanol) and the red-orange crystals were freed from all traces of solvent by being kept at 100°/0.05 mm for 3 days.

The 1,1'-azonaphthalene (500 mg) was dissolved in the acetyl chloride (115 ml) and the solution was solidified by cooling (liquid nitrogen bath). The flask containing the solid was evacuated (1 mm) and the acid chloride was allowed to slowly thaw. When nearly all of the solid acetyl chloride had melted, the mixture was cooled until it had resolidified. This procedure was repeated several times. The cold degassed solution was transferred to a photochemical reactor; and a strong flow of nitrogen was passed through it. The reactor was suspended in a cooling bath containing a dry ice-acetone mixture. The reaction mixture was maintained at -35 to -45° during the irradiation.

The solution was irradiated for 70 min with a high pressure mercury lamp. Removal of the acid chloride (reduced pressure) from the clear brown solution yielded a brown glass (650 mg). The infrared spectrum (chloroform) of this mixture showed strong bands at 3360 (N-H), 3200 (N-H), 1720 (C=O), 1705 (C=O), 1690 (C=O), and 1670 cm^{-1}.

Hydrolysis of the Photo-product.

A solution of the brown glass (205 mg) in aqueous ethanolic potassium hydroxide (15 ml) was boiled under reflux for 2.5 hr. After extraction with dichloromethane and subsequent removal of the solvent, the final product was chromatographed on alumina (petroleum-dichloromethane).

The first fraction afforded a mixture (59 mg, 11%), which after recrystallization from dichloromethane yielded 4 -chloro-1,1'-azonaphthalene (42 mg), m.p. 167-169° (alone or admixed with the authentic compound). Evaporation of the mother liquors to dryness yielded an orange solid which contained 4 -chloro-1,1'-azonaphthalene (major part) and 1,1'-azonaphthalene (gas chromatography).

A second fraction was eluted with dichloromethane-petroleum (15% V:V); and evaporation of the solvent gave a scarlet solid (18 mg).

Elution with dichloromethane-petroleum (20% V:V) yielded a purple solid (25 mg).

The fourth band eluted from the column (dichloromethane-petroleum 30% V:V) afforded 4-chloro-N,N'-diacetyl-1,1'-diamino- 2,2'-binaphthyl (77 mg) as a pale pink solid, m.p. 330-335°. The infrared spectrum of this compound was identical with that of a previously characterized sample, and admixture with that sample did not depress the melting point.

Dark Reaction of 1,1'-Azonaphthalene with Acetyl Chloride.

A solution of 1,1'-azonaphthalene (1.6 g) in acetyl chloride (150 ml) was heated under reflux for 12 hr in the dark. The acid chloride was removed by distillation (reduced pressure) and the residue was chromatographed on a column of alumina (petroleum-dichloromethane).

The first fraction (dichloromethane-petroleum 20% V:V) afforded unchanged 1,1'-azonaphthalene (1.48 g).

The material which remained on the column was eluted from the column with ethanol-dichloromethane (2-5% V:V). The solvent was removed from the fraction collected and a yellow-brown oil (64 mg) remained. The infrared spectrum (chloroform) showed none of the characteristics expected from N,N'-diacetyl-hydrazonaphthalenes or N,N'-diacetyl-diamino-binaphthyls.

WORK DESCRIBED IN PART II.

Materials and Reference Compounds.

The trans-azonaphthalenes and trans-phenylazonaphthalenes were available from earlier work (see Experimental I) as were the chloro-substituted azonaphthalenes and phenylazonaphthalenes required for gas chromatographic identification of hydrolysis-oxidation products (see Experimental V).

The acetyl chloride was a commercial preparation and was distilled in a stream of nitrogen just before use.

All the solvents were dried and distilled before use.

Preparation of cis-Azonaphthalenes and cis-Phenylazonaphthalenes.

Preparation of these compounds by the irradiation of solutions of the corresponding trans-isomers was attempted using the procedure described by Frankel et al.[10] These workers suspended a mercury lamp 5 cm above a solution of the trans-isomer in chloroform contained in an evaporating dish. The irradiation (3 hr) was carried out at 0° and a 70% conversion into the cis isomer was reported. However, upon repetition of their work, not more than a 5% yield of the cis isomer could be isolated.

The following is a general description of the procedure we adopted to prepare these cis compounds.

The trans isomer was dissolved in chloroform (100-150 ml) and the solution was placed in a photochemical reactor. This reactor incorporated a thermometer immersed in the solution to be irradiated.

The reaction vessel was partly submerged in a dry ice-acetone bath. The cooling jacket of the reactor was connected to a recycling pump and a cooling mixture of 1:1 ethanol-ethylene glycol was passed through the jacket, (see Diag. I). The coolant was pumped through a copper coil immersed in a dry ice-acetone bath ($T \simeq -60^{\circ}$) and the flow of this alcohol mixture could be varied to alter the temperature of the irradiated solution.

The solution was irradiated with a high pressure 125W Philips mercury lamp and maintained at a temperature of -20° to -30° during the irradiation. After a period of 2 hr the chloroform solution was passed through a column of alumina. All unchanged *trans* isomer was washed through the column with chloroform while the *cis* isomer remained adsorbed in a sharp zone at the top of the column. The chromatography was carried out in a darkened room at 0°; all solvents used were cooled to this temperature. The fraction containing the *trans* isomer was concentrated by evaporation to *c.* 110 ml and this solution was irradiated in the reactor. The separation of the two isomers from the *cis-trans* mixture formed was performed in the same manner and on the same column as that used for the first separation. After this sequence had been repeated several times, a usable quantity of the *cis* isomer was adsorbed at the top of the column.

The zone containing this isomer was eluted with chloroform containing 4% ethanol, and the resulting solutions were filtered. The solvent was removed under reduced pressure (temperature less than -5°)

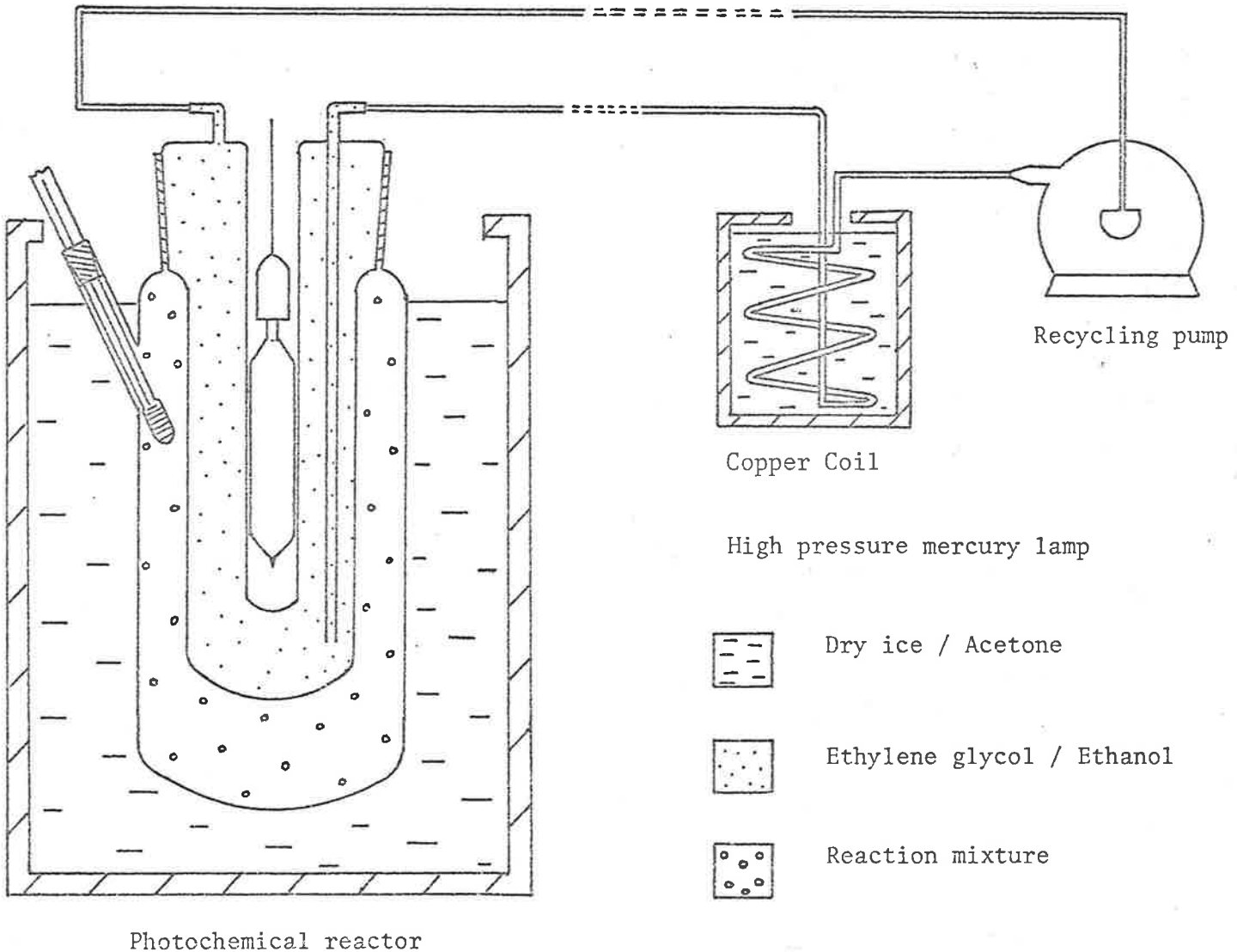

Recycling pump
Copper Coil
High pressure mercury lamp
Dry ice / Acetone
Ethylene glycol / Ethanol
Reaction mixture
Photochemical reactor

Diagram 1

so that the cis isomer attained the solid state as quickly as possible.

The solid cis isomer obtained in this way was immediately treated with acetyl chloride either in its pure state or diluted by an inert solvent (e.g. analytical grade dry benzene).

Gas Chromatography.

A Perkin-Elmer gas chromatograph was used with different columns (see below), the nature of which depended on the mixture being analysed. Nitrogen was used as the carrier gas; the flow rate was c. 100 ml/min. for 1/4" columns and 30 ml/min. for 1/8" columns. Samples of pure azonaphthalenes and chloroazonaphthalenes, and of mixed products (as used for peak identification and analysis, respectively), were injected as 2-4% (W:V) solutions in acetone (2-10 mμ per injection).

The mixtures containing substituted and unsubstituted 1-phenylazonaphthalenes were analysed with a 12 ft. by 1/8 in. aluminium/5% Carbowax 1500 column (polyethylene glycol) at 200-202°. The following retention times were observed: 1-phenylazonaphthalene (9) (13 min. 28 sec.); 1-(4'-chlorophenylazo)naphthalene (52) (24 min. 21 sec.); 1-(2'-chlorophenylazo)naphthalene (53) (28 min. 7 sec.); and 4-chloro-1-phenylazonaphthalene (55) (21 min. 25 sec.). An aluminium 6ft. by 1/4 in. 5% QF-1 column (Silicon-Fluoro/FS1265) was also used at 198-200° to separate these mixtures into their components. The retention times observed were: 1-phenylazonaphthalene (14 min. 37 sec.); 1-(4'-chlorophenylazo)naphthalene (19 min. 45 sec.); 1-(2'-chlorophenylazo)naphthalene

(23 min. 4 sec.); and 4-chloro-1-phenylazonaphthalene (18 min. 42 sec.).

The mixtures containing chlorinated and non-chlorinated 2-phenylazonaphthalenes were analysed using a 6 ft. by 1/4 in. aluminium/5% QF-1 column (Silicone-Fluoro/FS1265) at 210-212°. The following retention times were observed: 2-phenylazonaphthalene (10) (11 min. 33 sec.); 2-(4'-chlorophenylazo)naphthalene (33) (19 min. 11 sec.); 2-(2'-chlorophenylazo)naphthalene (34) (20 min. 9 sec.); and 1-chloro-2-phenylazonaphthalene (35) (21 min. 40 sec.).

The composition of the solutions containing mixtures of 2,2'-azonaphthalenes was determined using a 6 ft. by 1/4 in. aluminium/5% SE30 column (silicon gum rubber) at 268-270°. The following retention times were observed: 2,2'-azonaphthalene (4) (2 min. 9 sec.); and x -chloro-2,2'-azonaphthalene (69) (3 min. 14 sec.).

The analysis of mixtures containing 1,2'-azonaphthalene and substituted 1,2'-azonaphthalenes was accomplished by the use of a 5ft. by 1/8 in. aluminium/10% SE52 column (silicon gum rubber) at 270°. The following retention times were recorded: 1,2'-azonaphthalene (5) (7 min. 1 sec.); and 4-chloro-1,2'-azonaphthalene (84) (11 min.).

Calibration curves relating peak areas to the percentage of a particular compound in a mixture were not determined. Any product ratios (relative peak areas) given are very approximate.

1. Dark Reaction of cis-1-Phenylazonaphthalene with Acetyl Chloride. Preparation of cis-1-Phenylazonaphthalene (11).

trans-1-Phenylazonaphthalene (530 mg) was dissolved in chloroform (120 ml) and the solution was irradiated at -20° to -25° for 1.5 hr. The deep red solution formed was passed through a silica column and the trans isomer was eluted from the column with chloroform. The cis isomer remained adsorbed at the top of the column. The solution of the trans isomer was evaporated to a volume of c. 120 ml and the resulting mixture irradiated for 1.5 hr. The procedure described above was repeated on the photoisomerization mixture formed by this irradiation. The same column was used for the separation of the two isomers as that used for the first separation. After several such sequences the accumulated cis-2-phenylazonaphthalene was eluted from the column with methanol-chloroform (5% V:V). Reduced pressure distillation (temperature less than -5°) of the solvent from that fraction afforded a red-orange crystalline mass of cis-1-phenylazonaphthalene (11) (134 mg, 26%). This material was not purified further, and was used as soon as possible in the next step (see next paragraph). All of the above described procedures for isolating the cis compound were performed in the complete absence of light as far as possible.

Reaction of cis-1-Phenylazonaphthalene with Acetyl Chloride.

To the solid cis-1-phenylazonaphthalene (134 mg) was added acetyl chloride (1 ml) at 0-5° in the absence of light. A deep blue-purple

colouration developed immediately the acid chloride came into contact with the cis isomer. This colour gradually faded during the course of approximately 35 sec , being replaced by a red-brown colour. The reaction was quenched by the addition of cold water (10 ml) 60 sec after the moment of mixing. The mixture was vigorously agitated both before and during quenching. A brown-purple resinous material was formed, and both this and the aqueous layer were extracted with dichloromethane. The separated dichloromethane layer was washed (water), dried ($CaCl_2$), and evaporated to dryness to yield a blue-purple residue (260 mg of viscous oil). This mixture was chromatographed on a column of silica.

The first band was eluted with petroleum and this yielded trans-1-phenylazonaphthalene (9) (30 mg) when the eluate was evaporated to dryness. This compound was identified by direct comparison (mixed m.p. and infrared spectrum) with an authentic sample.

Elution with chloroform-petroleum (15-20% V:V) and evaporation of the solvent gave a semi-solid yellow compound (28 mg). This compound was not identified. The infrared spectrum (chloroform) did not show any absorptions attributable to the presence of amino, carbonyl, or azo groups in the molecule.

A third fraction was eluted from the column (chloroform-petroleum, 40-60%) and afforded a dark brown solid (35 mg). The infrared spectrum (chloroform) showed carbonyl absorptions at 1710 and 1690 cm^{-1} and the spectrum was practically identical with that of a fully characterized sample of 1-(N,N'-diacetyl-4'-chlorophenylhydrazo)naphthalene (56).

Further elution of the column was effected with chloroform, and the evaporation of the eluate to dryness left a red-brown oil (77 mg). The infrared spectrum (chloroform) showed a strong band at 1695 (C=O) cm^{-1} and a weaker band at 3230 (N-H) cm^{-1}.

The column was finally eluted with methanol-chloroform (10% V:V) and after removal of the solvent a red-purple solid (69 mg) remained. The infrared spectrum of this material showed bands inter alia at 3345 (N-H), 1695 (C=O), and 1675 cm^{-1}. This product was treated (3 hr) with boiling aqueous ethanolic potassium hydroxide (20% W:V) solution (10 ml). The final reaction mixture was diluted with water and the suspension formed was extracted with dichloromethane. The separated extract was washed (water), dried (Na_2SO_4), and evaporated to dryness to yield a pale brown solid (55 mg). The infrared spectrum of this product was identical with that of the material before the attempted hydrolysis. Thin-layer chromatography showed that no azo compounds were present in the hydrolysis product.

The products isolated from the second and third fractions were not pure, and each contained an appreciable quantity of material from the other fraction (by comparison of the infrared spectra). The two samples were combined (112 mg) and subjected to alkaline hydrolysis (refluxing aqueous alcoholic potassium hydroxide, 20% W:V) followed by aerial oxidation. The reaction mixture was poured into water. The suspension so formed was extracted (dichloromethane) and the extract washed, dried, and evaporated to dryness. A brown-red oil (90 mg)

remained and this was chromatographed on a preparative plate (silica-dichloromethane/petroleum 16% V:V). Two broad orange bands separated on the plate. Thin-layer chromatography indicated that both bands contained a mixture of compounds. The two bands were removed from the plate, extracted (chloroform), and the combined extracts were filtered and evaporated to dryness. The yellow-orange solid residue (58 mg) was dissolved in acetone and subjected to qualitative gas chromatography. The mixture was resolved into four peaks. By comparison with the retention times of authentic samples, these peaks were identified as belonging to 1-phenylazonaphthalene (9), 1-(4'-chlorophenylazo)naphthalene (52), 4-chloro-1-phenylazonaphthalene (55), and 1-(2'-chlorophenylazo)naphthalene (53). The first three compounds in the order presented were in the approximate ratio of 1:4:2. Only a very small quantity of 1-(2'-chlorophenylazo)naphthalene was present in the mixture. The peaks corresponding to the chloro substituted compounds could not be completely resolved, and the above relative peak areas (obtained by cutting out the peaks and weighing the paper contained therein) must be taken as being very approximate.

2. Dark Reaction of cis-2-Phenylazonaphthalene with Acetyl Chloride. Preparation of cis-2-Phenylazonaphthalene (12).

trans-2-Phenylazonaphthalene (1.2 g) was irradiated (3.25 hr) in chloroform (150 ml), the temperature of the solution being kept at

-20° to -25°. The mixture of cis and trans isomers so obtained was passed through an alumina column (0°). The trans isomer was eluted from the column with chloroform, while the cis isomer remained adsorbed at the top. The solution containing the trans isomer was concentrated (c. 150 ml), irradiated under the same conditions as described before and then chromatographed on the same column. This sequence was repeated twice more. The cis-2-phenylazonaphthalene was then eluted from the column with chloroform containing 3% (V:V) ethanol. The solvent was removed from this fraction under reduced pressure at a temperature below -10°. The residue consisted of deep red crystals of cis-2-phenylazonaphthalene (12) (157 mg). All these steps were carried out in the absence of light.

Reaction of cis-2-Phenylazonaphthalene with Acetyl Chloride.

Acetyl chloride (4 ml) was added to cis-2-phenylazonaphthalene (157 mg) at 0° in the absence of light. The mixture immediately acquired a deep purple-blue colour which after approximately 45 sec changed to a red-brown colour. The reaction was quenched after 60 sec by the addition of ice-water (20 ml) to the vigorously stirred reaction mixture. A blue-black gum was formed. This aqueous mixture was extracted with chloroform, and the extract was washed (water) and dried ($CaCl_2$). When the chloroform solution was evaporated to dryness it yielded a red-brown viscous oil (330 mg). The infrared spectrum (chloroform) of this mixture showed bands inter alia at 3300 (broad, N-H), 1680 (broad, C=O), 1710 (C=O), and 1695 (C=O) cm^{-1}. The reaction product was then chromatographed on a column of silica (petroleum-chloroform).

The first fraction (chloroform-petroleum 10% V:V) afforded trans-2-phenylazonaphthalene (10) (12 mg). This product was identified by direct comparison (mixed m.p. and infrared spectrum) with an authentic sample.

The second band was eluted with chloroform-petroleum (35-45% V:V) and evaporation of the solvent yielded a brown solid (45 mg). The infrared spectrum (chloroform) of this product showed strong carbonyl absorptions at 1710 and 1695 cm^{-1} and a weak N-H stretching absorption at 3240 cm^{-1}. The infrared and n.m.r. spectra of this mixture were similar to those of an authentic sample of 2-(N,N'-diacetyl-4'-chlorophenylhydrazo)-naphthalene (37).

The column was eluted with chloroform and removal of the solvent from this fraction gave a dark brown oil (85 mg). The infrared spectrum (chloroform) showed strong bands at 3240 (N-H) and 1695 (C=O) cm^{-1}.

A fourth fraction was eluted with methanol-chloroform (10% V:V) and yielded a dark brown solid (75 mg). The infrared spectrum (chloroform) showed bands at 3345 (N-H), 1695 (C=O), and 1675 cm^{-1}. This solid was treated with boiling aqueous ethanolic potassium hydroxide solution (20% W:V). After 2 hr the solution was cooled, diluted with water, and extracted with dichloromethane. The extract was washed (H_2O) and dried (Na_2SO_4). Evaporation of the solvent yielded unchanged starting material as shown by comparison with an authentic sample. The presence of azonaphthalenes in the hydrolysis mixture could not be detected using thin-layer chromatography.

