PHOTOCHEMICAL REACTIONS OF NAPHTHYLAZO, BIS(PHENYLAZO) AND RELATED COMPOUNDS.

A THESIS

PRESENTED FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

in the

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by

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CONTENTS

SUMMARY

The photochemical reactivities of azonaphthalenes and phenylazonaphthalenes in 22N sulphuric acid have been examined. 1-Phenylazonaphthalene was found to undergo photochemical cyclohydrogenation to naphtho[1,2-c]cinnoline, but 2-phenylazonaphthalene and 1,1'-, 1,2'-, and 2,2'-azonaphthalene were not converted to the corresponding cinnoline derivatives. Possible causes of the photochemical stability of these compounds are discussed.

A study has also been made of the photochemical reactions of the two conjugated bisazo compounds, 4-phenylazoazobenzene and 4,4'-bis(phenylazo)biphenyl in 22N and in concentrated sulphuric acid. 4-Phenylazoazobenzene was found to be unstable in 22N acid and only the two decomposition products 4-aminoazobenzene and 4-amino-3-(4'-aminophenyl)azobenzene were isolated. However, when the irradiation was carried out in 98% acid, good yields of two cyclised products, 2-amino-1-(4'-aminophenyl)benzo[c]cinnoline and 2-(4'-aminophenyl)aminobenzo[c]-cinnoline, were obtained. 4,4'-Bis(phenylazo)biphenyl was found to undergo cyclisation in both 22N and 98% sulphuric acid. In both media, the major products were the cyclised compounds, 2-(4'-aminophenyl)-benzo[c]cinnoline and 2-[4'-amino-3'-(4"-aminophenyl)phenyl]benzo[c]-cinnoline. Small amounts of the decomposition products, 4-(4'-aminophenyl)azobenzene and 4-[4'-amino-3'-(4"-aminophenyl)phenyl]azobenzene were also formed.

Neither 4-phenylazoazobenzene nor 4,4'-bis(phenylazo)biphenyl gave any doubly cyclised product on irradiation. In both cases, cyclisation around one azo linkage was accompanied by reduction and rearrangement at the other azo group. This phenomenon is discussed and an explanation is offered. The intermediate postulated to be formed during the irradiation of 4-phenylazoazobenzene, viz. 2-(2'-phenylhydrazino)-benzo[c]cinnoline, has been independently synthesised and subjected to the benzidine rearrangement in 98% sulphuric acid. This yielded the same two benzo[c]cinnolines which were formed during the irradiation of 4-phenylazoazobenzene in 98% acid. An attempt has been made to rationalise the course of this, and related rearrangements encountered during this work, on the basis of a recent mechanism proposed for the benzidine rearrangement.

The investigations with the conjugated bisazo compounds have led to an examination of the photochemistry of 3-phenylazobenzene, 4-phenylazobenzene and 2-phenylazobenzo[c]cinnoline in sulphuric acid. Irradiation of 3-phenylazobenzene was found to yield the two expected isomers, 1-phenylbenzo[c]cinnoline and 3-phenylbenzo[c]cinnoline; 4-phenylazobenzene gave 2-phenylbenzo[c]cinnoline. A pentacyclic product, probably benzo[1,2-c:4,5-c']dicinnoline was isolated following the irradiation of 2-phenylazobenzo[c]cinnoline.

Photochemical studies of compounds containing two azo groups in each molecule have been extended to two non-conjugated bisazo com-

pounds, 4,4'-bis(phenylazo)diphenylmethane and 4,4'-bis(phenylazo)-bibenzyl. With both these compounds, as with the conjugated bisazo compounds, cyclisation was found to occur around one azo linkage, apparently simultaneously with reduction at the other azo linkage.

The photochemical behaviour of azobenzene in 98% sulphuric acid has been examined. Yields of approximately 60% of benzo[c]cinnoline were obtained. This is in agreement with the postulated mechanism of cyclisation in concentrated acid involving disproportionation of the initially formed hydrazobenzene into azobenzene and aniline.

Irradiation of dilute solutions of 4-styrylazobenzene, 4-acetylstilbene, and 4-acetylstilbene anil, in sulphuric acid, has been found to produce spectral changes characteristic of cyclisation. However, no products could be isolated when experiments were carried out on a preparative scale.