The products from the second and third fractions could not be purified, each being contaminated by the other (infrared spectral data). The two fractions were combined and heated under reflux with aqueous ethanolic potassium hydroxide solution for 3 hr. The work-up procedure was essentially the same as that described for the attempted hydrolysis of the material from the fourth fraction (see previous paragraph). Removal of the solvent from the dichloromethane extract gave a red-brown oil (120 mg). This mixture was subjected to column chromatography (alumina-chloroform/petroleum 10% V:V) and a single broad band was collected. The solution was evaporated to dryness to give a yellow-orange solid (70 mg). Thin-layer chromatography (silica-dichloromethane/petroleum 20% V:V) showed two widely separated yellow-orange spots on the adsorbent. The mixture was dissolved in acetone (5% W:V) and analysed by means of gas chromatography. Four peaks were resolved and these were identified (comparison of retention times with those of authentic samples) as belonging to 2-phenylazonaphthalene (10), 2-(4'-chlorophenylazo)naphthalene (33), 2-(2'-chlorophenylazo)naphthalene (34), and 1-chloro-2-phenylazonaphthalene (35). The chloroazonaphthalene peaks overlapped to a considerable extent and consequently accurate comparative yields could not be determined. 2-Phenylazonaphthalene and 2-(4'-chlorophenylazo)naphthalene were the major products, both being present in approximately the same quantity. An unidentified compound appeared as a single peak with a retention time of 22 min 9 sec.

3. Dark Reaction of cis-2,2'-Azonaphthalene with Acetyl Chloride.

Preparation of cis-2,2'-Azonaphthalene (7).

A chloroform solution (150 ml) of trans-2,2'-azonaphthalene (500 mg) was irradiated for 2 hr at -25 to -30°. The mixture of cis and trans isomers formed was separated into its components by chromatography on alumina (chloroform) at 0°. The cis isomer remained on the column, and the partially evaporated solution (c. 150 ml) containing the trans isomer was returned to the reactor and irradiated for another 2hr. This was repeated three times, the same column being used on every occasion to separate the isomers. The cis isomer adsorbed at the top of the column was removed by elution with ethanol-chloroform (5% V:V). Evaporation of the solvent (reduced pressure) at a temperature less than -5° afforded yellow-orange crystals of cis-2,2'-azonaphthalene (7) (122 mg, 25%). All the steps involved in isolating the cis compound were carried out in the absence of light.

Reaction of cis-2,2'-Azonaphthalene with Acetyl Chloride.

cis-2,2'-Azonaphthalene (122 mg) was treated with acetyl chloride (2 ml) at 0° in the absence of light. The mixture was vigorously stirred and it immediately acquired a deep blue-purple colour. After a period of 60 sec from the instant of mixing, 10 ml of ice-water was stirred rapidly into the reaction mixture. The resulting aqueous suspension was extracted several times with dichloromethane. The combined extracts were washed (water), dried (Na_2CO_3), and afforded a dark blue resinous material

(164 mg) when evaporated to dryness. The infrared spectrum (chloroform) showed bands (inter alia) at 3200-3350 (complex, N-H) and 1675-1710 cm^{-1} (broad, C=O). This product was chromatographed on a preparative plate (silica) using chloroform-petroleum (10% V:V) as the eluting solvent.

Only one orange band appeared on the plate and this was removed; the compound was extracted from the adsorbent; and the extract was filtered and evaporated to dryness. The yellow-orange solid was identified as trans-2,2'-azonaphthalene (14 mg). The melting point of this product was not depressed upon admixture with an authentic sample, and the two infrared spectra were identical.

The remaining material on the plate was extracted from the silica and removal of the solvent yielded a dark blue semi-solid (142 mg).

This mixture was then subjected to alkaline hydrolysis-oxidation. The blue-black gum (142 mg) was heated under reflux with aqueous ethanolic potassium hydroxide (20% W:V) solution (10 ml) for 2 hr. Air was drawn through the mixture for an additional 1 hr. The mixture was cooled, diluted with water, and extracted three times with dichloromethane. The dried extract (Na_2SO_4) was evaporated to dryness and the dark-coloured residue (112 mg) was chromatographed on a preparative plate (silica-petroleum/dichloromethane 15% V:V).

Partial separation of two orange bands was achieved. These were removed and extracted separately. Thin-layer chromatography showed that each fraction contained a mixture of compounds. The two extracts were combined and evaporated to dryness. The yellow-orange solid (52 mg)

that remained was dissolved in acetone (2% W:V) and examined using qualitative gas chromatography. Only two peaks were resolved. The retention time of one peak was 2 min 9 sec and this was identical to the retention time of an authentic sample of 2,2'-azonaphthalene (4). The second peak had an identical retention time to that observed for a sample of x-chloro-2,2'-azonaphthalene (69) previously isolated from the photoreaction of 2,2'-azonaphthalene with acetyl chloride (see Experimental I.3). The peak areas were in the approximate ratio of 1:1.

4. Dark Reaction of cis-1,2'-Azonaphthalene with Acetyl Chloride. Preparation of cis-1,2'-Azonaphthalene (8).

A solution of trans-1,2'-azonaphthalene (600 mg) in chloroform (130 ml.) was irradiated for 2 hr at -20 to -25°. The deep red solution was then passed through an alumina column. Elution with cold (0°) chloroform (c. 300 ml) washed the trans isomer from the column and left the cis isomer adsorbed in a sharp band at the top of the column. The solution of the trans isomer was reduced in volume to c.120 ml. by distillation, and the concentrate was irradiated under the same conditions as before. The photoisomerization mixture was then chromatographed and the complete cycle repeated once again. The cis isomer that collected on the column was removed by elution with methanol-chloroform (4% V:V). The solvent in this fraction was distilled off under reduced pressure (temperature less than -5°) and the residue of cis-1,2'-azonaphthalene (8) was obtained as red-orange plates (162 mg, 28%). All of the above

isolation procedures were carried out where possible in the complete absence of light.

Reaction of cis-1,2'-Azonaphthalene with Acetyl Chloride.

Cold (0°) acetyl chloride (3 ml) was added to cis-1,2'-azonaphthalene (162 mg) in almost complete darkness. A deep blue-purple colouration developed the instant that the acetyl chloride came in contact with the azonaphthalene. The mixture was stirred vigorously, and after a time interval of 60 sec from the moment of mixing the acid chloride was destroyed by the addition of excess cold water (10 ml). The dark blue aqueous mixture was extracted with chloroform and the washed and dried extract was evaporated to dryness. A red-brown oily residue (285 mg) remained and this was chromatographed on silica (preparative plate) using chloroform-petroleum (10% V:V) as the solvent.

The single orange band was removed from the plate and extracted with chloroform. This extract afforded trans-1,2'-azonaphthalene (5) (22 mg), m.p. 144-145° (alone or admixed with the authentic compound).

The remaining silica on the plate was removed, washed with chloroform, and the washings filtered and evaporated to dryness. The infrared spectrum of this grey-blue gum showed bands inter alia at 3300-3200 (N-H), 1710-1690 (broad, C=O), and 1670 cm^{-1} (broad, C=O). Separation of this mixture into its components was not attempted. The mixture was immediately subjected to alkaline hydrolysis-oxidation.

The mixture (255 mg) was dissolved in ethanol (10 ml) and to this solution was added an aqueous potassium hydroxide solution (2 g in 1 ml

water). The reaction mixture was heated under reflux for 2 hr and air was bubbled through the cooled solution for a further 0.5 hr. Water (100 ml) was added to the red-brown solution and the suspension was extracted with dichloromethane. The separated dichloromethane layer was washed, dried (Na_2SO_4), and the solvent removed *in vacuo*.

The residual solid was chromatographed on a preparative plate (silica-dichloromethane/petroleum 16% V:V) and two closely spaced yellow-orange bands were gradually separated. These were removed separately and extracted with chloroform; and the extracts were examined using thin-layer chromatography. Both solutions were found to contain a similar mixture of compounds. The two extracts were combined and evaporated to dryness; and the residue (42 mg) was dissolved in acetone (5% W:V). Gas chromatography of this product gave two major and two minor peaks. The retention times for the two larger peaks were identical to those obtained for authentic samples of 1,2'-azonaphthalene (5) and 4-chloro-1,2'-azonaphthalene (84). The remaining peaks were not identified.

The adsorbent contained in the base line of the preparative plate was collected and washed with chloroform. Evaporation of the solvent from the washings yielded a dark brown resinous material (44 mg). The infrared spectrum (chloroform) of this mixture closely resembled that of a fully characterized sample of 4-chloro-N,N'-diacetyl-1,2'-diamino-1',2-binaphthyl (80) obtained from the photoreaction of 1,2'-azonaphthalene with acetyl chloride.

5. Dark Reaction of cis-1,1'-Azonaphthalene with Acetyl Chloride.

Preparation of cis-1,1'-Azonaphthalene (6).

trans-1,1'-Azonaphthalene (704 mg) was dissolved in chloroform (150 ml) and the solution was irradiated at -25 to -30° for 3 hr. The photoisomerization mixture was chromatographed on an alumina column (chloroform) at 0°.

The first fraction eluted from the column was evaporated to dryness. This yielded trans-1,1'-azonaphthalene (460 mg).

Further elution with methanol-chloroform (10% V:V) removed the cis isomer from the column. The solvent was removed from the eluate by reduced pressure distillation (temperature less than 0°) to give cis-1,1'-azonaphthalene (6) (238 mg, 35%) as deep red-orange crystals. The chromatography and solvent removal were carried out in the total absence of light.

Reaction of cis-1,1'-Azonaphthalene with Acetyl Chloride.

Acetyl chloride (3 ml) was added to cis-1,1'-azonaphthalene at 0° in almost complete darkness. A deep purple-black solution was formed immediately and the addition of more acetyl chloride (5 ml) gave a brown solution containing some suspended solid. After a short time (4 min) from the moment of mixing the acid chloride was destroyed by dropwise addition of ice-cold water. As the water was slowly added the deep purple-blue colour gradually returned. Further addition of water (8 ml) yielded a green-blue solution and an off-white precipitate. The suspension was left at room temperature for 15 hr and at the end of this

time the blue-black colour was again present. The aqueous suspension was extracted with dichloromethane, and the extract was washed with water. The blue-black colour faded and the organic layer became red-orange in colour. Removal of the solvent from the dried extract afforded a purple-black viscous oil (388 mg). The infrared spectrum (chloroform) of this mixture showed bands inter alia at 3290 (N-H), 1700 (broad, C=O), and 1680 cm^{-1} (C=O).

This oil was subjected to column chromatography (silica-petroleum/chloroform). The first fraction was eluted with chloroform-petroleum (15% V:V) and afforded 1,1'-azonaphthalene (3) (33 mg) as an orange solid. This compound was identified (mixed m.p. and infrared) by comparison with an authentic sample.

Elution with chloroform-petroleum (30-40% V:V) gave a second fraction and this yielded a pale purple oil (97 mg). The infrared spectrum (chloroform) showed strong carbonyl absorptions at 1715 and 1700 cm^{-1}. No bands were present in the region 3000-3500 cm^{-1}.

The third fraction was eluted with chloroform-petroleum (45-55% V:V) and gave a red-brown oil (210 mg). The infrared spectrum (chloroform) showed bands at 3200 (N-H) and 1690 (C=O) cm^{-1}, as well as weaker bands at 1710-1700 cm^{-1} (broad, C=O) which were attributed to the presence of compound(s) from the second fraction.

When allowance was made for this contaminant, the infrared spectrum closely resembled that of a previously characterized sample of 4-chloro-N,N'-diacetyl-1,1'-diamino-2,2'-binaphthyl (94) obtained from the

photoreaction of 1,1'-azonaphthalene with acetyl chloride. A portion of the oil (150 mg) was crystallized from aqueous ethanol (10% V:V). The collected solid was recrystallized several times from the same solvent mixture and yielded an off-white powdery solid (20 mg), m.p. 340-344° (alone or admixed with an authentic specimen of the above-mentioned binaphthyl). The infrared spectra of the two samples were identical.

The material isolated from the second fraction (97 mg) was treated with boiling aqueous ethanolic potassium hydroxide solution (20% W:V) for 2 hr. Air was passed through the cooled mixture for an additional 1 hr. The mixture was diluted with water and extracted with chloroform. The extract was washed, dried, and evaporated to dryness. The residue (82 mg) was chromatographed on a preparative plate (silica) using chloroform-petroleum (5% V:V) as the diluting solvent. No substituted or unsubstituted azonaphthalenes were isolated from the plate. The silica on the plate was removed, extracted (chloroform), and the extract evaporated to dryness. A dark brown solid remained (82 mg) and the infrared spectrum (chloroform) of this material was essentially identical with that of the starting material.

The red-brown oil (60 mg) from the third fraction was treated in a similar fashion to that described in the foregoing reaction. The mixture was recovered unchanged at the end of the reaction.

WORK DESCRIBED IN PART III.

Materials and Reference Compounds.

2-Phenylazonaphthalene (10), 2-(4'-chlorophenylazo)naphthalene (33), 2-(2'-chlorophenylazo)naphthalene (34) and 1-chloro-2-phenylazonaphthalene (35) were all available from previous work (see Experimental I). Azobenzene was a commercial preparation and was purified by column chromatography and recrystallization to give orange flakes, m.p. 67-68° (lit.[177] 68°).

4-Chloroazobenzene (30).

This compound was prepared according to the method described by Lewis and Mayfield.[104] After purification by column chromatography and recrystallization from methanol, 4-chloroazobenzene was obtained as orange needles, m.p. 86-87° (lit.[104] 86-87°).

Oxalyl Chloride.

A commercial sample was purified by distillation from linseed oil (10 ml per 100 ml of acid chloride) and obtained as a colourless liquid, b.p. 62-63° (lit.[161] 63.5°).

Malonyl Dichloride.

The procedure used was similar to that employed by Raha[160] to prepare this compound.

A mixture of dry malonic acid and freshly distilled thionyl chloride was heated (45-50°) for 2 days under an atmosphere of nitrogen.

The malonyl dichloride was fractionally distilled (collected b.p. 55-60°/ 18 mm) and collected as a colourless solid in a container surrounded by an acetone-dry ice cooling bath. The compound was found to be stable if kept at this temperature, but at room temperature it rapidly darkened to form a red-orange liquid. Care was exercised to ensure that the temperature in the distilling vessel did not exceed 80°, otherwise a violent reaction occurred. The freshly distilled malonyl dichloride was used in all reactions.

Reaction Sequences.

1. Photoreaction of 2-Phenylazonaphthalene with Oxalyl Chloride.

2-Phenylazonaphthalene (3 g) was dissolved in oxalyl chloride (115 ml) and the red-orange solution formed was irradiated for 75 min in a water-cooled photochemical reactor with a high pressure 125W mercury lamp. The ultraviolet spectrum of the solution indicated that no unchanged azonaphthalene was present. The reaction mixture was a very pale yellow in colour and contained a precipitate of off-white crystals. After being cooled to c. 15° (ethanol-dry ice) the suspension was filtered and the filtrate was put aside for further study.

The collected yellow needles were washed with light petroleum, and dried under vacuum (5 mm and room temperature) to yield green-yellow needles (2.9 g), m.p. 78-88°. The compound was found to be very unstable in the presence of moisture. It fumed when exposed to air, hydrogen chloride gas being evolved. All further attempts to purify it by

recrystallization (dry petroleum, chloroform, benzene) were not successful and meaningful analytical data could not be obtained. The infrared spectrum of this reaction product (chloroform) showed bands at 3310, 3375, 1780, 1710, 1630, 1600, 1500, and 1370 cm^{-1}.

The product from the photochemical reaction (200 mg) was dissolved in aqueous methanolic potassium hydroxide (10 ml) and boiled under reflux for 2 hr. After dilution with water the reaction mixture was extracted with ether. The ethereal solution was dried and then evaporated to dryness. The residue was chromatographed on alumina (petroleum-chloroform). Elution yielded 2-(4'-chlorophenylazo)naphthalene (33) (12 mg, 8%) and 2-phenylazonaphthalene (10) (122 mg, 84%). These compounds were identified by direct comparison (mixed m.p. and infrared spectrum) with samples of the authentic compounds.

Treatment of the Photo-product with Methanol.

The reaction product (1.3 g) was suspended in methanol (15 ml) and the mixture was boiled under reflux until all of the solid had dissolved. The solution was left to cool; and pale yellow crystals were deposited. Several recrystallizations (methanol) of this material afforded the methyl ester of x-chloro-N-oxalyl-2-phenylhydrazonaphthalene (136) as colourless crystals (900 mg, 70%), m.p. 154-155° (Found: C, 64.2; H, 4.19; O, 13.5; N, 8.2; mol.wt. (mass spectrum) 354. $C_{19}H_{15}N_2O_3Cl$ requires: C, 64.3; H, 4.23; O, 13.5; N, 7.9; Cl, 10.0%; mol.wt. 354.5). The infrared spectrum (chloroform) of the compound showed bands at 3310 (N-H), 1765 (C=O), 1700 (C=O), 1695, 1630, 1600, and 1500 cm^{-1}.

Treatment of the Photo-product with Ethanol.

The photo-product (1.1 g) was heated in ethanol (20 ml) until no more solid material was present. Upon cooling the solution deposited pale yellow crystals which after repeated recrystallization from ethanol gave the ethyl ester of x-chloro-N-oxalyl-2-phenylhydrazonaphthalene (135) as colourless crystals (790 mg, 70%), m.p. 136.5-137.5° (Found: C, 64.3; H, 4.56; O, 13.8; N, 7.4; Cl, 9.8; mol.wt. (mass spectrum) 368. $C_{20}H_{17}N_2O_3Cl$ requires: C, 65.1; H, 4.6; O, 13.2; N, 7.6; Cl, 9.6%; mol.wt. 368.5). The infrared spectrum (carbon tetrachloride) of the product showed bands at 3320 (N-H), 3000, 1745 (C=O), 1705 (C=O), 1625, 1600, 1570, 1360, 1250, 1230, and 1115 cm^{-1}.

An analytically pure sample (236 mg) of this compound (135) was heated under reflux with aqueous ethanolic potassium hydroxide (10 ml) for 1.5 hrs. Air was bubbled into the red-orange suspension for an additional 1 hr. The reaction mixture was extracted (benzene); and the extract was washed (water) and finally dried ($MgSO_4$). The residue obtained (142 mg) after evaporation of the benzene from the solution was dissolved in acetone (2% W:V) and subjected to gas chromatography at 258° using a 5 ft. by 1/8 in. 5% SE52 column with nitrogen as the carrier gas (flow rate c. 30 ml./min.). Only one major peak was observed; and this had an identical retention time to an authentic sample of 2-phenylazonaphthalene. One other very small peak had a retention time that was identical to that obtained for a sample of 2-(4'-chlorophenylazo)naphthalene.

Recrystallization of the hydrolysis product (aqueous ethanol) yielded red-orange flat needles (130 mg, 88%), m.p. 82-83° (separately or admixed with an authentic sample), of 2-phenylazonaphthalene.

The filtrate obtained from the filtration of the original photochemical reaction mixture was then examined. The excess oxalyl chloride was removed by distillation under reduced pressure (20 mm). The residue (660 mg) was a yellow-brown solid; and the mixture could not be separated into its components by column chromatography (alumina or silica). The infrared spectrum (chloroform) of the photo-product showed bands at 3300, 3050, 2300, 1785, 1740, 1710, 1695, 1600, and 980 cm^{-1}.

Purification of the mixture was attempted using fractional distillation under reduced pressure. The pale yellow-orange glass collected (b.p. 160-165°/0.05 mm) was analysed (C, 60.6; H, 4.44; O, 13.7; N, 9.14; Cl, 11.6%) but no useful information could be obtained from these figures. The infrared spectrum (chloroform) showed bands at 3320, 1740, 1690, 1595, and 1500 cm^{-1}.

The material recovered from the column was dissolved in aqueous ethanolic potassium hydroxide and boiled under reflux for 1.5 hr. The reaction mixture was diluted with water, extracted with dichloromethane, and after being dried the dichloromethane solution was evaporated to dryness. The residue was chromatographed on alumina (chloroform-petroleum).

The first major band eluted from the column (chloroform-petroleum, 20% V:V) gave a red-orange solid (130 mg) after evaporation of the

solvent. Comparative thin-layer chromatography and qualitative vapour phase chromatography indicated that this mixture contained mainly 2-(4'-chlorophenylazo)naphthalene; with some 2-phenylazonaphthalene, 2-(2'-chlorophenylazo)naphthalene and an unidentified compound also being present.

Elution with petroleum-chloroform (40% V:V) and evaporation of the solvent afforded a pink-white solid (46 mg), m.p. 57-58°. The infra-red spectrum of this product (chloroform) showed bands at 3450, 3350, and 1630 cm^{-1}.

The mass spectrum showed a probable (M-2) peak at m/e 266 and the isomer peaks were in the correct ratio for a molecule containing one chlorine atom.

Further elution of the column yielded red-brown gums of unknown composition and structure.

Dark Reaction of 2-Phenylazonaphthalene with Oxalyl Chloride.