Sulphuric acid solutions of 1-phenylazoazulene, 4-aminostilbene, and 4-benzalaminostilbene have been found to be photochemically stable.

***

STATEMENT

This thesis contains no material previously submitted for a 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.

Norman C. Jamieson.

ACKNOWLEDGEMENTS

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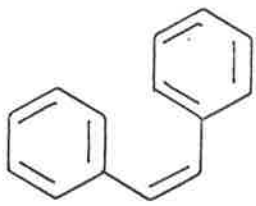
Grateful acknowledgement is made to the Petroleum Research Fund administered by the American Chemical Society for support of this work.

CHAPTER I

INTRODUCTION

1.1. Scope of Photochemical Cyclohydrogenations

Although it was discovered as long ago as 1873 that stilbene (1) could be thermally transformed into phenanthrene (2),[1] it was not until 1950 that the same reaction was first shown to occur photochemically.[2]



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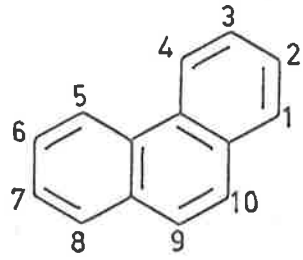

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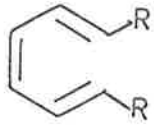
In the intervening years it had been noticed, during studies of the photochemically induced cis-trans isomerisation of stilbene, that a new compound of $\lambda_{max.}$ 247 mμ was produced.[3,4] However, no theories were advanced as to its identity. Somewhat later, Buckles[5] independently isolated and identified phenanthrene from solutions of stilbene which had been irradiated.

Of recent years there has been a considerable increased interest in such cyclisation reactions, which may be considered as being formally similar to the production of 1,3-cyclohexadiene (4, R = H) by the gas-phase photolysis of 1,3,5-hexatriene (3, R = H).[6]



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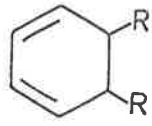

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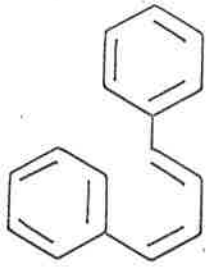
The cyclisation has also been shown to occur with conjugated dienes, thus 1,4-diphenyl-buta-1,3-diene (5) and 1,6-diphenyl-hexa-1,3,5-triene (7) will cyclise to 1-phenylnaphthalene (6) and chrysene (8) respectively.[7]



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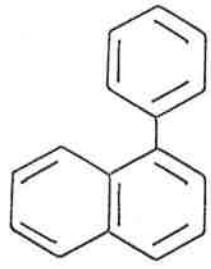

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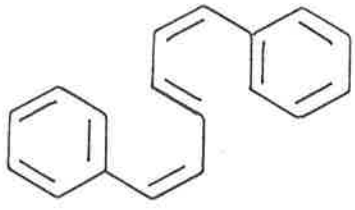

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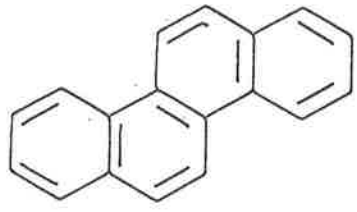

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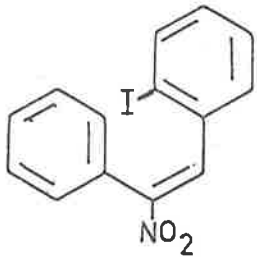
However, this review will be limited to the discussion of compounds of the type Ar-CH=CH-Ar, Ar-CH=N-Ar and Ar-N=N-Ar.

The photocyclisation of stilbene has been shown to be of value in preparing substituted phenanthrenes.[8] o-, p- and α -

substituted stilbenes gave 1-, 3- or 9-substituted phenanthrenes respectively, while m- substituted stilbenes yielded the expected mixture of 2- and 4- substituted phenanthrenes — detracting somewhat from the synthetic value of the reaction. Cyclisation was found to occur when the substituents were fluoro, chloro, bromo, methoxy, methyl, trifluoromethyl, carboxy or phenyl but failed with acetyl-, dimethylamino-, iodo- or nitro- bearing stilbenes. In the preparative experiments, iodine was present and the reaction mixtures were open to the air. The necessity for an oxidant will be considered during the discussion of the mechanism.