2-Phenylazonaphthalene (500 mg) was dissolved in oxalyl chloride (20 ml) and the solution was left in the dark at room temperature ($\simeq 20^{C}$) for 30 days. The oxalyl chloride was removed by distillation under reduced pressure and the residual red-orange oil chromatographed (alumina-petroleum). 2-Phenylazonaphthalene (470 mg, 94% recovery) was obtained from the first band eluted from the column.

2. Photoreaction of Azobenzene with Oxalyl Chloride.

Azobenzene (10 g) was dissolved in oxalyl chloride (105 ml) and the red-orange solution was irradiated in a water-cooled photochemical reactor for three hours with a high pressure mercury lamp. Oxygen-free nitrogen was bubbled through the solution during the irradiation. At the end of this period the solution was pale yellow, and a small quantity of precipitated solid was present. The excess oxalyl chloride was removed under reduced pressure leaving a dark yellow-green gum. Unsuccessful attempts were made to crystallize (dry ether, ether-chloroform) the product. After standing for several days the viscous material set to a hard glass. The mixture slowly decomposed on exposure to moist air with the evolution of hydrogen chloride gas.

The infrared spectrum (chloroform) showed bands at 3300, 3050, 2300, 1785, 1740, 1710, 1695, 1600, and 980 cm^{-1}. The mass spectrum showed an ion at m/e 399 which could be the molecular ion of a species with the formula $C_{16}H_9N_2O_4Cl_3$, M.W. 399. The isotope peaks had the correct relative abundance for a trichlorinated molecule.

Column Chromatography (silica).

Elution with chloroform-ethanol (2% V:V) and evaporation of the solvent from this fraction left a pale yellow-green glass (1.5 g). It was noted that the silica column cracked as the band passed down through it. The infrared spectrum of this glass (chloroform) showed bands at 3320, 2980, 2880, 2570, 2300, 1740, 1710, 1700, and 1685 cm^{-1}.

Column Chromatography (Alumina).

The crude photo-product (1 g) was preadsorbed on kieselguhr and chromatographed on an alumina column. The only fraction isolated was eluted from the column with chloroform-petroleum (20-40% V:V); and, after evaporation of the solvent it was obtained as a pale yellow glass (540 mg). The infrared spectrum of this product (chloroform) was essentially the same as that obtained for the fraction isolated from the silica column, except that the bands at 2880 and 2570 cm^{-1} were absent.

Reaction of the Photo-product with Ethanol.

A mixture of ethanol (25 ml) and the photo-product (1.2 g) was boiled under reflux (4 hrs). The pale orange solution was diluted with water and then extracted with chloroform. The extract was dried ($MgSO_4$) and the chloroform was removed by evaporation, leaving a red-orange oil (574 mg). The infrared spectrum of this material was identical to that obtained for the fraction isolated from the chromatography (alumina) of the photo-product. The spectrum showed bands at 3320, 2510, 2300, 1740, 1710, 1700, and 1685 cm^{-1}. The spectra of the chromatographed product and of the original photo-product were not identical.

The above fraction was then subjected to alkaline hydrolysis. The glass (1.5 g) was dissolved in aqueous ethanolic potassium hydroxide (50 ml) and heated under reflux for 2 hrs, while a stream of air was drawn through the mixture. The red-orange suspension was diluted with water and extracted with chloroform. After the extract was washed (water)

and dried ($MgSO_4$) the solvent was removed to give a red-orange oil. The oil was chromatographed on a preparative plate (silica-petroleum) and separated into two bands, one at the origin and a red-orange band near the top of the plate. Removal and extraction (chloroform) of the top band yielded a red-orange solid (640 mg, 80%) which was shown (gas chromatography) to be a mixture of 4-chloroazobenzene and 2-chloroazobenzene in the approximate ratio of 2:1. From the lower band was isolated an off-white solid (104 mg), m.p. 181-191°. The infrared spectrum (chloroform) showed strong bands at 3250 and 1690, 1600, 1540, and 1460 cm^{-1}. A Nujol mull of the same compound showed strong bands in the infrared at 3240 and 1645 cm^{-1}.

Treatment of the Photo-product with Water.

The photo-product (1 g) was heated under reflux with water (25 ml) for 3 hr. The cooled suspension was extracted with chloroform and dried ($MgSO_4$); and the solvent was removed. The infrared spectrum (chloroform) of the oily residue (780 mg) showed bands at 3320, 2570, 2300, 1740, 1710, 1700, and 1685 cm^{-1}. This spectrum was identical to those of samples obtained from the alumina column and the treatment of the photo-product with ethanol. Alkaline hydrolysis-oxidation of the mixture yielded a product that was found to contain 2-chloro- and 4-chloroazobenzene in the ratio of 1:2 (gas chromatography).

Treatment of the Photo-product with Ethanolic Potassium Hydroxide.

The photo-product (1.1 g) was dissolved in aqueous ethanolic potassium hydroxide solution; and the solution was boiled under reflux for 2.5 hrs. A pronounced deep red colour developed as the reaction proceeded. Air was drawn through the cooled mixture for 1 hr; the suspension was then diluted with water and extracted with dichloromethane. After the extract was washed (water) and dried ($MgSO_4$) the dissolved material was subjected to column chromatography (silica-petroleum/chloroform). The first band eluted from the column (chloroform-petroleum, 20% V:V) afforded a red-orange oil (514 mg, 90%) which slowly crystallized. Gas chromatographic analysis indicated that 2-chloro- and 4-chloroazobenzene were present in the approximate ratio of 1:2. Previous workers[104] obtained a more accurate figure of 64:100 for the product obtained from an identical reaction sequence.

3. Photoreaction of 2-Phenylazonaphthalene with Malonyl Dichloride.

A blood-red coloured solution of 2-phenylazonaphthalene (1.5 g) in freshly distilled (b.p. 58-67°, 16 mm) malonyl dichloride (50 ml) was irradiated in a photochemical reactor while oxygen-free nitrogen was bubbled through the solution. After a period of 2.5 hrs the solution was red-brown; and the ultraviolet spectrum showed that no unchanged azonaphthalene was present (λ_{max} 340 mμ absent). A very strong absorption was present at λ_{max} 300 mμ. Addition of samples of the reaction mixture to ethanol or chloroform gave solutions that

exhibited strong green-yellow fluorescence when exposed to ultraviolet light.

The reaction mixture was left standing at room temperature overnight while nitrogen was passed through the solution. At the end of this time the mixture had set solid due to the crystallization of an off-white compound. On many occasions this phenomenon occurred during the irradiation period. The reaction mixture was filtered under an atmosphere of nitrogen to yield a brown-yellow solid (156) (4.6 g) and a dark-coloured liquid filtrate. The filtrate was put aside for later study. Exposure to moist air caused the solid photo-product to decompose, with the evolution of hydrogen chloride. Eventually a dark brown gum was formed. Efforts to obtain this compound in pure form by recrystallization (chloroform, benzene, petroleum) were not successful. Hydrolysis with ethanolic potassium hydroxide did not yield any azo compound.

Treatment of the Photo-product (156) with Ethanol to yield Compound (157).

The yellow photo-product (6 g) was added gradually to a cooled vessel containing ethanol (50 ml). Vigorous effervescence occurred and hydrogen chloride gas was given off. The pale yellow precipitate (4.6 g) so formed was collected by filtration; and after multiple recrystallization from chloroform it gave compound (157) as colourless crystals (2 g), m.p. 121-122°. Purification could also be accomplished by sublimation (90-95°, 0.05 mm), which yielded colourless needles, m.p. 121-122°

(Found: C, 44.2; H, 3.18; O, 35.7; Cl, 16.3. $C_8H_7O_5Cl$ requires: C, 44.0; H, 3.20; O, 36.6; Cl, 16.3%; mol.wt. 218.5). The mass spectrum indicated a probable molecular ion at m/e 228 and the relative abundance of the isotope peaks suggested that no chlorine was present in this fragment.

The infrared spectrum of the compound (chloroform) showed bands at 2710, 2650 (complex), 1770, 1760, and 1635 cm^{-1}. The ultraviolet-visible spectrum (ethanol) possessed absorptions at λ_{max} 214 mμ (ε = 11,000) and λ_{max} 306 mμ (ε = 7,600).

The n.m.r. spectrum (deuterochloroform) showed signals at δ14.1 (singlet); 6.2 (singlet); 4.42 (quartet, J = 6.5 Hz); and 1.35 ppm (triplet, J = 6.5 Hz); and the corresponding integrated peak areas were in the ratio of 1:1:2:3. The resonance at δ14.1 ppm was removed by deuterium exchange (D_2O).

Treatment of Compound (157) with Ethanol at 78° to yield Compound (163).

The white solid (157) (2 g) was dissolved in ethanol (25 ml) and boiled under reflux for 3.5 hrs. The ethanol was removed *in vacuo* leaving a pale yellow liquid (163) (2.7 g). This liquid was distilled; and the fraction, b.p. 95-100°/0.05 mm, was collected as a colourless liquid (Found: C, 52.5; H, 6.65; O, 40.6. $C_{10}H_{14}O_6$ requires C, 52.2; H, 6.1 ; O, 41.7%; mol.wt., 230). The mass spectrum indicated a possible molecular ion at m/e 256. The ultraviolet spectrum (ethanol) showed absorption maxima at λ_{max} 246 mμ (ε = 3130) and 210 mμ (ε = 1420). The infrared spectrum (film) of this liquid showed bands at 3500, 3440,

2960, 1740, 1720, 1704, 1645, and 1610 cm^{-1}.

The n.m.r. spectrum (deuterochloroform) showed signals centred at δ14.0 (singlet); 4.25 (quartet, J = 7.0 Hz); 4.19 (quartet, J = 7.0 Hz); 4.72 (singlet); 3.72 (singlet); 1.43 (triplet, J = 7.2 Hz); 1.3 (triplet, J = 7.0 Hz); and 1.27 ppm (triplet, J = 7.6 Hz). The signal at 14.0 ppm was removed by deuterium exchange. The proton counts are recorded in Table V.

Treatment of the Liquid Filtrate from the Photoreaction.

The acid chloride solution from the filtration of the photoreaction was cooled and treated with water until no further reaction occurred on addition of water. The product was extracted (chloroform), the extract washed (water), and dried ($MgSO_4$). Removal of the solvent gave a yellow-green liquid (9.8 g) which was then dissolved in aqueous ethanolic potassium hydroxide for two hrs. The mixture was diluted with water and extracted with dichloromethane. The extract was dried (Na_2SO_4); and the dissolved material was chromatographed on an alumina column, (chloroform-petroleum). No azo compounds were isolated from the column. The only products eluted from the column were red-black gums of unknown structure. The infrared spectra of these mixtures (chloroform) showed bands at 3450, 3375, 1635, and 1610 cm^{-1}. Much dark-coloured material remained at the top of the column.

Photoreaction of 2-Phenylazonaphthalene with Malonyl Dichloride-Benzene.

2-Phenylazonaphthalene (5 g) was dissolved in malonyl dichloride (50 ml); and the solution was diluted to 100 ml by the addition of benzene (sodium dried, thiophene free). A benzene saturated stream of nitrogen was passed into the solution and the mixture was irradiated in a photochemical reactor with a high pressure mercury lamp for a period of 21 hrs. The reaction mixture had become black-brown; and, after the benzene was removed at room temperature by a stream of nitrogen, a dark brown elastic gum remained. This product was transferred in portions to a cooled vessel containing ethanol (100 ml). A slow evolution of hydrogen chloride gas occurred and a red-brown solution containing a yellow-orange solid in suspension was formed.

The solid was collected by filtration (20 g) and after several recrystallizations from chloroform formed colourless crystals, m.p. 121-122°. This compound was shown to be identical (infrared spectrum and mixed m.p.) to that isolated from the photoreaction where benzene was absent [compound (157)].

The ethanol was removed *in vacuo* from the filtrate and the red-brown liquid residue was extracted with boiling petroleum (3 x 150 ml). After each extraction the petroleum solution was decanted from the red-brown gum adhering to the sides of the vessel.

The solvent was evaporated from the petroleum extract leaving a yellow-brown liquid (12 g). The infrared spectrum of this mixture closely resembled that of an authentic sample of diethyl malonate. A

portion of this liquid (1.5 g) was heated under reflux with aqueous ethanolic potassium hydroxide solution for 1.5 hr. Extraction (dichloromethane) of the reaction mixture so obtained was followed by chromatography (alumina-petroleum/chloroform) of the material dissolved in the dichloromethane. No trace of azonaphthalenes was detected in the eluted fractions.

The infrared spectrum (film) of the petroleum insoluble red-brown gum showed bands at 3250, 3100, 1730, and 1715 cm^{-1}. This mixture was dissolved in chloroform, preadsorbed on kieselguhr and chromatographed (alumina) using a variety of eluting solvents. No material was obtained from fractions eluted with petroleum, chloroform, ethanol, and water-ethanol (10% V:V). Elution with acetic acid-ethanol (10% V:V) gave a fraction which afforded an orange oil. This residue was dissolved in ethanol (200 ml) and to this solution water (250 ml) was added. A precipitate was formed which was filtered off to yield a pale yellow-green solid (1.4 g), m.p. 330-340°. The infrared spectrum (chloroform) of this compound possessed bands at 3300, 3100, 1730, and 1600 cm^{-1}. The compound could not be purified sufficiently by recrystallization for microanalysis. The mass spectrum indicated a possible molecular ion at m/e 292, and no chlorine was present in this species. A sodium-fusion test also gave no positive indication of chlorine. Treatment with aqueous ethanolic potassium hydroxide did not yield any azo compounds.

Irradiation of Malonyl Dichloride.

Freshly distilled malonyl dichloride (50 ml; b.p. 52-56°, 16 mm) was irradiated in a Pyrex reactor (125W high pressure mercury lamp) for

24 hrs. The acid chloride was initially a pale yellow in colour and was kept under an atmosphere of oxygen-free nitrogen during the irradiation period. Samples of the reaction mixture were removed from the reactor at irradiation times of 1, 2, 4, 8, and 24 hrs; and the infrared spectrum of each sample was recorded. Before the irradiation was begun, the infrared spectrum of the malonyl dichloride (film) showed bands at 2950, 2900, 1800 (inflexion), and 1780 cm^{-1}. After being exposed to ultraviolet radiation for 24 hrs the liquid in the reactor was yellow-brown in colour, and the infrared spectrum of this material was identical with the spectrum of non-irradiated malonyl dichloride.

The malonyl dichloride was removed by distillation (b.p. 50-54°, 17 mm), leaving a red-brown oily residue. An identical residue (infrared spectrum) was obtained by distilling an authentic sample of malonyl dichloride under the same conditions.

Ethanol was added dropwise to the residue until evolution of hydrogen chloride ceased. No precipitate was formed; and the excess ethanol was removed under reduced pressure. The infrared spectrum (film) of the residue did not bear any resemblance to that obtained from a sample of the compound (157) derived from the photoreaction of 2-phenylazonaphthalene with malonyl dichloride.

Dark Reaction of 2-Phenylazonaphthalene with Malonyl Dichloride.

A solution of 2-phenylazonaphthalene (1 g) in malonyl dichloride (20 ml) was left at room temperature in a sealed tube under a nitrogen

atmosphere for 7 days. No precipitate was formed during this period; and the red-brown solution was then cooled and treated dropwise with ethanol until no further reaction occurred. The mixture was dissolved in chloroform; and the solution washed with water several times and dried ($MgSO_4$). After evaporation of the solvent the residue was subjected to column chromatography (alumina-petroleum/chloroform). The first fraction eluted (chloroform-petroleum, 5% V:V) contained 2-phenylazo-naphthalene (10) (928 mg), m.p. 82-83°.

4. Photoreaction I of Azobenzene with Malonyl Dichloride.

Azobenzene (1.5 g) was dissolved in malonyl dichloride (45 ml); and the red-orange solution was irradiated with a high pressure mercury lamp. After irradiation for 5 hrs the reaction mixture had set solid in the reactor and was a pale yellow in colour. Filtration of the mixture gave a canary-yellow solid and a dark brown liquid filtrate.

The solid photo-product was washed with dry petroleum and then added gradually, with stirring, to a cooled flask containing ethanol (40 ml). The yellow-orange suspension formed was left standing over-night and then filtered. The pale yellow solid (22 g) which was collected was recrystallized four times from chloroform. It formed colourless crystals (13 g), m.p. 119-121°. The compound was identical (infrared spectrum and mixed melting point) with a sample of the compound (157) isolated from the photoreaction of malonyl dichloride with 2-phenylazo-naphthalene.

The alcoholic filtrate was freed of all traces of ethanol and

boiled under reflux with aqueous methanolic potassium hydroxide for 2 hr. Air was drawn through the mixture for 1 hr; and the suspension was then extracted with dichloromethane. The extract was washed (water) and dried ($MgSO_4$); and the product contained in the extract was chromatographed on a preparative plate (silica-chloroform/petroleum 10% V:V). The only yellow-orange band present on the plate was extracted (chloroform); and after evaporation of the solvent a residue of an orange solid (35 mg, 2%) was obtained. After recrystallization from petroleum this compound formed orange plates of 4-chloroazobenzene (30), m.p. 86-87°, which was identified by direct comparison (mixed m.p. and the infrared spectrum) with an authentic sample.

The dark brown filtrate obtained from the filtration of the photoreaction mixture was then examined. Unreacted malonyl dichloride (2 ml) was removed by distillation under reduced pressure (52-56°, 18 mm); and the brown residue was treated with ethanol until no further reaction occurred. The mixture remaining after evaporation of the excess alcohol from the solution (last traces under reduced pressure) was heated with aqueous methanolic potassium hydroxide for 1 hr. Extraction of the reaction mixture with chloroform and evaporation of the solvent from the extract, yielded a yellow-brown gum which was then subjected to chromatography on a preparative plate (silica-chloroform/petroleum 20% V:V). The single yellow-orange band formed was removed from the plate and extracted with ether; and the solvent was removed to give a yellow-orange solid (16 mg). Recrystallization from light petroleum afforded 4-chlorobenzene as red-orange plates, m.p. 86-87°. This product was

identical to the previously isolated sample of 4-chloroazobenzere. The total yield of crude 4-chloroazobenzene was 51 mg (3%).

Photoreaction II of Azobenzene with Malonyl Dichloride.

A solution of azobenzene (200 mg) in malonyl dichloride (50 ml) was irradiated for 3 hrs in the absence of oxygen. Ultraviolet spectroscopy showed that no unchanged azobenzene was then present in the clear green-yellow solution. The infrared spectrum of a sample taken from the reaction mixture (film) was markedly different from that of the mixture before irradiation.

A further quantity of azobenzene (1.1 g) was added; and after a further period of irradiation (2.5 hrs) the solution was again pale yellow in cclour and no precipitate was formed.

An additional quantity of azobenzene (2 g) was then added and the mixture was irradiated again. Approximately 25 min after this last addition the reaction mixture had set to a solid mass, and no azobenzene remained.

The reaction mixture was filtered; and the collected pale yellow solid was washed (light petroleum). This product was added in portions to a cooled vessel containing methanol (40 ml). A vigorous reaction ensued (hydrogen chloride gas evolved), and cooling was required to keep the temperature at 5-10°. The off-white precipitate (20 g) was removed from the solution by filtration and washed several times with cold methanol. Further purification of this compound (169) by recrystallisation from chloroform yielded pale cream coloured crystals (5 g), m.p.

134-135° (Found: C, 41.3; H, 2.41; O, 38.9; Cl, 17.5; mol.wt. (mass spectrum) 204. $C_7H_5O_5Cl$ requires: C, 41.07; H, 2.44; O, 39.12; Cl, 17.35%; mol.wt. 204.5). The infrared spectrum showed bands at 3100, 3050, 2700 (complex), 1780, and 1760 cm^{-1}.

Absorptions appeared in the ultraviolet spectrum (ethanol) at λ_{max} 307 mμ (ε = 5990) and λ_{max} 214 mμ (ε = 8870). The n.m.r. spectrum (deuterochloroform) showed signals at δ3.9 (singlet); 6.18 (singlet); and 13.9 ppm (singlet). The resonance at 13.9 ppm was removed by deuterium exchange (D_2O).

A deep red colour was obtained when the compound (169) was treated with ferric chloride solution, and this indicates that it possesses an enolic hydroxy group.

A sample of the solid (169) was shaken with ethanol at room temperature (≃ 18°) for 5 min; and upon addition of alcoholic silver nitrate solution a faint white precipitate was formed. Under similar conditions at 30° a dense flocculent white precipitate was deposited. When compound (169) was treated with aqueous silver nitrate at room temperature only a faint white suspension appeared; but if the compound was first heated to 80-90° in water and silver nitrate solution was then added, a dense white precipitate was formed.

The compound (169) could also be readily sublimed (100-105°, 0.05 mm) as colourless crystals, m.p. 133-135°. This material was shown to be identical to the non-sublimed solid (infrared spectrum and mixed m.p.).

Treatment of Compound (169) with Methanol at 78° to yield Compound (170).

Compound (169) (3.2 g) was heated under reflux in methanol (25 ml) for 2.5 hrs. The removal of the methanol (reduced pressure) left a clear liquid which was further purified by distillation. Compound (170) was contained in the fraction b.p. 116-120°/0.05 mm. (Found: C, 47.03; H, 5.40; O, 47.2. $C_8H_{12}O_6$ requires C, 47.06; H, 5.88; O, 47.1%; mol.wt. 204). A peak at m/e 202 in the mass spectrum could be attributed to an $(M-2)^+$ fragment.

Bands appeared in the infrared spectrum at 2910, 1740, 1720 (inflexion), 1640, 1610, 1450, and 1280 (broad, complex) cm^{-1}. The ultraviolet spectrum (ethanol) showed absorptions at λ_{max} 248 mμ (ε = 3130) and λ_{max} 210 mμ (ε = 1500). The n.m.r. spectrum (deuterochloroform) showed singlets at δ3.63, 3.70, 3.74, 3.80, 3.85, and 13.2 ppm. The signal at δ13.2 ppm was removed by deuterium exchange (D_2O). The integrated peak areas were in the ratio of 1:3:3:1:1 in the order presented above.

WORK DESCRIBED IN PART IV.

1. Total Product Ratios.

Materials.

The benzoyl chloride, acetyl chloride, and propionyl chloride were commercial preparations which were purified by distillation before being used.

The remaining acid chlorides utilized were prepared by treating the respective carboxylic acid with thionyl chloride.[162] Trimethyl acetyl chloride was obtained as a colourless liquid, b.p. 105-106° (lit.[163] 105-106°). Dimethylacetyl chloride (colourless liquid) had b.p. 92-93° (lit.[164] 92-93°). Trichloroacetyl chloride was isolated by distillation as a colourless liquid, b.p. 104-106° (lit.[165] 106°). Dichloroacetyl chloride and monochloroacetyl chloride were both colourless liquids, the former had b.p. 107-109° (lit.[166] 107-108°) and the latter had b.p. 104-105° (lit.[167] 105°). The benzene employed was of analytical grade and was redistilled from sodium wire before use.

The 1-phenylazonaphthalene (9), 2-phenylazonaphthalene (10), 1,1'-azonaphthalene (3), 1,2'-azonaphthalene (5), and 2,2'-azonaphthalene (4) were available from earlier work (see Experimental I). 2-(2'-Chlorophenylazo)naphthalene (34), 2-(4'-chlorophenylazo)naphthalene (33), 1-(2'-chlorophenylazo)naphthalene (53), 1-(4'-chlorophenylazo)naphthalene (52), 4-chloro-1,1'-azonaphthalene (96), 4-chloro-1,2'-azonaphthalene (84), and x-chloro-2,2'-azonaphthalene (69) had also been previously prepared (see Experimental I and V).

General Procedure Adopted.

The azo compound (250 mg) was dissolved in the acid chloride (115 ml) and this solution was placed in a photochemical reactor and exposed to ultraviolet radiation emitted from a high pressure mercury lamp. In some cases a solution of the azonaphthalene in benzene (100 ml) containing the dissolved acid chloride (10 equivalents) was irradiated under identical conditions. Oxygen-free nitrogen was bubbled through the reaction mixture during the irradiation.

Samples of known volume were removed from the mixture at 5 min. intervals, accurately diluted with spectroscopic ethanol, and examined by ultraviolet spectroscopy. In this fashion the rate of reaction of the azo compound was observed, and the time needed for completion of the reaction was determined (Tables VI-IX).

The unchanged acid chloride (and benzene when employed) was then removed by distillation under reduced pressure. Comparative thin-layer chromatography (silica) was used to further verify that no unchanged azonaphthalene remained. The residue was then subjected to alkaline hydrolysis and aerial oxidation by heating the mixture with aqueous ethanolic potassium hydroxide (50 ml) for 1 hr. The reaction mixture was cooled, diluted with water (150 ml) and extracted with dichloromethane. The extract was dried ($MgSO_4$) and the dissolved product adsorbed on kieselguhr before being chromatographed on a column of alumina (petroleum-chloroform). The mixture of azo compounds was eluted as one broad band; and the solvent was removed by evaporation. The combined

yield (substituted and unsubstituted azonaphthalenes) was ascertained, and the mixture was then dissolved in acetone (4% solution) in readiness for analysis by quantitative gas chromatography.

Gas Chromatography.

A Perkin-Elmer 881 gas chromatograph was used with a 5 ft. by 1/8" aluminium/10% SE52 column (Silicon gum rubber) at 260-280° (depending on the mixture being analysed) with nitrogen as the carrier gas (flow rate c. 30 ml/min.).

The samples of pure phenylazonaphthalenes and azonaphthalenes (substituted and unsubstituted), of mixtures of known composition, and of mixed products (as used for peak identification, calibration, and analysis respectively), were injected as 4% (W:V) solutions in acetone (4-10µl per injection).

The column temperature was maintained at 258-260° for the analysis of mixtures of phenylazonaphthalenes. The following retention times were observed: 2-phenylazonaphthalene (2 min. 32 sec.); 2-(4'-chlorophenylazo)naphthalene (4 min.); 2-(2'-chlorophenylazo)naphthalene (6 min. 3 sec.); 1-phenylazonaphthalene (2 min. 51 sec.); 1-(4'-chlorophenylazo)naphthalene (4 min. 25 sec.); 1-(2'-chlorophenylazo)naphthalene (6 min. 26 sec.); and 1-chloro-2-phenylazonaphthalene (3 min. 44 sec.).

Analyses of mixtures of 2,2'- and 1,2'-azonaphthalenes were accomplished with column temperatures of 280° and 270° respectively.

The following retention times were observed: 2,2'-azonaphthalene (5 min. 34 sec.); x-chloro-2,2'-azonaphthalene (9 min. 29 sec.); 1,2'-azonaphthalene (7 min. 1 sec.); and 4-chloro-1,2'-azonaphthalene (11 min.).

A number of standard mixtures containing substituted and unsubstituted azonaphthalenes and phenylazonaphthalenes in widely varying amounts were analysed to obtain calibration graphs for each system. The ratios of the recorded peak areas were plotted against the percentage composition of the mixtures and smooth curve graphs were obtained. These calibration graphs were used to determine the relative amounts of each azo compound in the mixture obtained from the hydrolysis and subsequent chromatography of the photo-products.

2. Photo-products.

Photoreaction of 2,2'-Azonaphthalene with Trichloroacetyl chloride.

2,2'-Azonaphthalene (2 g) was partly dissolved in trichloroacetyl chloride (115 ml) and the pale yellow-orange suspension was irradiated in a photochemical reactor with a high pressure mercury lamp for 7 hr. The suspension was agitated by a flow of nitrogen passing into the reaction mixture. During the irradiation the solid material gradually dissolved and the mixture became green-yellow in colour. The excess acid chloride was removed by distillation under reduced pressure (b.p. 60°, 90 mm) leaving a green-black gum. The infrared spectrum of this product (chloroform) showed bands inter alia at 3350 (N-H), 1760 (C=O),

and 1720 (C=O) cm^{-1}. Thin-layer chromatography (silica) indicated that no unchanged 2,2'-azonaphthalene was present. Chromatographic separation of the photo-product into its components was not achieved.

The recovered photo-product was subjected to alkaline hydrolysis (boiled with aqueous ethanolic potassium hydroxide) followed by aerial oxidation. The reaction mixture was poured into water (500 ml), and the suspension formed was extracted with chloroform (150 ml). The extract was washed with water and finally dried (Na_2SO_4). The residue obtained after evaporation of the solvent was chromatographed on a column of alumina (petroleum-chloroform).

The first fraction eluted from the column (chloroform-petroleum, 80% V:V) contained a red-orange solid (78 mg) which was recrystallized from chloroform to give orange-brown needles (47 mg, 15%), m.p. 273.5-274.5° (Found: C, 68.3; H, 3.49; N, 7.72; Cl, 20.5. $C_{20}H_{12}N_2Cl_2$, M.W. 350, requires C, 68.5; H, 3.43; N, 8.0; Cl, 20.0%). The mass spectrum showed a molecular ion at m/e 350 and the isomer peaks had the correct relative abundance for a dichlorinated species. This compound was shown by direct comparison (mixed m.p. and ultraviolet spectrum) to be identical with a sample of a dichloro-2,2'-azonaphthalene (73) obtained from the irradiation of x-chloro-2,2'-azonaphthalene in acetyl chloride, followed by hydrolysis/oxidation of the photo-product (see Experimental I.4).

Evaporation of the mother liquors to dryness gave an orange solid, the mass spectrum of which showed fragment ions at m/e 350 and m/e 326,

which would correspond to molecular ions arising from a monochloro- and a dichloro-2,2'-azonaphthalene. However, separation of this mixture into its components could not be accomplished.

Continued elution (chloroform) afforded a second fraction which after removal of the solvent yielded a dark brown gum (740 mg). The infrared spectrum of this material (chloroform) showed bands inter alia at 3450 (N-H), 3360 (N-H), 1720 (C=O), 1695 (C=O), and 1615 cm^{-1}.

The abovementioned gum was treated with 80% sulphuric acid (20 ml) at 140-145° for 5 mins. After cooling, the solution was poured onto crushed ice with vigorous stirring. A brown suspension was formed, which after filtration afforded a dark brown solid. This was treated with ammonium hydroxide (10%) and dried to give a dark brown solid (520 mg). Extraction with chloroform gave a brown solution and an insoluble black gum. The chloroform extract was thoroughly dried and then saturated with dry hydrogen chloride gas. The solution became a deep burgundy red in colour but no precipitate was formed. The chloroform-insoluble gum was dissolved in concentrated ammonia solution; and the solution was diluted with water and extracted with chloroform. The extract was dried and saturated with hydrogen chloride gas. As before, no precipitate was formed. Further attempts to resolve the mixture into its components, by chemical and chromatographic means, were unsuccessful.

Photoreaction of 2-Phenylazonaphthalene with Trichloroacetyl Chloride.

A solution of 2-phenylazonaphthalene (1.5 g) in trichloroacetyl

chloride (115 ml) was irradiated in a reactor with a mercury lamp for 8 hr under an atmosphere of nitrogen. The reaction mixture after this period was a dark green-brown; and the ultraviolet spectrum (ethanol) of a sample of this mixture indicated the absence of unchanged azonaphthalene. The acid chloride was removed by distillation (26-28°, 11 mm); and the residue was dissolved in chloroform (150 ml). The chloroform solution was washed with sodium carbonate solution, dried (Na_2SO_4), and evaporated to dryness to give a yellow-green oil (4.3 g). The infrared spectrum (chloroform) of this photo-product showed bands at 3260 (N-H), 2995 (C-H), 2275, 1750 (C=O), 1705 (C=O), 1600, and 760 (C-Cl) cm^{-1}.

The mixture was chromatographed on silica (petroleum-chloroform). Elution with chloroform-petroleum (60-70% V:V) gave the first fraction (A), and removal of the solvent left orange crystals (96 mg). Recrystallization (dichloromethane) afforded orange needles of 2-(4'-chlorophenylazo)naphthalene (33) (32 mg, 2%), m.p. 140-142° (alone or admixed with the authentic sample). The ultraviolet and infrared spectra were identical with those of the authentic compound.

The second fraction (B) (chloroform-petroleum, 90-95% V:V), yielded a scarlet oil (1.2 g) which could not be crystallized. The infrared spectrum (film) showed bands inter alia at 3300 (N-H), 3000 (C-H), 1700-1725 (C=O), 1630, and 1600 cm^{-1}.

Continued elution with ethanol-chloroform (1% V:V) gave a third fraction (C), which after evaporation of the eluate gave a black-brown

gum (1.8 g). The infrared spectrum (chloroform) of this material showed strong bands at 3350 (N-H), 1720 (C=O), 1620, 1600, 1510, and 1530 cm^{-1}.

The mixture isolated from the second fraction (B) was rechromatographed on an alumina column using petroleum-chloroform as the eluting solvent. A single broad orange band was eluted from the column with chloroform-petroleum (40-60% V:V); and evaporation of the solvent left an orange solid (44 mg). Several recrystallizations (chloroform) of this product afforded orange needles (206 mg, 12%) of 1-chloro-2-phenylazonaphthalene (35), m.p. 109-110° (alone or admixed with an authentic specimen), (Found: C, 71.9; H, 4.15; N, 10.4; Cl, 13.6. $C_{16}H_{11}N_2Cl$, M.W. 266.5; requires C, 72.0; H, 4.13; N, 10.5; Cl, 13.3). The mass spectrum showed a molecular ion at m/e 266, and the isotope peaks were in the correct ratio for a monochlorinated ion. The second fraction (chloroform-petroleum 85-95% V:V) afforded a red oil (108 mg). The infrared spectrum showed strong bands at 3400 (N-H), 3350 (N-H), 1630, and 1610 cm^{-1}.

The dark brown gum (1.8 g) obtained from the third fraction (C) was rechromatographed on alumina (petroleum-dichloromethane). One broad band was eluted using dichloromethane-petroleum (50-90% V:V) as eluate. Removal of the solvent yielded a residue (58 mg) which after recrystallization from petroleum gave orange needles of 1-chloro-2-phenylazonaphthalene (35) (15 mg, 1%), m.p. 108-110° (alone or admixed with the authentic compound). The second fraction (ethanol-chloroform 5% V:V) was evaporated to dryness; and the infrared spectrum (chloro-

form) of the residual black gum (465 mg) showed strong bands at 3350 (N-H), 1720 (C=O), 1620, 1600, 1530, and 1510 cm^{-1}. This residue was heated under reflux with aqueous ethanolic potassium hydroxide solution for 7 hr. Air was drawn through the cooled reaction mixture for 0.5 hr and the suspension so formed was extracted with dichloromethane. After being washed with water and dried (Na_2SO_4), the dichloromethane solution was evaporated to dryness. The residue was chromatographed on a preparative plate (silica-dichloromethane/petroleum 20% V:V). Several visible bands were separated on the plate. The two bands at highest R_f were deep orange; and removal and extraction of these gave orange solids. The uppermost band yielded 2-(4'-chlorophenylazo)naphthalene (8 mg, 0.5%), m.p. 140-143°; the other band gave 1-chloro-2-phenylazonaphthalene (21 mg, 1%), m.p. 106-108°. Each compound was identified by direct comparison (mixed m.p. and ultraviolet spectrum) with an authentic sample.

Photoreaction of 2-(4'-Chlorophenylazo)naphthalene with Trichloroacetyl Chloride.

A solution of 2-(4'-chlorophenylazo)naphthalene (250 mg) in trichloroacetyl chloride (115 ml) was irradiated under an atmosphere of nitrogen with a high pressure mercury lamp until the ultraviolet spectrum (ethanol) of a sample of the mixture indicated that no azonaphthalene remained (2 hr). The acid chloride was distilled off (reduced pressure 24°, 12 mm); and the residue was dissolved in chloroform; and the chloroform solution was washed (water) and dried (Na_2SO_4). Removal of

the solvent gave a yellow-green oil (340 mg). The infrared spectrum of this product showed intense bands at 3400 (N-H), 3260 (N-H), 1760 (C=O), 1720 (C=O), and 1705 (C=O) cm^{-1}. The photo-product was taken up in dichloromethane and applied to a preparative plate (silica); and the chromatogram was developed with chloroform-petroleum (20% V:V). Four bands were evident on the plate.

The topmost yellow-orange band, after removal from the plate and extraction with ether, yielded a red-orange oil (2 mg) when the solvent was evaporated.

The orange band just below this was treated in the same way. This afforded a yellow-orange solid (20 mg). Thin-layer chromatography (silica) showed this material as a single spot. However, several recrystallizations (petroleum, chloroform, ethanol) failed to produce an exact melting point (92-112°). This was probably due to the presence of two or more chromatographically inseparable dichlorinated compounds. Gas chromatography gave two peaks, neither of which had the same retention time as an authentic sample of 2-(4'-chlorophenylazo)naphthalene. The mass spectrum of the mixture showed a molecular ion at m/e 300; and the isotope peaks were in the correct ratio for two chlorine groups being in the molecule.

The remaining material on the plate was recovered (chloroform extraction) and treated with boiling aqueous ethanolic potassium hydroxide. Extraction of the reaction mixture (dichloromethane) was followed by drying of the extract ($MgSO_4$) and removal of the solvent to yield a

black-brown gum. This mixture was subjected to preparative plate chromatography in a similar fashion to that described in the previous paragraph. The two upper-most bands (yellow-orange) were separately collected and extracted. Thin-layer chromatography showed that each was a mixture containing two compounds. Attempts to achieve complete separation of the components of this mixture were unsuccessful. The combined yield of the two fractions was 72 mg. Comparative thin-layer chromatography and qualitative gas chromatography showed that one component of the mixture was 2-(4'-chlorophenylazo)naphthalene. The mass spectrum of the mixture possessed a molecular ion at m/e 300, with the isotope peaks having the correct relative abundance for two chloro groups.

The remaining two bands were collected and extracted, but the red-orange semi-solid so obtained (9 mg) could not be identified. The infrared spectrum (chloroform) showed bands inter alia at 3420, 3350 (N-H), 1630, and 1610 cm^{-1}.

Photoreaction of 2-Phenylazonaphthalene with Trichloroacetyl Chloride in Benzene.

To a solution of 2-phenylazonaphthalene (250 mg) in analytical grade benzene (10 ml.) was added trichloroacetyl chloride (4 ml, d. 1.66). A flow of nitrogen was maintained through the mixture; and the solution was irradiated with a high pressure mercury lamp. The photoreaction of the azo compound was followed by ultraviolet spectroscopy, aliquots of the solution being removed from the reaction at various times and quenched in ethanol. It was found that c. 20% of the azonaphthalene

had reacted after 7.5 hr. A further portion of acid chloride (4 ml) was added; and the above procedure repeated. Additional quantities (4 ml) of the trichloroacetyl chloride were introduced into the reaction mixture after irradiation times of 9 hr and 12 hr. After being exposed to ultraviolet light for a total of 80 hr the red-brown solution was found still to contain some azonaphthalene. The excess acid chloride and benzene were removed by distillation under reduced pressure; and the residue was dissolved in chloroform, washed (Na_2CO_3 solution), and dried ($MgSO_4$). After the solvent was evaporated, a black-brown gum (264 mg) remained. The gum was dissolved in dichloromethane. Thin-layer chromatography (silica) showed that no azo compound was present. Preparative plate chromatography (silica, chloroform-petroleum/20% V:V) gave two partly resolved bands, which were removed from the plate and extracted (chloroform) to give an orange solid (12 mg). This mixture was shown by gas chromatography to consist of 2-(2'-chlorophenylazo)naphthalene, 2-phenylazonaphthalene, and 1-chloro-2-phenylazonaphthalene.

The compounds remaining on the plate were recovered and subjected to alkaline hydrolysis (aqueous ethanolic potassium hydroxide) and aerial oxidation. The washed (water) and dried (Na_2SO_4) chloroform extract of this reaction mixture was evaporated to dryness; and the residue was subjected to preparative plate chromatography (silica-dichloromethane/petroleum 20% V:V). The combined yield of the three azo compounds obtained from the plate was 5 mg. Gas chromatography indicated that these compounds were the same as those described in the previous paragraph.

Several oils and gums were isolated from other bands on the plate; but the quantities were too small and too impure for identification purposes.

V. APPROACHES TO THE SYNTHESES OF CHLOROAZONAPHTHALENES

Syntheses of Mono-chlorinated Phenylazonaphthalenes.

1-Naphthylamine.

A commercial sample was purified by steam distillation, followed by recrystallization from aqueous ethanol to give colourless needles, m.p. 48.5-49.5° (lit.[117] 50°).

2-Naphthylamine.

Purification of the commercial product was accomplished by recrystallization several times from water to form tan-coloured leaflets, m.p. 111-112° (lit.[117] 113°).

4-Chloronitrobenzene.

This compound was distilled before use and was obtained as a pale yellow liquid, b.p. 240-244° (lit.[118] 242°).

2-Chloronitrobenzene.

Commercial 2-chloronitrobenzene was redistilled before use to give a pale yellow liquid, b.p. 243-247° (lit.[118] 245°).

1-(4'-Hydroxyphenylazo)naphthalene.

This compound was prepared from phenol and 1-naphthylamine diazonium chloride.[120] The product was purified by column chromatography followed by recrystallization (ethanol) to give 1-(4'-hydroxyphenylazo)-naphthalene as red needles, m.p. 135-136° (lit.[120] 136°).

2-(4'-Hydroxyphenylazo)naphthalene.

Diazotised 2-naphthylamine was coupled with phenol according to the procedure described by Grandmougin and Freimann.[119] The 2-(4'-hydroxyphenylazo)naphthalene was recrystallized from ethanol to form red-scarlet needles, m.p. 238-239° (lit.[119] 240°).

2-(4'-Chlorophenylazo)naphthalene (33).

The method used was a modified version of that described by Martynoff[115] for the preparation of 2-phenylazonaphthalene.

Freshly powdered sodium hydroxide (17 g) was added in portions to a mixture of 2-naphthylamine (26.7 g) and 4-chloronitrobenzene contained in a flask that was being heated on a Woods' metal-bath. The suspension was stirred during the addition which was carried out over a 30 min period. The temperature was maintained at 210-220°; the reaction was strongly exothermic and if the temperature exceeded 230° a violent explosion occurred. Large amounts of steam were evolved, and the reaction mixture rapidly darkened and became a black, viscous mass. The mixture was kept at 215° for a further 15 min and then hydrochloric acid (10%) was cautiously added to the cooled material until the excess sodium hydroxide was neutralized. The black granular product was collected by filtration, pulverised, and then extracted with boiling chloroform until the extract was colourless. After being dried (Na_2SO_4) the chloroform solution was concentrated; and the dissolved material was adsorbed on to kieselguhr. This mixture was placed on an alumina column and chromatographed (petroleum-chloroform).