The synthesis of 9-nitrophenanthrene (10) has been achieved in good yield by irradiation of solutions of α-nitro-2'-iodo-cis-stilbene (9).[9]



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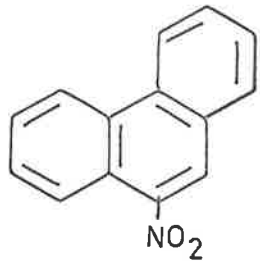

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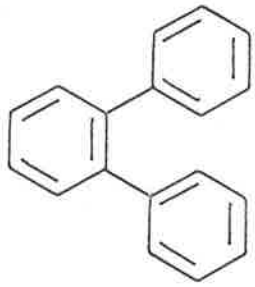
The failure of o-terphenyl (11) to photocyclise to triphenylene (12)[10] led Mallory to postulate[10] that a necessary condition for cyclisation was that the central double bond be olefinic. However, later work has shown the reaction to proceed smoothly and in good yield in the presence of iodine.[11]



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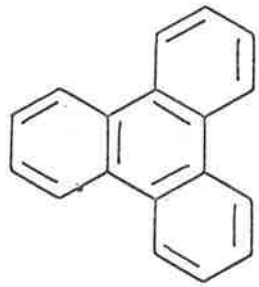
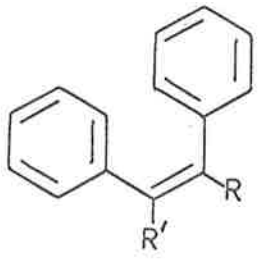


(12)

It is generally accepted[12] that an oxidant is required for the photocyclisation of stilbenes to phenanthrenes and reports to the contrary[7,13] have been explained on the basis of the adventitious presence of atmospheric oxygen. When α-α'-dicyanostilbene (13, R = R' = CN) was irradiated in the presence of oxygen or iodine, the expected 9,10-dicyanophenanthrene (14, R = R' = CN) was obtained.[14] However, when the irradiation was carried out in the absence of oxidants, an almost quantitative yield of trans-9,10-dicyano-9,10-dihydrophenanthrene (15, R = R' = CN) was isolated.[14] Similar



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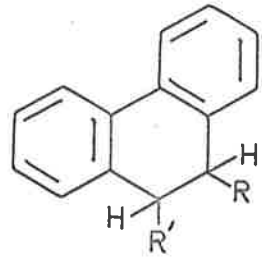
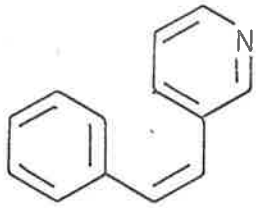


(15)

results were obtained with diphenylmaleic anhydride (13, RR' = CO.O.CO) and diphenylmaleimide (13, RR' = CO.NH.CO).

Increased yields of 9,10-disubstituted phenanthrenes have been reported when the cyclisations were carried out in the presence of copper halides.[15]

Contrary to earlier reports[8,10] that stilbazoles resist. photochemical cyclodehydrogenation, Loader, Sargent and Timmons[16] have isolated benzo[f]isoquinoline (17) in good yield following brief irradiation of 3-stilbazole (16). The 2- and 4- stilbazoles also underwent cyclisation although somewhat more slowly. 4-Styryl-quinoline gave a poor yield of benzo[i]phenanthridine. Similar results have been reported by Bortolus.[17] In view of the comparative



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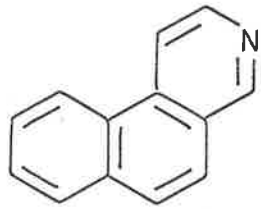


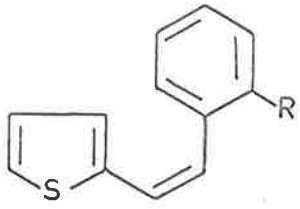
(17)

inaccessibility of benzo[f]- and benzo[h]- isoquinolines, the authors consider the reaction to be of synthetic value.

Spectral studies on the related 1,2-dipyridylethylenes[18] indicate that these compounds too will undergo cyclisation.

Thiophene analogues of stilbene have also been shown to cyclise on irradiation.[19] Thus naphtho[2,1-b]thiophene (19, R = H) was isolated in almost quantitative yield following irradiation, in the presence of iodine, of 2-styrylthiophene (18, R = H). Similarly, 11-thiabenzo[a]fluorene (21, R = H) was obtained from 3-styryl-

benzo[b]thiophene (20, R = H).



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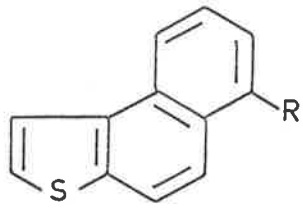

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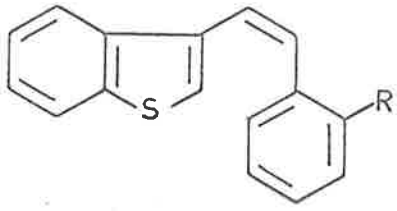

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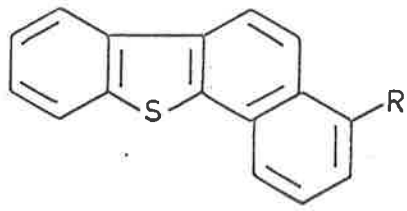
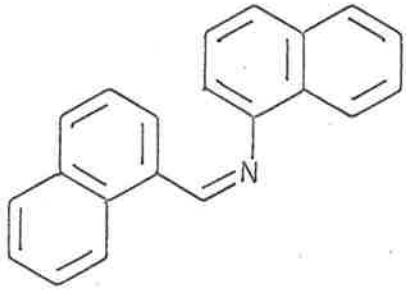


(21)

It is of interest that when the o-tolyl substrates were irradiated (18, 20, R = Me), in addition to the expected methyl substituted products (19, 21, R = Me), some unsubstituted products were obtained.

Replacement of a -CH= group in stilbene by nitrogen gives a Schiff base. Initial attempts to cyclise such compounds were unsuccessful.[10,13,20] However, Cava and Schleissinger[21] have found that irradiation of an ethanolic solution of the Schiff base (22) formed from 1-naphthylamine and 1-naphthaldehyde, yields dibenzo[c,i] phenanthridine (23). The reaction mixture in this case was open to the air. No reaction occurred in degassed benzene.

This successful cyclisation led Mallory *et al*[22] to re-



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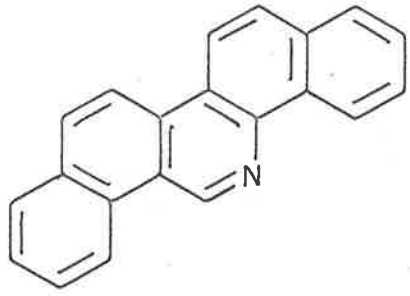
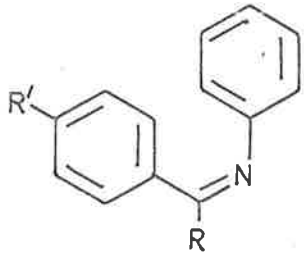


(23)

examine their earlier work[10] in which it was stated that benzalaniline (24, R = R' = H) could not be cyclised. They confirmed their previous findings that at room temperature, no cyclisation occurs and continued irradiation destroys the benzalaniline. This observation is explained by the rapid cis-trans thermal isomerisation of benzalaniline.[23] However, on cooling the irradiated solution to 10°, they were able to detect small amounts (2%) of cyclised product although prolonged irradiation again destroyed the benzalaniline. Additional evidence for the stereochemical explanation of non-cyclisation is the observation that N-diphenylmethyleneaniline (24, R = Ph, R' = H), which has no trans-isomer, cyclised readily, though slower than triphenylethylene, to give 6-phenylphenanthridine (25, R = Ph, R' = H).



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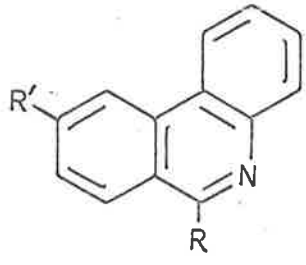
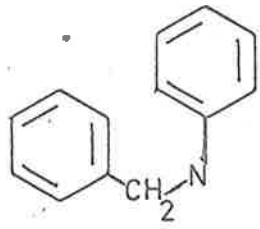


(25)

A small yield of 9-dimethylaminophenanthridine (25, R = H, R' = NMe_2) has been isolated[24] following the irradiation of p-dimethylaminobenzylideneaniline (24, R = H, R' = NMe_2). The major products of this interesting irradiation were azobenzene and 4,4'-bis(dimethylamino)-stilbene, presumably formed via a diazetidine intermediate.