Elution with chloroform-petroleum (5% V:V) and evaporation of the solvent yielded a red-orange solid. Recrystallization of this product from ethanol, methanol, or chloroform gave 2-(4'-chlorophenylazo)-naphthalene (33) as long orange needle-like crystals (11 g, 26%), m.p. 142-143° (Found: C, 72.1; H, 4.33; mol.wt. (mass spectrum), 266. $C_{16}H_{11}N_2Cl$ requires C, 72.0; H, 4.12%; mol.wt. 266.5).

A second fraction was eluted from the column with chloroform-petroleum (10-15%). The solvent was removed by distillation; and the residue was recrystallized (ethanol) to give red-scarlet needles of 2-(4'-hydroxyphenylazo)naphthalene (3.6 g, 9%), m.p. 238-239° (lit.[119] 240°). The m.p. was not depressed upon admixture with the authentic compound.

1-(4'-Chlorophenylazo)naphthalene (52).

A well stirred mixture of 1-naphthylamine (26.7 g) and 4-chloro-nitrobenzene (25.5 g) was maintained at 220-230° while powdered sodium hydroxide (17 g) was gradually added over a 25 min period. The procedure followed thereafter was almost identical to that described for the preparation of 2-(4'-chlorophenylazo)naphthalene.

The crude reaction product was extracted with benzene and the benzene solution was washed (water), dried (Na_2SO_4) and evaporated to dryness. The residue was subjected to column chromatography (silica-petroleum/dichloromethane). The first fraction eluted from the column (dichloromethane-petroleum 5% V:V) was obtained as yellow-orange needles (350 mg, 1%), m.p. 187-189°, after sublimation (130°, 0.8 mm) and

recrystallization from methanol. The product was shown to be 1,1'-azonaphthalene by direct comparison (mixed m.p. and infrared spectrum) with an authentic sample.

The second band was eluted with dichloromethane-petroleum (8% V:V). Removal of the solvent yielded 1-(4'-chlorophenylazo)naphthalene (52) as a red-orange crystalline solid. This product was recrystallized (methanol) to give orange needles (1.7 g, 4%), m.p. 126.5-127° (Found: C, 71.8; H, 4.15; mol.wt. (mass spectrum), 266. $C_{16}H_{11}N_2Cl$ requires C, 72.0; H, 4.12%; mol.wt., 266.5).

Further elution with dichloromethane-petroleum (10% V:V) gave 1-(4'-hydroxyphenylazo)naphthalene (540 mg, 2%). Recrystallization from ethanol yielded scarlet needles, m.p. 134-135° (lit.[120] 136°). The structure of this compound was confirmed by comparison (mixed m.p. and infrared spectrum) with an authentic sample.

2-(2'-Chlorophenylazo)naphthalene (34).

This compound was prepared by condensation of 2-naphthylamine (26.7 g) with 2-chloronitrobenzene (25.5 g) in the presence of sodium hydroxide (17 g) at 220-225°. The experimental details were similar to those described for the synthesis of 2-(4'-chlorophenylazo)naphthalene. The crude material was chromatographically purified (alumina-chloroform/petroleum 5%) and the 2-(2'-chlorophenylazo)naphthalene (34) (4.5 g, 11%) so obtained formed red-orange plates when recrystallized from methanol, m.p. 115.5-116.5° (Found: C, 72.0; H, 4.21; mol.wt. (mass spectrum), 266. $C_{16}H_{11}N_2Cl$ requires C, 72.0; H, 4.12%; mol.wt. 266.5.)

1-(2'-Chlorophenylazo)naphthalene (53).

1-Naphthylamine (26.7 g) and 2-chloronitrobenzene (25.5 g) were condensed in the presence of sodium hydroxide (17 g), the experimental procedure being essentially similar to that involved in the preparation of 2-(4'-chlorophenylazo)naphthalene. The black reaction mixture was extracted with several portions of hot benzene; and the combined extracts were dried (Na_2SO_4) and evaporated to dryness; and the residue was chromatographed (silica-petroleum/chloroform). The first yellow-orange band was eluted with chloroform-petroleum (2% V:V). Evaporation of the solvent left a red-orange solid, which after recrystallization from methanol afforded orange plates of 1-(2'-chlorophenylazo)naphthalene (53) m.p. 111.5-112.5°, (Found: C, 72.0; H, 4.48; N, 10.5; mol.wt. (mass spectrum), 266. $C_{16}H_{11}N_2Cl$ requires C, 72.0; H, 4.12; N, 10.5%; mol.wt., 266.5).

4-Amino-1-phenylazonaphthalene and 1-Amino-2-phenylazonaphthalene.

These compounds were prepared by coupling diazotised aniline with 1-naphthylamine using the procedure described by Turner.[121] The two amino compounds were separated individually from the reaction mixture by column chromatography (alumina-petroleum/chloroform). Further purification of each compound by recrystallization (petroleum) yielded 4-amino-1-phenylazonaphthalene as scarlet plates, m.p. 122-123° (lit.[122] 120°, lit.[121] 122°) and 1-amino2-phenylazonaphthalene as red-orange plates, m.p. 161-162° (lit.[121] 161-161.5°).

4-Chloro-1-phenylazonaphthalene (55).

4-Amino-1-phenylazonaphthalene (1 g) was dissolved in absolute ethanol (10 ml), and to the red-orange solution was added concentrated hydrochloric acid (1.4 g, d 1.18) and water (2 ml). The amine hydrochloride separated from the stirred solution as red-purple flakes. The stirred suspension was then cooled to 0° (ice-salt bath) and a solution of sodium nitrite (0.3 g in 1 ml water) was added dropwise over a period of 10 min. After the addition was complete the suspension was gradually warmed to room temperature (c. 20°) and then left at that temperature for 10 hr. Any excess sodium nitrite (determined using starch-iodide paper) which remained in the yellow-brown mixture was destroyed by the addition of urea. The precipitated diazonium chloride was then collected by filtration, washed with ether, and dried by suction. The diazonium salt was found to be quite stable under these conditions.

The impure diazonium salt was then added in small portions to a well stirred solution ($0-5^{\circ}$) of cuprous chloride (1.5 g) in concentrated hydrochloric acid (3 ml, d 1.18). After the addition was complete (10 min.) the stirred suspension was allowed to attain room temperature. It was then heated on a boiling water-bath for 2 hr. Nitrogen was evolved and a drop of ether or ethanol was occasionally added to the suspension to minimise frothing. The final reaction mixture was extracted with boiling chlofoform (200 ml); and the extract was washed (water) and dried ($MgSO_4$); and the solvent was removed under reduced pressure. The residue was adsorbed on kieselguhr and then chromatographed on a column

of alumina (petroleum-ether). The first band eluted from the column (ether-petroleum 30% V:V) afforded a pale orange compound. This was recrystallized from ethanol to give bright orange needles of 4-chloro-1-phenylazonaphthalene (55) (62 mg, 6%), m.p. 112-113° (Found: C, 72.3; H, 4.48; N, 10.5; mol.wt. (mass spectrum), 266. $C_{16}H_{11}N_2Cl$ requires C, 72.0; H, 4.12; N, 10.5%; mol.wt., 266.5). Further elution with ether-petroleum (40%) gave a fraction which after removal of the solvent yielded 4-amino-1-phenylazonaphthalene (260 mg), m.p. 120-122° (alone or admixed with an authentic sample).

Attempted Synthesis of 2-Chloro-1-phenylazonaphthalene (54).

1-Nitro-2-naphthylamine.

This compound was prepared by the nitration of 2-naphthylamine in the manner described by Hodgson[127] or Hartmann.[128] After several recrystallizations from hot ethanol the 1-nitro-2-naphthylamine formed yellow needles, m.p. 120-121° (lit.[127] 122°, lit.[128] 123-124°).

2-Chloro-1-nitronaphthalene.

This compound was prepared by the action of cuprous chloride on diazotised 1-nitro2-naphthylamine.[127] Final purification by recrystallization from ethanol yielded pale yellow needles, m.p. 98-99° (lit.[127] 99°).

2-Chloro-1-naphthylamine.

The preparation of this compound was achieved by reduction of 2-chloro-1-nitronaphthalene with iron powder and ferrous ammonium

sulphate in an aqueous medium.[129] The product was purified by recrystallization (ethanol) and obtained as colourless needles, m.p. 55-56° (lit.[129] 56°).

2-Chloro-1-phenylazonaphthalene (54).

The procedure adopted was similar to that described by Martynoff[113] for the preparation of other unsubstituted and substituted phenylazonaphthalenes.

Nitrobenzene (0.7 g) and 2-chloro-1-naphthylamine (1 g) were heated together at 210° while powdered sodium hydroxide (1 g) was added at such a rate that the temperature of the reaction mixture did not exceed 215°. Steam was evolved; and the mixture rapidly darkened and became very viscous. After 20 min the reaction product was cooled, pulverized, washed with hydrochloric acid (2M), and then extracted with chloroform. The extract was washed (water) and dried ($MgSO_4$). The dissolved material was then subjected to column chromatography (alumina-petroleum/chloroform. None of the required 2-chloro-1-phenylazonaphthalene was isolated from the column.

1-Chloro-2-phenylazonaphthalene (35).

2-Nitronaphthol.

This compound was prepared by the nitrosation of 1-naphthol and subsequent oxidation of the 2-nitroso-1-naphthol so formed with hydrogen peroxide.[130] After steam distillation the product was recrystallized (ethanol) to form yellow needles, m.p. 127-128° (lit.[130] 128°).

2-Nitro-1-naphthylamine.

This compound was synthesised from 2-nitro-1-naphthol according to the method of Hodgson et al.[127] 2-Nitro-1-naphthylamine was obtained after recrystallization (methanol) as pale yellow crystals, m.p. 142-143° (lit.[127] 144°).

1-Chloro-2-nitro-naphthalene.

Diazotised 2-nitro-1-naphthylamine was treated with cuprous chloride in the manner described by Hodgson et al.[127] After steam distillation, followed by recrystallization from ethanol, the compound was isolated as long pale yellow needles, m.p. 74.5-75.5° (lit.[127] 76°).

1-Chloro-2-naphthylamine.

(a) 1-Chloro-2-naphthylamine was prepared from 1-chloro-2-nitronaphthalene by the reduction of the latter compound with stannous chloride and concentrated hydrochloric acid.[131] Recrystallization from ethanol gave long colourless needles, m.p. 57-58° (lit.[132] 56°, lit.[133] 59-60°).

(b) 1-Chloro-2-naphthylamine was also prepared directly from 2-naphthylamine by chlorination of the p-toluene sulphonyl derivative as reported by Kuhlmann.[133] No experimental details of his method were available in the literature reference; and the following is a description of the procedure that was devised.

The p-toluene sulphonyl derivative of 2-naphthylamine was prepared[144] by treating the amine with p-toluene sulphonyl chloride.

After recrystallization from methanol the product was obtained as grey needles, m.p. 132-133° (lit.[145] 133°). This material was kept at 80° and 0.5 mm pressure for 24 hr to remove all traces of the solvent.

The sulphonamide (56 g) was partly dissolved in benzene (560 ml) (thiophene-free and sodium-dried), which was contained in a flask equipped with a nitrogen inlet, a constant pressure dropping funnel, and a condenser fitted with a calcium chloride drying tube. A vigorous stream of nitrogen was introduced into the colourless stirred suspension; and freshly distilled sulphuryl chloride (39 g) dissolved in benzene (38 ml) was slowly added at room temperature during a 30 min period (c. 20°). During the addition the suspended solid slowly dissolved to yield a pale green-brown solution. The stirred solution was then warmed to 35-40° and left under an atmosphere of nitrogen until no more sulphur dioxide and hydrogen chloride gas were evolved, (c. 2.5 hr). All of the benzene and unchanged sulphuryl chloride was then removed in vacuo, yielding a viscous green-yellow oil. This product was hydrolysed by cautious addition of 80% sulphuric acid (352 ml) at room temperature, followed by slow heating to 155°. The temperature was then maintained at 155-165° for 5 min. The black-brown solution was allowed to cool and was then poured carefully into a vigorously stirred mixture of water (500 ml) and ice (500 g). The resulting solution was rendered basic by the addition of sodium hydroxide solution (30%). The brown precipitate so formed was removed by filtration and extracted with boiling dichloromethane; the extract was washed (water) and dried ($MgSO_4$). Removal of the solvent

yielded a pale pink solid (22 g). This material was then chromatographed on a column of alumina (petroleum). The first compound eluted from the column was 1,4-dichloro-2-naphthylamine. This product was recrystallized from hexane as colourless needles (189 mg, 1%), m.p. 91-92° (lit.[146] 91-92°). The mass spectrum showed a molecular ion at m/e 211 and the isotope peaks were in the correct ratio for a molecule containing two chloro groups.

The second fraction (chloroform-petroleum, 3% V:V) yielded a pale pink solid (21 g). This was further purified by recrystallization from hexane to yield 1-chloro-2-naphthylamine (19.8 g, 89%) as long colourless needles, m.p. 59-60° (lit.[132] 56°, lit.[133] 59-60°). This compound was identical (infrared spectrum and mixed m.p.) with the product obtained by Hodgson's method.[131]

(c) 1-Chloro-2-naphthylamine was also prepared by the chlorination of 1-chloro-2-acetamidonaphthalene (chlorine gas) and subsequent hydrolysis of the 1,4-dichloro-2-acetamidonaphthalene so formed, as described by Clemo.[146] Direct comparison (infrared spectrum and mixed m.p.) with the product obtained from the previous reaction (b) indicated that the two compounds were identical.

1-Chloro-2-phenylazonaphthalene (35).

By a similar method to that described for the preparation of 2-(4'-chlorophenylazo)naphthalene, 1-chloro-2-naphthylamine (3 g) and nitrobenzene (2.2 g) were condensed at 220-230° in the presence of dry

powdered sodium hydroxide (1.6 g). A violent reaction occurred if the temperature exceeded 235°. The crude reaction product was extracted with chloroform, the chloroform solution then being dried (Na_2SO_4) and evaporated to dryness. The residue was chromatographed on an alumina column (petroleum--chloroform).

An orange band was eluted with petroleum as the first fraction. Removal of the solvent left an orange solid which, after recrystallization from hexane or light petroleum, formed orange plates of azobenzene (70 mg), m.p. 67-68° (alone or admixed with an authentic sample). The infrared spectra of the authentic compound and the product were identical.

The second fraction was eluted from the column with chloroform-petroleum (10% V:V) and afforded 1-chloro-2-phenylazonaphthalene (35) which, after recrystallization from hexane, was obtained as yellow-orange needles (29 mg, 1.5%), m.p. 113-114° (Found: C, 71.9; H, 4.15; N, 10.4; Cl, 13.6; mol.wt. (mass spectrum), 266. $C_{16}H_{11}N_2Cl$ requires C, 72.0; H, 4.13; N, 10.5; Cl, 13.3%; mol.wt. 266.5).

Further elution with chloroform-petroleum (15% V:V) yielded unchanged 1-chloro-2-naphthylamine (900 mg). No unchanged nitrobenzene was eluted from the column.

Unsuccessful Preparation of 1-Chloro-2-phenylazonaphthalene (35).

β-Naphthol was treated with chlorine gas; and the product from the reaction was treated with freshly distilled phenylhydrazine.[159] None of the azo compound described by Zincke and Kegel[159] was isolated from the reaction mixture.

Unsuccessful Preparation of 1-Chloro-2-(4'-aminophenylazo)naphthalene.

1-Chloro-2-naphthylamine was diazotised and the diazonium salt solution was treated with a solution of aniline hydrochloride at 0°. The experimental details were similar to those described by Turner[121] for the synthesis of 1-(4'-aminophenylazo)naphthalene. The crude product was chromatographically purified, but none of the required 1-chloro-2-(4'-aminophenylazo)naphthalene was eluted from the column.

Syntheses of Multi-chlorinated Phenylazonaphthalenes.

2,4-Dichloroaniline.

This compound was a commercial preparation. Several recrystallizations from aqueous methanol yielded colourless needles, m.p. 62-63° (lit.[133] 63°).

1-Nitronaphthalene.

The commercially available material was purified by steam distillation and then recrystallized from aqueous ethanol to give yellow needles, m.p. 61-62° (lit.[143] 61.5°).

2,4,6-Trichloroaniline.

This compound was prepared by the chlorination of aniline hydrochloride using the method described by Chattaway and Irving.[148] After recrystallization from methanol the 2,4,6-trichloroaniline was obtained as colourless needles, m.p. 78-79° (lit.[148] 78.5°).

4-Amino-1-(2',4'-dichlorophenylazo)naphthalene and 1-Amino-2-(2',4'-dichlorophenylazo)naphthalene.

1-Naphthylamine hydrochloride was prepared by passing hydrogen chloride through a solution of 1-naphthylamine in dry benzene or chloroform. The amine hydrochloride was collected by filtration and was freed from all traces of solvent by being kept at 5 mm pressure for 2 hr at room temperature.

2,4-Dichloroaniline hydrochloride was prepared in a similar fashion from 2,4-dichloroaniline.

1-Naphthylamine hydrochloride (3.1 g) was suspended in water (55 ml) and the mixture was slowly added to a sodium acetate-acetic acid solution (3.3M sodium acetate, 0.33M acetic acid; 17.5 ml) at 0°C.

A mixture of 2,4-dichloroaniline hydrochloride (4 g), hydrochloric acid (2.7 g, d 1.18), ice (7 g), and water (21 ml) was treated with 2M sodium nitrite solution until an excess of sodium nitrite was present (starch-iodide paper). The sodium nitrite solution was added over a period of 20 min , and the temperature of the stirred mixture was kept at 0-5°. The yellow suspension was filtered into a cooled flask and the cold diazonium salt solution so obtained was added dropwise to the cold 1-naphthylamine hydrochloride suspension, which was kept vigorously stirred. The addition required a period of 20 min , and the scarlet solution was left for a further 1.5 hr at 0-5°. The suspension was filtered; and the scarlet amine hydrochloride was converted to the free base by treatment with concentrated ammonia solution. The filter cake was washed with water

and dried. This yielded a powdery scarlet solid (5.8 g). This material was dissolved in chloroform and subjected to thin-layer chromatography (silica gel-dichloromethane/petroleum 20% V:V). Two major components of the mixture were widely separated on the plate.

The contents of the chloroform solution were adsorbed on kieselguhr and then subjected to column chromatography (alumina-petroleum/dichloromethane). The first band eluted from the column (dichloromethane-petroleum, 30% V:V) contained 1-amino-2-(2',4'-dichlorophenylazo)-naphthalene. This product after several recrystallizations from petroleum formed bright red-orange plates (155 mg, 2.6%), m.p. 179-180° (Found: C, 61.3; H, 3.58; N, 13.7; Cl, 22.5; mol.wt. (mass spectrum), 315. $C_{16}H_{11}N_3Cl_2$ requires C, 61.0; H, 3.49; N, 13.3; Cl, 22.2%; mol.wt., 315).

The second major fraction contained 4-amino-1-(2',4'-dichlorophenylazo)naphthalene (1.6 g). This was further purified by recrystallization from methanol to yield scarlet-black flat needles (936 mg, 16%), m.p. 207-208° (Found: C, 61.0; H, 3.67; N, 13.5; Cl, 22.3; mol.wt. (mass spectrum), 315. $C_{16}H_{11}N_3Cl_2$ requires C, 61.0; H, 3.49; N, 13.3; Cl, 22.2%; mol.wt. 315).

1-(2',4'-Dichlorophenylazo)naphthalene.

This compound was prepared by the deamination of 4-amino-1-(2',4'-dichlorophenylazo)naphthalene. The method used was similar to that described by Shine et al.[149] for the deamination of 4-amino-1,2'-azonaphthalene.

4-Amino-1-(2',4'-dichlorophenylazo)naphthalene (1 g) was dissolved

in ethanol (35 ml); and to this solution was added concentrated sulphuric acid (2.5 g, d 1.84). The purple-scarlet suspension was then heated under reflux while saturated sodium nitrite solution was added dropwise to it. The addition was continued until the purple colour was dispelled. At that stage none of the amino compound remained in the mixture. The red-brown suspension was poured into cold water (300 ml); and the mixture was stirred vigorously. The black-red solid which separated was removed by filtration and dissolved in dichloromethane. The solution was dried ($CaCl_2$); and the dissolved product was adsorbed on kieselguhr and chromatographed (alumina-petroleum/dichloromethane). 1-(2',4'-Dichlorophenylazo)naphthalene was eluted from the column with dichloromethane-petroleum (5% V:V). After several recrystallizations from petroleum the compound was obtained as red-orange plates (220 mg, 44%), m.p. 119-120° (Found: C, 64.2; H, 3.39; N, 9.6; Cl, 23.6; mol.wt. (mass spectrum), 300. $C_{16}H_{10}N_2Cl_2$ requires C, 64.0; H, 3.34; N, 9.4; Cl, 23.45; mol.wt. 300).

Separation of 1-(2',4'-dichlorophenylazo)naphthalene from the crude mixture was also achieved by preparative plate chromatography (silica-dichloromethane/petroleum 17% V:V).

Alternative Preparation of 1-(2',4'-Dichlorophenylazo)naphthalene.

This compound was also obtained by deamination of the crude mixture isolated from the preparation of 4-amino-1-(2',4'-dichlorophenylazo)-naphthalene. This material contained much unidentified material together

with some 1-amino-2-(2',4'-dichlorophenylazo)naphthalene.

The crude material (6.8 g) was dissolved in ethanol (250 ml); and concentrated sulphuric acid (16.5 g), d 1.84) was added to the solution. The mixture was then treated in the same way as was described for the deamination of pure 4-amino-1-(2',4'-dichlorophenylazo)naphthalene.

Chromatography and multiple recrystallization of the product gave 1-(2',4'-dichlorophenylazo)naphthalene as red-orange plates (672 mg, 8%), m.p. 119-120°. This compound was identical (mixed m.p. and infrared spectrum) with that isolated from the deamination of the pure amino compound. In addition to this product a second azo compound was eluted from the column with dichloromethane-petroleum (10% V:V). This material after recrystallization from petroleum formed orange plates (98 mg), m.p. 190-191°. This was shown to be 1,1'-azonaphthalene by comparison (mixed m.p. and ultraviolet spectrum) with an authentic sample.

4-Amino-1-(2',4',6'-trichlorophenylazo)naphthalene and 1-Amino-2-(2',4',6'-trichlorophenylazo)naphthalene.

These compounds were prepared by the condensation of 1-naphthylamine (2.8 g) with the diazonium salt of 2,4,6-trichloroaniline (3.7 g). The experimental procedure was similar to that involved in the preparation of 4-amino-1-(2',4'-dichlorophenylazo)naphthalene.

The crude reaction product was adsorbed on kieselguhr and subjected to column chromatography (alumina-petroleum/dichloromethane). The first band eluted from the column (dichloromethane-petroleum 45% V:V)

was found by thin-layer chromatography to consist of several compounds. The impure solid (635 mg) was rechromatographed under the same conditions. The major fraction (dichloromethane-petroleum 35% V:V) was evaporated to dryness. Recrystallization of the residue from petroleum yielded 1-amino-2-(2',4',6'-trichlorophenylazo)naphthalene as red-orange needles (548 mg, 8.5%), m.p. 149.5-150° (Found: C, 54.7; H, 3.15; N, 12.0; Cl, 30.2; mol.wt. (mass spectrum), 350. $C_{16}H_{10}N_3Cl_3$ requires C, 54.8; H, 2.86; N, 12.0; Cl, 30.4%; mol.wt. 350.5).

Elution with dichloromethane-petroleum (50-70%) gave mixtures of unidentified compounds (1.9 g) containing traces (thin-layer chromatography) of the two required azonaphthalenes. A brown band was eluted from the column using dichloromethane-petroleum (80-90% V:V). Removal of the solvent yielded a scarlet-black solid (3.1 g). Thin-layer chromatography showed that this material was a mixture. It was therefore rechromatographed under the same conditions as before. The first fraction (dichloromethane-petroleum 70% V:V) was collected and the solvent was removed *in vacuo*. The residual reddish-black oil (2.2 g) was further purified by crystallization from petroleum (b.p. 65-80°). In this way 4-amino-1-(2',4',6'-trichlorophenylazo)naphthalene was obtained as black-scarlet prisms (873 mg, 14%), m.p. 122-123° (Found: C, 54.9; H, 2.96; N, 11.8; Cl, 30.1; mol.wt. (mass spectrum), 350. $C_{16}H_{10}N_3Cl_3$ requires C, 54.8; H, 2.86; N, 12.0; Cl, 30.4%; mol.wt. 350.5.

Attempted Synthesis of 2-(2',4',6'-Trichlorophenylazo)naphthalene.

Deamination of 1-amino-2-(2',4',6'-trichlorophenylazo)naphthalene

was carried out by the same method as that described for the deamination of 4-amino-1-(2',4'-dichlorophenylazo)naphthalene.

1-Amino-2-(2',4',6'-trichlorophenylazo)naphthalene in a refluxing ethanol solution (20 ml) containing concentrated sulphuric acid (0.7 ml, d 1.84) was treated with saturated sodium nitrite solution. The reaction mixture was processed in the same way as that described for 4-amino-1-(2',4'-dichlorophenylazo)naphthalene. Removal of the solvent from the extract yielded a semi-solid red oil (127 mg). Thin-layer chromatography (silica-dichloromethane/petroleum 21% V:V) showed the presence of six compounds in the mixture. The separation of these compounds was achieved using preparative plate chromatography (silica-dichloromethane/petroleum 20% V:V).

The yellow band of highest R_f was removed, and the compound extracted with chloroform. Evaporation of the solvent and further purification of the residue by recrystallization (petroleum) gave brown-orange needles of 1-ethoxy-2-(2',4',6'-trichlorophenylazo)naphthalene (48 mg, 33%), m.p. 121-122° (Found: C, 57.1; H, 3.44; N, 7.1; mol.wt. (mass spectrum), 379. $C_{18}H_{13}N_2Cl_3O$ requires C, 56.9; H, 3.46; N, 7.4%; mol.wt. 379.5).

The scarlet coloured band of second highest R_f yielded a scarlet solid after extraction with chloroform. This compound, 1-hydroxy-2-(2',4',6'-trichlorophenylazo)naphthalene, was recrystallized from light petroleum as scarlet needles (28 mg, 21%), m.p. 154-155° (Found: C, 55.2; H, 3.22; mol.wt. (mass spectrum), 351. $C_{16}H_9N_2Cl_3O$ requires C, 55.5; H, 2.66%; mol.wt. 351.5).

1-(2',4',6'-Trichlorophenylazo)naphthalene.

4-Amino-1-(2',4',6'-trichlorophenylazo)naphthalene (1 g) was dissolved in ethanol (100 ml); and to this solution was added concentrated sulphuric acid (1.5 ml, d 1.84). To the refluxing mixture was added saturated sodium nitrite solution. The reaction mixture was then treated in the same way as was described for the deamination of 4-amino-1-(2',4'-dichlorophenylazo)naphthalene. Removal of the solvent from the final extract yielded a red-brown oil (900 mg). The oil was then chromatographed (alumina-petroleum/dichloromethane).

The first fraction eluted from the column (dichloromethane-petroleum 20% V:V) contained the 1-(2',4',6'-trichlorophenylazo)naphthalene. The brown-orange solid obtained was recrystallized from petroleum as fine orange-brown needles (670 mg, 70%), m.p. 101.5-102.5° (Found: C, 57.4; H, 2.92; N, 8.4; Cl, 31.5; mol.wt. (mass spectrum), 335. $C_{16}H_9N_2Cl_3$ requires C, 57.2; H, 2.68; N, 8.4; Cl, 31.8%; mol.wt. 335.5).

2-Nitronaphthalene.

(a) 2-Naphthylamine was diazotised; and the cold filtered diazonium salt solution was added to a solution of sodium cobaltinitrite in water.[152] The pale yellow diazonium cobaltinitrite was collected by filtration and dried.

The solid diazonium salt was added portion-wise to a solution containing sodium nitrite, copper sulphate, and cuprous oxide, according

to the procedure described by Hodgson and Ward.[153] The reaction mixture was steam distilled; and the 2-nitronaphthalene was collected as a pale yellow solid which, after recrystallization from aqueous ethanol, gave bright yellow plates, m.p. 78-79° (lit.[154] 79°).

(b) 2-Naphthylamine was diazotised in fluoroboric acid solution[151] to yield the diazonium fluoroborate as a buff-coloured solid. This salt was purified by dissolution in acetone and precipitation from the solution by the addition of ether. It was obtained as a pale-pink solid.

The replacement of the diazo group by a nitro group was carried out in a similar fashion to that described in (a) for the diazonium cobaltinitrite. The 2-nitronaphthalene was purified by steam distillation and recrystallization (methanol).

The yields from both the fluoroborate and cobaltinitrite diazonium salts were of the same order of magnitude (c. 30%).

1-Chloro-2-nitronaphthalene.

1-Chloro-2-naphthylamine was diazotised and the diazonium salt was isolated as the diazonium cobaltinitrite.[152,153]

The solid diazonium salt (5 g) was added in small portions to a vigorously stirred solution of sodium nitrite (10 g) and crystalline copper sulphate (10 g) in water (60 ml), containing suspended cuprous oxide (4 g). The addition was carried out at room temperature over a period of 5 min. The stirred mixture was left for a further 2.5 hr and then made alkaline with 10% sodium hydroxide solution. Steam distillation

of the suspension gave a yellow solid (321 mg). Recrystallization from ethanol gave 1-chloro-2-nitronaphthalene as yellow needles (125 mg, 5%), m.p. 74-75° (lit.[127] 76°). The structure was confirmed by comparison (mixed m.p. and infrared spectrum) with an authentic sample available from previous work.

1-(4'-Chlorophenylazo)naphthalene (52).

4-Chloroaniline (15 g) and 1-nitronaphthalene (20.2 g) were condensed in the presence of powdered sodium hydroxide (14 g) at 220-235°. The procedure used was essentially the same as that described for the synthesis of 2-(4'-chlorophenylazo)naphthalene from 4-chloronitrobenzene and 2-naphthylamine.

The black granular reaction mixture was extracted with hot benzene, and the material contained in the extract was chromatographed on an alumina column using dichloromethane-petroleum (5% V:V) as the eluting solvent. The first fraction afforded 1-(4'-chlorophenylazo)-naphthalene (52) which, after recrystallization from petroleum, was isolated as orange needles (81 mg, 2.5%), m.p. 126-127° (alone or admixed with an authentic sample).

1-(2',4'-Dichlorophenylazo)naphthalene.

2,4-Dichloroaniline (9.3 g) was coupled with 1-nitronaphthalene (10 g) in the presence of powdered sodium hydroxide (7 g) at 215-225°. The method followed was identical to that used in the preparation of 1-(4'-chlorophenylazo)naphthalene from 4-chloroaniline and 1-nitro-naphthalene.

The dissolved material in the benzene extract was subjected to chromatography (alumina-petroleum/dichloromethane). Elution with dichloromethane-petroleum (25% V:V) afforded 1-(2',4'-dichlorophenylazo)-naphthalene. This material was recrystallized from benzene. It formed scarlet flat needles (340 mg, 3%), m.p. 115-116°. Comparison (mixed m.p. and infrared spectrum) with an authentic sample confirmed its identity.

1-(2',4',6'-Trichlorophenylazo)naphthalene.

In an experimental procedure similar to that involved in the preparation of 1-(4'-chlorophenylazo)naphthalene, 2,4,6-trichloroaniline (10 g), and 1-nitronaphthalene (8.9 g) were condensed in the presence of sodium hydroxide (5.6 g) at 225-230°. The crude product was chromatographically purified (alumina-petroleum/chloroform). Elution with chloroform-petroleum (10% V:V) yielded unchanged 2,4,6-trichloroaniline (4.3 g). The second fraction (chloroform-petroleum 20% V:V) afforded a red-orange solid which after recrystallization from petroleum formed orange-brown needles of 1-(2',4',6'-trichlorophenylazo)naphthalene (21 mg, 0.1%), m.p. 101-102° (alone or admixed with an authentic sample).

Syntheses of Chloroazonaphthalenes.

Attempted Synthesis of 1-Chloro-2,2'-azonaphthalene.

1-Chloro-2-naphthylamine (1 g) and 2-nitronaphthalene (1 g) were heated together (210-215°); and dry powdered sodium hydroxide was added over a period of 10 min. The reaction that ensued was strongly exothermic and water vapour was evolved. The cooled mixture was extracted with

dichloromethane and the extract was dried ($MgSO_4$). The dichloromethane was removed by evaporation and the dark-coloured residue was chromatographed on an alumina column (petroleum-chloroform). Elution of the column yielded none of the required 1-chloro-2,2'-azonaphthalene; and the presence of unchanged 1-nitronaphthalene and 1-chloro-2-naphthylamine was not detected.

Attempted Synthesis of 1'-Chloro-1,2'-azonaphthalene.

The procedure followed was almost identical to that previously described for the attempted synthesis of 1-chloro-2,2'-azonaphthalene.

1-Chloro-2-naphthylamine (1 g) and 1-nitronaphthalene (1 g) were heated (210-220°) in the presence of powdered sodium hydroxide. The material obtained from the benzene extract of the reaction product was subjected to column chromatography (alumina-petroleum/chloroform). Elution of the column yielded none of the required 1'-chloro-1,2'-azonaphthalene and no unchanged starting materials.

4-Amino-1,2'-azonaphthalene.

This compound was prepared by the condensation of diazotised 2-naphthylamine with 1-naphthylamine.[150] The 4-amino-1,2'-azonaphthalene was separated from the crude reaction mixture by chromatography (alumina-petroleum/chloroform). After recrystallization from ethanol it was obtained as scarlet needles, m.p. 152-153° (lit.[150] 152°).

4-Chloro-1,2'-azonaphthalene (84).

(a) The method used for the diazotisation of 4-amino-1,2'-azonaphthalene closely resembled that described by Saunders[155] for the diazotisation of 4-aminoazobenzene.

4-Amino-1,2'-azonaphthalene (4 g) was ground in a glass mortar with a mixture of boiling water (6 ml) and concentrated sulphuric acid (6 ml, d 1.84). The dark purple suspension was rinsed into a 100 ml flask with 20 ml of hot water (70-80°). Diazotisation was then performed with sodium nitrite solution (1.15 g in 7 ml water), which was added to the warm (28-30°), stirred suspension at such a rate that no oxides of nitrogen were evolved from the reaction mixture (50 min). The mixture was continually stirred at 28° for 72 hours. At the end of this period the vessel was filled with the red-brown crystalline diazosulphate. This was collected by filtration, washed with water and ether, and then dried by suction.

The dry diazosulphate was added over a period of 15 min to a stirred solution of cuprous chloride (4 g) in concentrated hydrochloric acid (12 ml, d 1.19) at 0-5°. A further 6 ml of hydrochloric acid was added to reduce the viscosity of the paste formed. After being stirred for an additional 3 hr at 0-5°, the suspension was gradually warmed to room temperature and then heated on a boiling water-bath for 3 hr. The evolution of nitrogen caused extensive forthing, and ether was added to minimise this. After dilution with water (150 ml) the suspension was extracted with chloroform; and the extract was washed (water) and dried ($MgSO_4$). The product contained in the chloroform solution was

preadsorbed on kieselguhr and subjected to column chromatography (alumina-petroleum/dichloromethane).

The first fraction was eluted with dichloromethane-petroleum (10% V:V). This afforded a red-orange solid (510 mg), which was found (thin-layer chromatography) to contain two compounds. The product was therefore subjected again to chromatography (silica-petroleum/dichloromethane). Careful elution of the column with petroleum, containing gradually increasing amounts of dichloromethane, separated the two compounds. The first fraction (dichloromethane-petroleum 17% V:V) yielded a red-orange compound (49 mg), m.p. 189-190°. This compound was shown by direct comparison (infrared spectrum and mixed m.p.) to be identical with the dichloroazonaphthalene isolated from the second band eluted from the alumina column. The second fraction was eluted with dichloromethane-petroleum (26% V:V) and found to contain 4-chloro-1,2'-azonaphthalene (84). After several recrystallizations from dichloromethane this material formed pale orange plates (395 mg, 9%), m.p. 188.5-189.5° (Found: C, 75.5; H, 4.24; N, 8.9; Cl, 11.7; mol.wt. (mass spectrum), 316. $C_{20}H_{13}N_2Cl$ requires C, 75.8; H, 4.11; N, 8.9; Cl, 11.2%; mol.wt. 316.5).

The second fraction isolated from the chromatography of the crude Sandmeyer reaction product was eluted from the column with dichloromethane-petroleum (20-25% V:V). The solution was evaporated to dryness and the residue (550 mg) was found (thin-layer chromatography) to consist of a major and a minor component. This mixture was chromatographed (silica); and the first band eluted from the column (dichloromethane-petroleum 15%

V:V) yielded a red-orange solid. This was recrystallized several times from dichloromethane to form long red-orange needles of a dichloroazonaphthalene (365 mg, 7.5%), m.p. 191-192° (Found: C, 68.3; H, 3.47; N, 8.0; Cl, 20.4; mol.wt. (mass spectrum), 350. $C_{20}H_{12}N_2Cl_2$ requires C, 68.6; H, 3.43; N, 8.0; Cl, 20.0%, mol.wt. 350).

(b) n-Amyl nitrite was prepared from n-amyl alcohol;[156] and the product was obtained after distillation (b.p. 102-106°) as a colourless liquid. This compound was freshly prepared just before use.

The method used for the diazotisation of 4-amino-1,2'-azonaphthalene was similar to that described by Saunders[157] for the preparation of benzene diazonium sulphate.

4-Amino-1,2'-azonaphthalene (500 mg) was dissolved in ethanol (100 ml) and the resulting solution was cooled to 0-5°C. Enough concentrated sulphuric acid (d 1.84) was added until the initially formed purple precipitate of amine salt redissolved. Amyl nitrite (300 mg) was added dropwise while the solution was stirred (temperature 0-5°); and the suspension was left at this temperature for a further period of 2 hr. The dark brown-purple suspension was then added rapidly to a cold (0°C) solution of cuprous chloride (1 g) in concentrated hydrochloric acid (3 ml, d 1.18); and the reaction mixture allowed to stand (0-5°) for 1 hr. The mixture was then allowed to attain room temperature. This was followed by heating at 40-50°C for 1 hr. Frothing in the reaction vessel was kept to a minimum by addition of small quantities of ether whenever necessary. After being cooled, the suspension was extracted

with ether. The extract was washed, firstly with sodium bicarbonate solution, and then with water. It was finally dried ($CaCl_2$); and the product contained in the ether extract was chromatographed (alumina-chloroform/petroleum). Elution with chloroform-petroleum (10% V:V) yielded an orange solid. This compound, 4-chloro-1,2'-azonaphthalene, was obtained as pale yellow needles (64 mg, 15%), m.p. 188-189°, after recrystallization from ethanol. Comparison (mixed m.p. and infrared spectrum) with a sample of 4-chloro-1,2'-azonaphthalene previously prepared showed the two samples to be the same compound. A dichloro azonaphthalene was not present in the fractions eluted from the column.

4-Amino-1,1'-azonaphthalene.

This compound was prepared by coupling 1-naphthylamine with diazotised 1-naphthylamine according to the procedure of Michaelis and Eidmann.[158] The crude aminoazonaphthalene was purified by recrystallization from aqueous ethanol to give 4-amino-1,1'-azonaphthalene as red-black needles with a deep green lustre, m.p. 174-175° (lit.[158] 175°).

4-Chloro-1,1'-azonaphthalene (96).

(a) This compound was prepared from 4-amino-1,1'-azonaphthalene (11.8 g), the experimental procedure for the synthesis being essentially similar to that involved in the preparation of 4-chloro-1,2'-azonaphthalene. The chloroform extract of the crude reaction product was subjected to column chromatography (alumina-petroleum/dichloromethane).

The first fraction was eluted with dichloromethane-petroleum (15-20% V:V). This afforded a yellow-orange solid (1.7 g). Thin-layer chromatography (silica-dichloromethane/petroleum 20% V:V) showed the presence of two compounds. The mixture was rechromatographed on an alumina (1000 g) column; and the chloroform content of the solvent was increased in 0.5% increments. The first band (chloroform-petroleum 20% V:V) yielded a yellow-orange solid which was a mixture of one main compound and traces of a second compound. Several recrystallizations from ethanol-chloroform (9:1) gave 4-chloro-1,1'-azonaphthalene (96) as yellow-orange needles (900 mg, 8%), m.p. 179-180° (Found: C, 75.7; H, 4.12; N, 8.8; Cl, 11.4; mol.wt. (mass spectrum), 316). $C_{20}H_{13}N_2Cl$ requires C, 75.9; H, 4.11; N, 8.8; Cl, 11.2%; mol.wt. 316.5).

Continued elution of the first column gave a second fraction (chloroform-petroleum 30% V:V) which, after removal of the solvent, yielded an orange solid (406 mg), m.p. 172-198°. Thin-layer chromatography and the mass spectrum of the substance, indicated that this fraction was a mixture of mono- and dichloroazonaphthalenes. Multiple recrystallization of the mixture from chloroform yielded the least soluble dichloro compound as red-orange needles (58 mg, 0.5%), m.p. 229-230° (Found: C, 68.9; H, 3.46; N, 8.0; Cl, 20.3; mol.wt. (mass spectrum), 350. $C_{20}H_{12}N_2Cl_2$ requires C, 68.6; H, 3.43; N, 8.0; Cl, 20.0%; mol.wt. 350).

The mother liquors obtained from the recrystallizations of both fractions were chromatographed on silica using petroleum-dichloromethane

as eluant. The compound: absorbent ratio was 1000:1. Once again the separation was not complete; and several recrystallizations were required to obtain pure samples of each compound.

(b) The diazonium sulphate of 4-amino-1,1'-azonaphthalene was also prepared using n-amyl nitrite as the diazotising agent. The method used was identical to that described for the analogous diazotisation of 4-amino-1,2'-azonaphthalene.