The incorporation of a C_2 fragment from the solvent, ethanol, during photochemical cyclodehydrogenation of an aromatic Schiff base has also been encountered.[25]

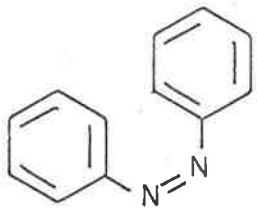
An independently discovered cyclisation of benzalaniline to phenanthridine under conditions quite different from those so far considered has been reported.[26] The solvent used was concentrated sulphuric acid and it is of interest that in addition to phenanthridine, some benzylaniline (26) was isolated. This phenomenon of cyclisation



(26)

being accompanied by reduction appears to be peculiar to photolyses performed in acidic solvents. Although Srinivarsan and Powers[27] have detected bibenzyl following the irradiation of cis-stilbene in degassed cyclohexane, bicyclohexyl was also formed and no phenanthrene could be detected. It seems unlikely therefore that the bibenzyl was formed from a reaction between dihydrophenanthrene and stilbene.

Replacement of both -CH= groups in stilbene with nitrogen atoms gives an aromatic azo compound. It has been known for some time that irradiation of aromatic azo compounds in neutral solution results in cis-trans isomerisation.[28] Azobenzene (27) can be cyclised thermally in aluminium chloride melts to benzo[c]cinnoline[29] (28), a reaction which has been applied more recently to the synthesis of some polycyclic benzo[c]cinnolines.[30]



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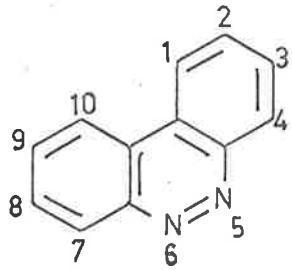
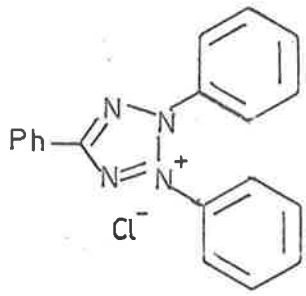


(28)

Benzo[c]cinnoline has also been synthesised by a reaction sequence using a photochemical ring closure as the key step.[31] Thus when 2,3,5-triphenyltetrazolium chloride (29) was irradiated in alcoholic solution, 2,3-diphenylene-5-phenyltetrazolium chloride (30) was produced. Reduction of this compound with Raney nickel gave



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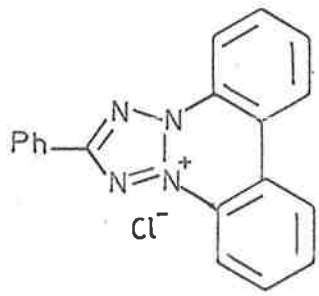

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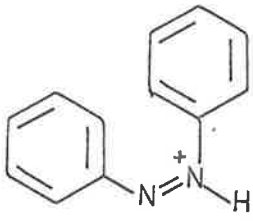
benzo[c]cinnoline in good yield. The preparative scope of this reaction can be widened by using suitably substituted substrates.

However, the first observation that irradiation of acidic solutions of azobenzene gives rise to benzo[c]cinnoline was made by Lewis in 1960.[32] In the same year, a similar photocyclisation of azobenzene was found to occur in acetic acid solution in the presence of aluminium chloride.[13] Lewis showed[33] that under the conditions of acidity used, both cis- and trans- azobenzene existed as their first conjugate acids (31 and 32), and that irradiation initially caused the cis-trans equilibrium (31 $\rightleftharpoons$ 32) to be established. Prolonged



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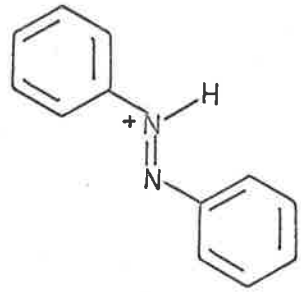
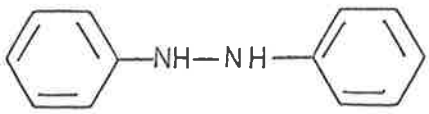


(32)

irradiation resulted in the formation of benzo[c]cinnoline at a rate approximately 100 times slower than that of the cis-trans equilibration. In later experiments,[34] benzidine was shown to be formed in approximately the same yield as benzo[c]cinnoline. In view of Nesmeyanov and Golovnya's report that protonated azobenzene is a powerful abstractor of hydride ions,[35] it was concluded that the hydrogen eliminated in

the cyclisation process reduced a second molecule of azobenzene to hydrazobenzene (33) which then rearranged under the acidic conditions to give benzidine (34).