4-Amino-1,1'-azonaphthalene (500 mg) was diazotised with n-amyl nitrite in ethanolic sulphuric acid solution. The diazonium salt so obtained was then treated with a solution of cuprous chloride in concentrated hydrochloric acid in the manner previously described for the preparation of 4-chloro-1,1'-azonaphthalene.

The crude product was chromatographed on an alumina column. The first fraction to be eluted (chloroform-petroleum 20% V:V) yielded 4-chloro-1,1'-azonaphthalene (72 mg, 17%), m.p. 178-180° (alone or admixed with a fully characterized sample). None of the dichloro azonaphthalene was isolated from the mixture.

VI. APPROACHES TO THE SYNTHESES OF N,N'-DIACETYLHYDRAZONAPHTHALENES.

Materials:

2-Phenylazonaphthalene.

This compound was available from previous work (see Part I).

2-(4'-Chlorophenylazo)naphthalene and 2-(2'-chlorophenylazo)naphthalene.

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

The acetyl chloride was a commercial preparation and was distilled (b.p. 51-52°) just before use.

The acetic anhydride was fractionally distilled from anhydrous sodium acetate and was obtained as a colourless liquid, b.p. 139-140°.

The acetic acid was commercially available, and this product was mixed with a quantity of acetic anhydride and distilled from solid potassium permanganate. The dried and purified acid was collected as a colourless liquid, b.p. 117-118°.

The pyridine used was distilled (b.p. 114-115°) from potassium hydroxide pellets and the distillate was stored over an additional quantity of pellets until required.

The dichloromethane was dried by distillation from phosphorus pentoxide and was obtained as a colourless liquid, b.p. 41-42°.

The tetrahydrofuran obtained commercially was refluxed over calcium hydride, distilled from calcium hydride, distilled (b.p. 64-65°) from sodium, and then stored over sodium wire.

Reduction of Azo Compounds and Hydrazo Compounds.

The method used was a modification of that described by Olah[173] for the reduction of substituted azobenzenes to hydrazobenzenes. A notable variation was the use of aluminium chloride as the metal halide catalyst for the reduction. This was in contrast to the results obtained by Olah[173] which showed that aluminium halides did not catalyse the reduction of azobenzenes.

The following is a general description of the procedure used to reduce phenylazonaphthalenes and azonaphthalenes (substituted and unsubstituted) to the corresponding hydrazo compounds.

The purified azonaphthalene (1 g) was dissolved in dry tetrahydrofuran (50 ml) contained in a flame-dried flask, and the mixture was vigorously stirred. A flow of oxygen-free dry nitrogen was passed through the solution. Finely powdered lithium aluminium hydride (4 moles) was added to the solution and brisk effervescence occurred. The solution deepened in colour (deep red or red-brown), and after the evolution of gas had ceased a catalytic quantity (c. 0.01M) of aluminium chloride or ferric chloride was added. Dense white fumes filled the reaction vessel the instant the metal halide was added and the dark colouration immediately changed to the more normal red-orange colour. This colour gradually faded until after 0.5-1.5 hr (depending on the azonaphthalene being reduced) the suspension was a pale yellow-green. The flow of nitrogen through the mixture was maintained while the excess lithium aluminium hydride was destroyed by the dropwise addition of saturated ammonium chloride

solution to the cooled suspension. Additional tetrahydrofuran was added to the stirred suspension and the mixture was then filtered. The grey filter cake was washed several times with tetrahydrofuran. The original filtrate and the washings were combined and evaporated (reduced pressure) to dryness yielding an off-white solid. This hydrazo compound was dissolved in nitrogen saturated dry benzene (10 ml) and the solution was refluxed in an atmosphere of nitrogen. A Dean-Stark apparatus for azeotropic water separation was used to dry the solution. When free from water, the solvent was evaporated from the solution, and the solid residue of hydrazonaphthalene was suspended in cold petroleum and collected by filtration as a white solid. Further purification was not carried out and this product was used in subsequent acetylation procedures.

The reduction proceeded smoothly with tetrahydrofuran or ether as the solvent. The former had the advantage of being a much better solvent for both the azo compounds and the hydrazo compounds. It had the disadvantage that the reaction product was often contaminated with n-butanol, which resulted from attack by the mixed hydride reducing mixture on the solvent.

Gas Chromatography.

The procedure used for gas chromatographic analysis was identical to that previously described in part II of the Experimental.

1. Synthesis of 2-(N,N'-Diacetylphenylhydrazo)naphthalene (36) from 2-Phenylhydrazonaphthalene.

2-Phenylhydrazonaphthalene.

2-Phenylazonaphthalene (1 g) was dissolved in ether (50 ml) and lithium aluminium hydride (4 moles) was added to the stirred solution. A small quantity (c. .02M) of ferric chloride was introduced and the mixture was kept under an atmosphere of nitrogen. After a period of 20 min the solution was a pale green-yellow colour. The excess reducing agent was destroyed (saturated ammonium chloride) and the precipitate was removed by filtration. The solvent was evaporated from the filtrate (nitrogen atmosphere) to yield 2-phenylhydrazonaphthalene (920 mg, 92%) as a pale yellow oil which rapidly turned orange upon exposure to air. Addition of petroleum caused the oil to crystallize giving pale yellow crystals of the hydrazo compound, m.p. 102-104° (lit.[174,175] 104°). The infrared spectrum (film) showed bands at 3320 (N-H), 3260 (N-H), 3000, 2950, 2900, 2850, 1635, 1605, 1525, 1500, 1480, 850, 820, 755, and 690 cm^{-1}.

This procedure was duplicated for each of the following acetylation reactions, the hydrazo compound in each case being used in its entirety as soon as possible after being prepared.

Acetylation of 2-Phenylhydrazonaphthalene using:

(a) Acetyl Chloride.

2-Phenylhydrazonaphthalene (900 mg) was dissolved in acetyl chloride (50 ml) and the mixture was heated under reflux for 12 hrs in

an atmosphere of nitrogen. The excess acid chloride was removed by distillation (reduced pressure) and a pale brown oily residue was obtained. This material was dissolved in chloroform, washed (water), and dried (Na_2SO_4). Evaporation of the solvent yielded a pale brown resinous material. The infrared spectrum (film) of this mixture showed strong bands at 3250 (N-H), 1680 (C=O), and 1665 cm^{-1}. The mass spectrum suggested that there was a molecular ion at m/e 318.

The product was boiled with a 20% W:V solution of potassium hydroxide in aqueous ethanol (10% V:V) for 3 hr. The reaction mixture was diluted with water and extracted (chloroform); and the extract was chromatographed on an alumina column (chloroform-petroleum).

The first fraction (chloroform-petroleum 5% V:V) yielded 2-phenylazonaphthalene (1¼ mg). This compound was identified by direct comparison (mixed m.p. and infrared spectrum) with an authentic sample.

The column was finally eluted with methanol-chloroform (5% V:V) and this fraction afforded unchanged starting material (880 mg). The infrared spectrum (film) of this product was virtually identical with that of the mixture before treatment with ethanolic potassium hydroxide.

(b) N,N'-Dimethylaniline-Acetyl Chloride/Tetrahydrofuran.

2-Phenylhydrazonaphthalene (500 mg) was dissolved in tetrahydrofuran (25 ml.) and freshly distilled N,N-dimethylaniline (8 g) was added to the solution. This mixture was cooled to -35° (dry ice-ethanol) and acetyl chloride (2.7 g) was introduced dropwise into the

solution over a 15 minute period. Nitrogen was bubbled continuously through the mixture. The reaction mixture was warmed gradually to room temperature and then heated under reflux for 30 hrs. The tetrahydrofuran was distilled from the deep blue-purple solution under reduced pressure and the residue was dissolved in chloroform. This solution was washed several times with 5% hydrochloric acid and water, and then dried ($MgSO_4$). Removal of the solvent yielded a pale purple liquid (1.4 g) with a fruity odour. The infrared spectrum (film) showed bands at 3250, 1730, 1695, 1680, and 1660 cm^{-1}. This material was extracted several times with petroleum. The insoluble viscous oil that remained (630 mg) was chromatographed on an alumina column (chloroform-petroleum).

The major fraction (methanol-chloroform 5% V:V) afforded a pale brown oil (570 mg). The infrared spectrum (film) of this mixture was essentially the same as that of the product obtained in 1(a). Alkaline hydrolysis-oxidation under the conditions described in part (a) did not yield any 2-phenylazonaphthalene.

(c) N,N-Dimethylaniline-Acetyl Chloride.

Acetyl chloride (2.7 g, 8 mole) was added slowly to a cooled solution (0°) of 2-phenylhydrazonaphthalene (500 mg) in N,N-dimethylaniline (8 g) . The stirred mixture was then heated at 100° in an atmosphere of nitrogen for 6 hr. Chloroform was added to the cooled mixture and the solution so formed was washed with water (200 ml), 10% hydrochloric acid, and finally once more with water. The solution was dried ($MgSO_4$) and the solvent was removed *in vacuo* to give a pale green

viscous oil (580 mg) which could not be crystallized. The infrared spectrum (film) showed bands inter alia at 3250 (N-H), 1680, and 1665 cm^{-1}. The spectrum was virtually the same as those of the products isolated from the acetylation reactions 1(a) and 1(b). As before, this material was found to be stable to aqueous alcoholic potassium hydroxide (20% V:V).

(d) Pyridine-Acetyl Chloride/Dichloromethane.

A solution of 2-phenylhydrazonaphthalene (740 mg) in dichloromethane (30 ml) was cooled to -60° (liquid nitrogen bath). To this cold stirred mixture (under a nitrogen atmosphere) was gradually added acetyl chloride (20 ml). The suspension was allowed to attain room temperature and then heated under reflux for 5 hrs. Water (30 ml) and dichloromethane (50 ml) were added to the cooled reaction mixture. The organic layer was separated and washed with 3.5% hydrochloric acid, water, saturated sodium bicarbonate solution, and finally with water. The dichloromethane extract was dried ($CaCl_2$) and removal of the solvent gave a yellow-brown viscous oil (980 mg). The infrared spectrum (carbon tetrachloride) of this mixture showed weak absorptions at 3260 (N-H) cm^{-1} and 1680 (C=O) cm^{-1} together with very strong absorptions at 1705 (C=O) and 1690 (C=O) cm^{-1}. This residue was chromatographed on a column of silica (petroleum-chloroform).

The main fraction (chloroform-petroleum 20-30% V:V) was eluted as a broad pale yellow band. Evaporation of the solvent afforded a pale yellow glass (520 mg, 53%) which could not be crystallized. The infrared

spectrum (carbon tetrachloride) showed strong carbonyl absorptions at 1705 and 1690 cm^{-1}. No bands appeared in the region 3200-3500 cm^{-1}. The n.m.r. spectrum (deuterochloroform) showed a sharp singlet at δ2.0 ppm (6 protons), assigned to the acetyl protons, and a broad multiplet at δ7.4-8.2 ppm (12 protons), assigned to the aromatic ring protons. The mass spectrum suggested a molecular ion at m/e 318.

The 2-(N,N'-diacetylphenylhydrazo)naphthalene (36) (318 mg) so obtained, was treated with boiling aqueous ethanolic potassium hydroxide solution (20 ml) for 2 hrs. The mixture was diluted with water and the orange-brown precipitate collected by filtration. This solid was chromatographed (petroleum-chloroform) on an alumina column. The first fraction was eluted with chloroform-petroleum (10% V:V) and yielded 2-phenylazonaphthalene (195 mg, 85%), m.p. 83-84° (alone or admixed with an authentic sample).

(e) Acetic Anhydride.

A modified version of the method described by Nietzki and Zehnter[176] for the diacetylation of 1-phenylhydrazonaphthalene was used to prepare 2-(N,N'-diacetylphenylhydrazo)naphthalene (36).

Preparation of 2-(N-Acetylphenylhydrazo)naphthalene.

A vigorously stirred mixture of 2-phenylhydrazonaphthalene (1 g) and acetic anhydride (20 ml) was kept at a temperature of 55-60° (oil bath) for 3 hr under an atmosphere of nitrogen. The excess acetic anhydride was removed by distillation under reduced pressure (5 mm).

The pale yellow solid that remained was treated with boiling petroleum for 10 min. The insoluble material (900 mg) was collected by filtration and recrystallized several times from methanol to give white crystals of 2-(N-acetylphenylhydrazo)naphthalene (520 mg, 50%), m.p. 136-138° (Found: C, 77.8; H, 5.77; N, 10.1; O, 6.3; mol.wt. (mass spectrum), 276. $C_{18}H_{16}N_2O$ requires: C, 78.2; H, 5.79; N, 10.1; O, 5.8%; mol.wt. 276). The infrared spectrum (chloroform) showed bands at 3250 (N-H), 1670-1660 (C=O), 1630, 1600, 1500, 1510, 1380, and 1300 cm^{-1}. The n.m.r. spectrum (deuterochloroform) showed a singlet at δ2.27 ppm and δ2.30 ppm (integrated areas 1:1), assigned to acetyl protons, and a broad multiplet at δ6.7-8.0 ppm, assigned to the aromatic ring protons.

Preparation of 2-(N,N'-Diacetylphenylhydrazo)naphthalene (36).

2-(N-Acetylphenylhydrazo)naphthalene (658 mg) was dissolved in acetic anhydride (25 ml) and the mixture was heated under reflux for 11 hr. Care was taken to ensure that no moisture entered the reaction mixture, and the reflux was carried out in an atmosphere of dry nitrogen. The acetic anhydride was then removed from the reaction mixture at 70° in a stream of nitrogen. The residue was dissolved in ether (50 ml) and this solution was washed several times with water, dried ($MgSO_4$), and evaporated to dryness. The infrared spectrum (film) of the oily residue showed bands at 3260 (weak, N-H), 3020, 2930, 2830, 1705 (C=O), 1690 (C=O), and 1670 cm^{-1}.

This mixture (840 mg) was subjected to column chromatography

(alumina). The major fraction eluted from the column (chloroform-petroleum 25-35%) afforded a pale brown viscous oil (500 mg, 63%). This compound was identical (infrared, n.m.r., and mass spectra) with the 2-(N,N'-diacetylphenylhydrazo)naphthalene (36) isolated from the acetylation of 2-phenylhydrazonaphthalene with pyridine-acetyl chloride [see 1(d)].

The infrared spectrum of the above-mentioned product was superimposed on that of the material isolated from the photoreaction of 2-phenylazonaphthalene with acetyl chloride (see Experimental I). This comparison showed that N,N'-diacetyl-2-phenylhydrazonaphthalene was not present in the photo-product to any great extent.

2. Synthesis of 2-(N,N'-Diacetyl-4'-chlorophenylhydrazo)naphthalene (37).

2-(4'-Chlorophenylhydrazo)naphthalene (108).

2-(4'-Chlorophenylazo)naphthalene (1.5 g) was dissolved in tetrahydrofuran (50 ml) and dry oxygen-free nitrogen was passed into the solution. Lithium aluminium hydride (c. 10 moles) was then added gradually to the solution. The initial orange colour of the solution rapidly changed to deep red-brown; and vigorous effervescence occurred. A catalytic amount (c.0.05 moles) of finely powdered ferric chloride was added; and the suspension was stirred for 15 min. Saturated ammonium chloride solution was added slowly to the pale yellow mixture until no visible reaction occurred on addition of a further quantity of the salt

solution. The grey-white precipitate was removed by filtration and washed with tetrahydrofuran. The combined filtrates were evaporated to dryness (reduced pressure), and refluxing benzene was used to remove all traces of moisture from the residue. Removal of the benzene by reduced pressure distillation yielded a pale yellow oil (1.3 g, 86%). The infra-red spectrum of this product showed bands inter alia at 3320 (N-H), 3010 (C-H), 1635, 1605, and 1500 cm^{-1}. The addition of petroleum to this oil caused it to crystallize. The 2-(4'-chlorophenylhydrazo)naphthalene (108) so obtained was not purified further and was used as soon as possible in the acetylation reactions. If left in contact with air this product rapidly reverted to 2-(4'-chlorophenylazo)naphthalene.

The above preparation was carried out before every acetylation reaction, and all of the freshly prepared hydrazonaphthalene was used in the reaction.

Acetylation of 2-(4'-Chlorophenylhydrazo)naphthalene using:

(a) Acetyl Chloride.

A solution of 2-(4'-chlorophenylhydrazo)naphthalene (700 mg) in acetyl chloride (65 ml) was left for 14 hr at room temperature (c. 20°). The mixture was vigorously agitated during this period and oxygen and moisture were excluded from the system (nitrogen atmosphere).

A pale yellow deliquescent solid (183 mg) was removed from the reaction mixture. This material was insoluble in chloroform and was not converted into an azo compound when subjected to alkaline hydrolysis-oxidation.

The pale yellow filtrate was heated under reflux for 6 hr. The acid chloride was removed by reduced pressure distillation and yielded a pale orange glass (890 mg). This residue was chromatographed on a column of silica (petroleum-chloroform).

Several minor bands were eluted from the column (total yield 80 mg). None of these showed the characteristic 1710 and 1695 cm^{-1} carboryl absorptions in their infrared spectra that would be expected of N,N'-diacetyl-hydrazonaphthalenes.

The major fraction (methanol-petroleum 5% V:V) afforded a pale orange glass (800 mg). The infrared spectrum (chloroform) showed bands inter alia at 3280 (broad, N-H), 1690 (C=O), and 1660 cm^{-1}. The mass spectrum showed a molecular ion at m/e 352.

The product could not be crystallized; and thin-layer chromatography (silica) indicated that it was a mixture of compounds.

Treatment of the mixture with boiling aqueous ethanolic potassium hydroxide solution for 2 hr followed by extraction of the reaction mixture and chromatography of the extract, did not yield any 2-(4'-chlorophenylazo)naphthalene. The infrared spectrum of the material collected was virtually identical to that of the mixture before treatment with alkali.

(b) N,N'-Dimethylaniline-Acetyl Chloride/Tetrahydrofuran and N,N'-Dimethylaniline-Acetyl Chloride.

The procedures followed for the treatment of 2-(4'-chlorophenylhydrazo)naphthalene with the above reagents were essentially the same as

those described for the acetylation of 2-phenylhydrazonaphthalene [see 1(b) and 1(c)].

In both cases no N,N'-diacetyl hydrazonaphthalene was formed, and the infrared spectrum of the isolated product was identical with that of the product isolated from the foregoing reaction [see 2(a)].

(c) Pyridine-Acetyl Chloride/Dichloromethane.

2-(4'-Chlorophenylhydrazo)naphthalene (600 mg) was partially dissolved in dry dichloromethane (30 ml) and the suspension was cooled (c.-40°) in a dry ice-acetone bath. A nitrogen atmosphere was maintained throughout this reaction and precautions were taken to exclude all traces of moisture from the mixture. Pyridine (2.1 g) was added to the stirred mixture. Acetyl chloride (15 ml) was then introduced dropwise over a period of 20 min. The cold suspension became a deep red-brown as the acid chloride was added. After the addition was complete the mixture was slowly warmed to room temperature (red colour disappeared) and the cream-coloured suspension was heated under reflux for 20 hr. The reaction mixture was then poured slowly into stirred ice-water and extracted with chloroform (200 ml). The extract was washed (5% hydrochloric acid and then water), dried ($MgSO_4$), and evaporated to dryness to give a pale yellow glass (880 mg). The infrared spectrum of this mixture showed a broad band at 3320 cm^{-1} (N-H) and a strong absorption at 1660-1720 (C=O) cm^{-1}. This residue was chromatographed on an alumina column (petroleum-chloroform).

Elution with ethanol-chloroform (3-5%) and evaporation of the solvent from this fraction gave 2-(N,N'-diacetyl-4'-chlorophenylhydrazo)-naphthalene (37) as a pale yellow glass (650 mg, 80%). The infrared spectrum (chloroform) of this material showed carbonyl absorptions at 1710 and 1695 cm^{-1}. No bands appeared in the region 3100-3500 cm^{-1}. The mass spectrum of this product showed a molecular ion at m/e 352.

Alkaline hydrolysis-oxidation of this product afforded 2-(4'-chlorophenylhydrazo)naphthalene in 85% yield [see 4 (a)].

The infrared and n.m.r. spectra of this diacetylated hydrazo-naphthalene were identical to those of the product isolated from the photoreaction of 2-phenylazonaphthalene with acetyl chloride.

(d) Acetic Anhydride.

Preparation of 2-(N-Acetyl-4'-chlorophenylhydrazo)naphthalene.

A suspension of 2-(4'-chlorophenylhydrazo)naphthalene (1g) in acetic anhydride (30 ml) was stirred overnight at 60-70° (nitrogen atmosphere). The excess acetic anhydride was removed at 70-80° in a stream of nitrogen. The yellow-orange solid that remained was treated with boiling ether-petroleum (10% V:V), and after cooling the mixture was filtered. A pale pink solid (1.4 g) was collected. The infrared spectrum (chloroform) of this product showed bands at 3350 (N-H), 3300 (N-H), 1675 (C=O), 1630, 1595, and 1495 cm^{-1}. The mass spectrum indicated a molecular weight of 310. The n.m.r. spectrum (deuterochloroform) shows sharp singlets at δ2.27 and 2.30 ppm (integrated signal areas in the ratio 1:1), assigned to acetyl group protons and a complex signal at δ6.67-8.0 ppm, assigned to

the aromatic ring protons.

Alkaline hydrolysis-oxidation of this product yielded 2-(4'-chlorophenylazo)naphthalene in 90% yield [see 4(b)].

Preparation of 2-(N,N'-Diacetyl-4'-chlorophenylhydrazo)naphthalene (37).

The impure mono-acetylated product (1 g) isolated from the previously described reaction was dissolved in acetic anhydride and the mixture was heated under reflux for 12 hr.

The final reaction mixture was cooled and the white precipitate removed by filtration. This compound was insoluble in chloroform, soluble in water, and absorbed moisture when exposed to air.

The red-brown filtrate was heated to 70-80° and the acetic anhydride was removed in a stream of nitrogen. The red-brown gum which remained was chromatographed on an alumina column (petroleum-chloroform).

Elution with chloroform-petroleum (20-30%) separated a broad brown band from the column. The solvent was removed (reduced pressure) and a yellow-orange glass (900 mg, 80%) remained. The infrared spectrum (chloroform) of this product showed bands at 1705, 1695, (2 x C=O), 1600, 1500, 1380, 1325, and 1075 cm^{-1}. The infrared spectrum of this 2-(N,N'-diacetyl-4'-chlorophenylhydrazo)naphthalene (37) was almost identical with that of the product from the photoreaction of 2-phenylazonaphthalene with acetyl chloride. The infrared spectrum of the photoproduct showed additional bands at 1065, 1025, and 965 cm^{-1}.

This synthetic 2-(N,N'-diacetyl-4'-chlorophenylhydrazo)naphthalene was identical (infrared spectrum) with a sample of the compound prepared

before [see 2(c)]. All attempts to crystallize this product were unsuccessful.

The column was finally eluted with chloroform-petroleum (50-60% V:V), and this fraction when evaporated to dryness left a red-brown viscous oil. This material was dissolved in ether and left to stand undisturbed overnight. Off-white crystals were deposited and these were collected and dried (121 mg), m.p. 235-245°. The infrared spectrum of this compound showed bands at 3280 (N-H), 1690 (C=O), and 1660 cm^{-1}. The mass spectrum indicated molecular ion at m/e 352. This material could not be convertedinto a coloured azo compound by alkaline hydrolysis-oxidation.

3. Synthesis of 2-(N,N'-Diacetyl-2'-chlorophenylhydrazo)naphthalene (38).

2-(2'-Chlorophenylhydrazo)naphthalene (109).

2-(2'-Chlorophenylazo)naphthalene (1.5 g) was dissolved in tetrahydrofuran (50 ml.) and reduced to the hydrazo compound with lithium aluminium hydride-aluminium chloride (reduction period 1.5 hr). The method used was identical to that previously described for the reduction of 2-(4'-chlorophenylazo)naphthalene (Experimental VI.2).

Removal of the solvent from the dry benzene solution of the reduction product afforded 2-(2'-chlorophenylhydrazo)naphthalene as a pale yellow viscous oil (1.4 g, 95%). The infrared spectrum (dichloromethane) of this compound showed bands at 3400 (N-H), 3320 (N-H), 3000, 1625

(broad), 1520, 1395, 1400, 1310, 1075, 855, and 830 cm^{-1}. This product could not be crystallized.

A fresh sample of the hydrazo compound was prepared each time it was needed.

Acetylation of 2-(2'-Chlorophenylhydrazo)naphthalene.

(a) Pyridine-Acetyl Chloride/Dichloromethane.

Pyridine (3.5 g) was added to a solution of 2-(2'-chlorophenylhydrazo)naphthalene (1 g) in dichloromethane (50 ml). The stirred solution was cooled to -40° (dry ice-acetone) and acetyl chloride (25 ml) was added gradually over a period of 40 min. A continuous flow of nitrogen was passed through the reaction mixture. The cream-coloured suspension was warmed to room temperature and then heated under reflux for 12 hr (nitrogen atmosphere). The cooled mixture was poured cautiously into ice-cold water with vigorous stirring. Dichloromethane was added and the aqueous layer extracted several times with that solvent. The extract was washed (3% hydrochloric acid and water) and dried ($CaCl_2$); and the solvent was evaporated to give a pale yellow viscous oil (1.5 g). This material was then subjected to column chromatography (silica-petroleum/chloroform).

The major fraction eluted from the column (chloroform-petroleum 40% V:V) yielded a brown oil (920 mg). The infrared spectrum (chloroform) of this material showed strong carbonyl absorptions at 1705 and 1695 cm^{-1}. The infrared and n.m.r. spectra were essentially identical with those of a fully characterised sample of 2-(N,N'-diacetyl-2'-chlorophenylhydrazo)-

naphthalene [see Experimental VI.3(b)]. The mass spectrum showed a molecular ion at m/e 352.

The oily reaction product could not be crystallized. When treated with boiling aqueous ethanolic potassium hydroxide (20% W:V) this material was converted to 2-(2'-chlorophenylhydrazo)naphthalene [see Experimental VI.4(a)].

(b) Acetic Anhydride.

Preparation of 2-(N-Acetyl-2'-chlorophenylhydrazo)naphthalene.

An acetic anhydride solution (25 ml.) of 2-(2'-chlorophenylhydrazo)-naphthalene (1.4 g) was stirred for 6 hr under an atmosphere of nitrogen (temperature 70-80°). The unchanged acetic anhydride was removed in a stream of nitrogen at 60-70°. The off-white gummy solid that remained was heated under reflux with petroleum (b.p. 85-100°). The suspension was cooled and the white precipitate (1.5 g, 95%) was filtered off. A small sample of this 2-(N-acetyl-2'-chlorophenylhydrazo)naphthalene was recrystallized from aqueous methanol (5% V:V) to form colourless needles, m.p. 135-136°. The mass spectrum showed a molecular ion at m/e 310. The n.m.r. spectrum (deuterochloroform) showed a sharp singlet at δ2.27 ppm (3 protons), assigned to the acetyl protons, and a complex signal at δ6.67-7.87 ppm (11 protons), assigned to the aromatic ring protons. The infrared spectrum showed bands at 3310 (N-H), 2990, 2910, 1690 (C=O), 1680 (C=O), 1630, 1595, 1500-1510, 1380, and 1320 cm^{-1}.

Preparation of 2-(N,N'-Diacetyl-2'-chlorophenylhydrazo)naphthalene (38).

The crude mono-acetylated compound (1.3 g) was dissolved in acetic anhydride (25 ml) and the mixture was boiled under reflux for 30 hr. The reaction mixture at the end of this period contained an insoluble compound. This was removed by filtration and dried. It was found to be insoluble in chloroform and benzene, soluble in water, and deliquescent when exposed to air.

The acetic anhydride was removed from the pale yellow filtrate *in vacuo*. A yellow oil remained and this was dissolved in chloroform. The solution was washed with water several times, dried ($MgSO_4$), and evaporated to dryness to yield a pale yellow glass. This was dissolved in ether; and the solution was vigorously stirred. An off-white solid precipitate was formed; and this was collected and washed with ether to give 2-(N,N'-diacetyl-2'-chlorophenylhydrazo)naphthalene (38) as a white solid (1.4 g, 88%), m.p. 131-133°. Further recrystallization from chloroform-ether afforded (38) as colourless needles, m.p. 132-133° (Found: C, 68.2; H, 4.84; N, 8.0; O, 9.1; Cl, 10.2; mol.wt. (mass spectrum), 352. $C_{20}H_{17}O_2ClN_2$ requires C, 68.2; H, 4.83; N, 8.0; O, 9.1; Cl, 9.9%; mol.wt., 352.5). The mass spectrum (deuterochloroform) showed a sharp singlet at δ2.0 ppm (6 protons), assigned to the acetyl group protons, and a complex signal at δ7.36-8.23 ppm (11 protons), assigned to the aromatic ring protons. The infrared spectrum (chloroform) showed bands at 3000, 1705 (C=O), 1695 (C=O), 1600, 1470, 1280, and 1320 cm^{-1}.

The infrared spectrum of the synthetic 2-(N,N'-diacetyl-2'-

chlorophenylhydrazo)naphthalene was not superimposable on that of the product from the photoreaction of 2-phenylazonaphthalene with acetyl chloride.

4. Treatment of Several Phenylhydrazonaphthalenes with Aqueous Ethanolic Potassium Hydroxide.

(a) 2-(x'-Chlorophenylhydrazo)naphthalenes.

2-(4'-Chlorophenylhydrazo)naphthalene.

The hydrazo compound (550 mg) was dissolved in ethanol (50 ml) and to this was added a solution of potassium hydroxide (11 g) in water (7 ml). The pale yellow mixture was heated under reflux for 2.5 hr in an atmosphere of nitrogen. The mixture was cooled, and air was drawn through it for 1 hr. The red-orange suspension was diluted with water and filtered. The orange solid so obtained (500 mg) was dried, and a sample of it was dissolved in acetone (5% W:V). This solution was injected (5 µl) into a gas chromatograph and only one peak appeared. The retention time of this peak was identical with that of an authentic sample of 2-(4'-chlorophenylazo)naphthalene. No trace of 2-phenylazonaphthalene was detected.

2-(2'-Chlorophenylhydrazo)naphthalene.

The procedure used was identical to the procedure described for the foregoing reaction. Gas chromatographic analysis of the isolated azonaphthalene (510 mg) showed that the only compound present was 2-(2'-chlorophenylazo)naphthalene. No dechlorinated product was present.

(b) 2-(N-Acetyl-x'-chlorophenylhydrazo)naphthalene.

2-(N-Acetyl-4'-chlorophenylhydrazo)naphthalene.

The mono-acetylated hydrazo compound (310 mg) was heated under reflux with aqueous ethanolic potassium hydroxide (20 ml, 20% W:V) for 3 hr. Air was drawn through the mixture for 1 hr. The suspension was diluted with water; and the precipitate was filtered off and dried (250 mg). A small quantity of this product was dissolved in acetone (5% W:V) and subjected to qualitative gas chromatography. Only one peak appeared, and this was identified as belonging to 2-(4'-chlorophenylazo)-naphthalene.

2-(N-Acetyl-2'-chlorophenylhydrazo)naphthalene.

This compound was treated in the same way as was described for the 4'-chloro isomer. Gas chromatographic analysis of the orange product (260 mg) showed that 2-(2'-chlorophenylazo)naphthalene was the only compound present. The presence of 2-phenylazonaphthalene was not detected.

(c) 2-(N,N'-Diacetyl-x'-chlorophenylhydrazo)naphthalenes.

2-(N,N'-Diacetyl-4'-chlorophenylhydrazo)naphthalene (37).

This compound (synthetic) (350 mg) was treated with boiling aqueous ethanolic potassium hydroxide (20 ml, 20% W:V) for 4 hr. Air was bubbled into the cooled solution for an additional 1 hr. The red-orange precipitate was collected by filtration and dried (255 mg). Gas chromatography showed the presence of 2-(4'-chlorophenylazo)naphthalene together with a very small quantity of 2-phenylazonaphthalene.

2-(N,N'-Diacetyl-2'-chlorophenylhydrazo)naphthalene (38).

This compound was subjected to alkaline hydrolysis-oxidation in the same manner as was described for the 4'-chloro diacetyl compound. Qualitative analysis by gas chromatography showed that the orange hydrolysis product (550 mg) consisted of only 2-(2'-chlorophenylazo)-naphthalene. 2-Phenylazonaphthalene was not present.

VII. APPROACHES TO THE SYNTHESES OF N,N'-DIACETYLDIAMINOBINAPHTHYLS

4-Chloro-1,2'-azonaphthalene and 4-chloro-1,1'-azonaphthalene were available from earlier work (see Experimental V).

4-Chloro-1,2'-hydrazonaphthalene, 4-chloro-1,1'-hydrazonaphthalene, 1,1'-hydrazonaphthalene, and 1,2'-hydrazonaphthalene were prepared by metal hydride reduction of the corresponding azo compounds. The method used was similar to that employed for reducing phenylazonaphthalenes to phenylhydrazonaphthalenes (see Experimental VI).

7H-Dibenzo-[a,g]carbazole (90).

This compound was prepared by the acid-catalysed rearrangement of 1,2'-hydrazonaphthalene.[149] The product from the reaction was recrystallized from methanol and afforded colourless needles of 7H-dibenzo[a,g]carbazole, m.p. 234-235° (lit. 235-236°,[149] 231°[193]).

13H-Dibenzo-[a,i]carbazole (100).

13H-Dibenzo-[a,i]carbazole was prepared by the methods of Vesely[194] and King et al.[195] In each case, the crude product was recrystallized several times from methanol to give colourless needles of compound (100), m.p. 214-215° (lit.[194] 216°).

Synthesis of 4-Chloro-N,N'-diacetyl-1,1'-diamino-2,2'-binaphthyl (94).

4-Chloro-1,1'-hydrazonaphthalene.

4-Chloro-1,1'-azonaphthalene (800 mg) was dissolved in sodium-dried tetrahydrofuran (50 ml), and the mixture was kept thereafter under an atmosphere of nitrogen. To the stirred solution was added lithium

aluminium hydride (10 moles). After the mild effervescence had ceased, aluminium chloride (200 mg) was gradually introduced into the suspension. A vigorous reaction occurred and the suspension rapidly lost its orange-red colour. After a period of 20 min the pale yellow mixture was cooled in an ice-salt bath. The excess reducing agent was then destroyed by the dropwise addition of a saturated ammonium chloride solution. The solid precipitate so formed was removed by filtration; the filter cake was washed with tetrahydrofuran (100 ml); and the collected solutions were combined. The solution was dried ($MgSO_4$) and the solvent was removed by distillation under reduced pressure to give a pale yellow oily residue, (795 mg, 99%). The infrared spectrum (film) of the crude 4-chloro-1,1'-hydrazonaphthalene showed bands inter alia at 3280, 3000, 1590, 1580, 1410, and 1385 cm^{-1}. The oil could not be crystallized, and was used in all subsequent reactions without further purification.

4-Chloro-1,1'-diamino-2,2'-binaphthyl (93).

4-Chloro-1,1'-hydrazonaphthalene (500 mg) was dissolved in sodium-dried benzene (150 ml). Dry HCl gas was then passed into the stirred solution, and after a period of 20 hr the precipitated amine hydrochloride was collected by filtration and dried. The pale grey hydrochloride (440 mg) was converted into the free base by treatment with ammonium hydroxide (50%, 1 ml). The pink-white diamino compound was collected and dried by suction. The infrared spectrum ($CHCl_3$) of this material contained a strong, broad band at 3320 cm^{-1} (N-H). The

crude 4-chloro-1,1'-diamino-2,2'-binaphthyl was found to decompose when it was heated in common organic solvents, and attempts to purify the compound by recrystallization were not successful. The impure material was therefore utilised in all subsequent reactions.

4-Chloro-N,N'-diacetyl-1,1'-diamino-2,2'-binaphthyl (94).

4-Chloro-1,1'-diamino-2,2'-binaphthyl (100 mg) was suspended in acetyl chloride (15 ml) and the mixture was heated under reflux for 4 hr. During this period the solid slowly dissolved to give a brown-yellow solution. The acetyl chloride was then removed in vacuo and the off-white solid residue was dissolved in dichloromethane. The solution was washed (water) and dried (Na_2SO_4). The solution was then evaporated to dryness, and the cream-coloured solid that remained was recrystallized several times from methanol-chloroform (5:1; V:V) to give 4-chloro-N,N'-diacetyl-1,1'-diamino-2,2'-binaphthyl (94) as off-white crystals (60 mg, 41%), m.p. 344-345°.

This product was shown to be identical (mixed m.p. and infrared spectrum) with the compound isolated from the photoreaction of 1,1'-azonaphthalene with acetyl chloride.

bis-Salicylidene-4-chloro-1,1'-diamino-2,2'-binaphthyl (95).

An impure sample of 4-chloro-1,1'-diamino-2,2'-binaphthyl (250 mg) was dissolved in ethanol (2 ml) and to this mixture was added salicylaldehyde (300 mg). The mixture was heated at 70° for 15 min,

during which time a bright yellow precipitate was formed. The yellow solid was collected by filtration and purified by recrystallization from ethanol. bis-Salicylidene-4-chloro-1,1'-diamino-2,2'-binaphthyl (95) was thereby obtained as bright yellow crystals (200 mg, 40%), m.p. 278-279° (Found: C, 76.24; H, 4.40; N, 5.1; O, 6.9; Cl, 8.5; mol.wt. (mass spectrum) 526. $C_{34}H_{23}N_2O_2Cl$ requires: C, 77.5; H, 4.37; N, 5.32; O, 6.1; Cl, 6.8%; mol.wt. 526.5).

Carbazole Formation.

5-Chloro-13H-dibenzo[a,i]carbazole (101).

The procedure used resembled that described by King et al.[195] and Colin et al.[196] for the preparation of 3-acetoamidocarbazole and 2,4,5,7-tetramethylcarbazole respectively.

A sample (500 mg) of the crude 4-chloro-1,1'-diamino-2,2'-binaphthyl was suspended in 25% sulphuric acid (25 ml) contained in a sealed glass tube. The tube and its contents were heated at 200° for a period of 16 hr. The final reaction mixture was cooled; and the suspended solid was collected by filtration and washed with 50% ammonium hydroxide solution. The dried product so obtained was extracted with chloroform; and then to the filtered extract was added an equal volume of petroleum. The precipitated solid was collected and recrystallized from ethanol/petroleum (10:1) to afford a cream-coloured solid (105 mg), m.p. 105-111°.

When exposed to ultraviolet light a solution of this material

in benzene exhibited the deep purple fluorescence typical of dibenzocarbazoles. The infrared spectrum ($CHCl_3$) showed a strong band at 3220 cm^{-1} (N-H) and the overall spectrum was similar to that of 13H-dibenzo[a,i]carbazole (100). The ultraviolet-visible spectrum was essentially identical with that of 13H-dibenzo[a,i]carbazole, showing absorption maxima at 235, 259, 293, 335, and 349 mμ. The mass spectrum showed singly charged fragments at m/e 301 ($M^+_\cdot$, base peak), 266 (M-35) and 239 (M-62). Doubly charged species appeared at m/e 150.5, 133, and 119.5.

Synthesis of 4-Chloro-N,N'-diacetyl-1,2'-diamino-1',2-binaphthyl (80).

In a similar manner to that previously described for the preparation of 4-chloro-N,N'-diacetyl-1,1'-diamino-2,2'-binaphthyl, 4-chloro-N,N'-diacetyl-1,2'-diamino-1',2-binaphthyl (80) was synthesized from 4-chloro-1,2'-azonaphthalene. The crude product after recrystallization from ethanol-chloroform (10:1; V:V) afforded compound (80) as colourless crystals, m.p. 330-331°. Direct comparison (mixed m.p. and infrared spectra) with a sample of photochemically prepared 4-chloro-N,N'-diacetyl-1,2'-diamino-1',2-binaphthyl showed that the two products were identical.

bis-Salicylidene-4-chloro-1,2'-diamino-1',2-binaphthyl (82).

This compound was prepared by treatment of 4-chloro-1,2'-diamino-1',2-binaphthyl (250 mg) with salicylaldehyde (300 mg) in ethanolic solution (≃3 ml.) at 70-80°. The yellow precipitated solid

was collected and was then purified by recrystallisation (ethanol) to yield bis-salicylidene-4-chloro-1,2'-diamino-1',2-binaphthyl (82) as canary-yellow crystals (150 mg, 30%), m.p. 218.5-219.5° (Found: C, 76.1; H, 4.44; O, 6.7; N, 5.0; Cl, 8.2; mol.wt. (mass spectrum) 526. $C_{34}H_{23}N_2O_2Cl$ requires: C, 77.5; H, 4.37; N, 5.32; O, 6.1; Cl, 6.8%; mol.wt. 526.5).

Carbazole Formation.

12-Chloro-7H-dibenzo-[a,g]carbazole (90).

The procedure followed was essentially the same as that previously described for the synthesis of 5-chloro-13H-dibenzo-[a,i]-carbazole, except that the diaminobinaphthyl used was 4-chloro-1,2'-diamino-1',2-binaphthyl (930 mg).

The crude product was extracted with boiling ethanol; the extract was then filtered and petroleum was added to the hot filtrate until precipitation occurred. The suspension was then cooled and filtered. Recrystallization of the collected solid from ethanol-petroleum yielded off-white plate-like crystals (315 mg), m.p. 170-180°. Further recrystallization did not improve the m.p.

The infrared spectrum (chloroform) of this material exhibited a strong absorption at 3220 cm^{-1} (N-H) and the spectrum resembled that of 7H-dibenzo-[a,g]carbazole.

A solution (ethanol) of the product produced strong violet fluorescence when exposed to ultraviolet light. The ultraviolet-visible spectrum (ethanol) was similar to that of 7H-dibenzo-[a,g]-

carbazole. Absorptions occurred at λ_{max} 235, 247, 265, 292, 303, 351, and 359 mμ.

The mass spectrum indicated fragments at m/e 301 ($M_{\cdot}^{+}$, base peak), 266 (M-35), and 239 (M-62). Doubly charged ion-radicals appeared at m/e 150.5, 133, and 119.5.

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