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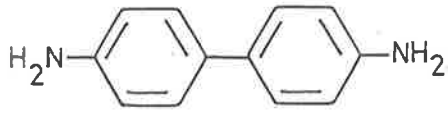


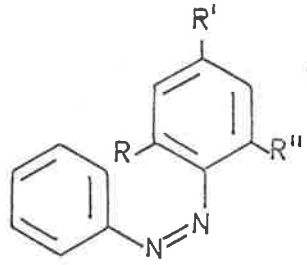
(34)

It is of interest that the fading in colour observed on irradiation of azobenzene in iso-propanol and iso-octanol has been attributed to hydrogen abstraction from the solvent to give the colourless hydrazo compound.[36]

The photochemical cyclisation in acid has also been found to proceed with methyl-substituted azobenzenes[37] and those substituted with halogens or carboxy groups.[38] 4-Substituted azobenzenes gave 2-substituted benzo[c]cinnolines. 3-Substituted azobenzenes gave a mixture of 1- and 3- substituted benzo[c]cinnolines — the proportion of the unhindered 3-isomer being greater than that of the sterically-hindered 1-isomer. Irradiation of 2-substituted azobenzenes gave, in addition to the expected 4-substituted benzo[c]cinnoline, some unsubstituted benzo[c]cinnoline due to the ejection of the substituent. The fate of the ejected substituent was not ascertained but the reaction has a parallel in the ejection of a methoxy group from the 2-position on photochemical cyclisation of 2-methoxy stilbene,[8] the ejection of a methyl group during the cyclisation of methyl substituted styryl-thiophenes[19] and the ejection of a methyl group on cyclisation of

3-methyl-2-styrylpyridine.[17]

Even more interesting was the cyclisation of 2,4,6-trimethylazobenzene (35, R = R' = R" = Me). In addition to the



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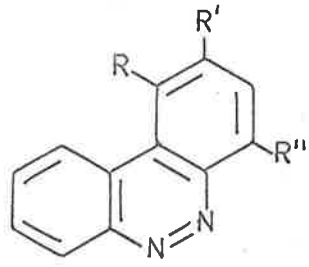
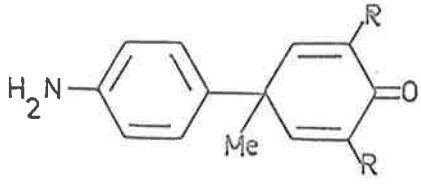


(36)

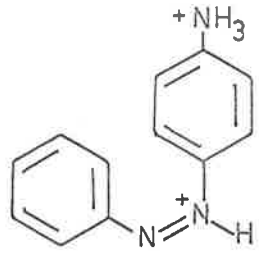
expected 2,4-dimethylbenzo[c]cinnoline (36, R = H; R' = R" = Me), a small yield of 1,2,4-trimethylbenzo[c]cinnoline (36, R = R' = R" = Me) was isolated.

In all the above cyclisations of substituted azobenzenes, the expected benzidine rearrangement product was also isolated except in the case of 4-methylazobenzene (35, R = R" = H, R' = Me) and 2,4,6-trimethylazobenzene (35, R = R' = R" = Me). In these cases, abnormal rearrangement products 4-(4'-aminophenyl)-4-methylcyclohexa-2,5-dienone (37, R = R' = H) and 4-(4'-aminophenyl)-2,4,6-trimethylcyclohexa-2,5-dienone (37, R = R' = Me) respectively were produced.[37]



(37)

It has been reported[39] that acidic solutions of 4-amino-azobenzene and 4-dimethylaminoazobenzene resist photochemical cyclisation. As there is little doubt that 4-aminoazobenzene exists in concentrated sulphuric acid as the diprotonated species (38), the failure of this compound to undergo cyclisation has been attributed[40] to the establishment of a prototropic equilibrium mixture (38 $\rightleftharpoons$ 39).



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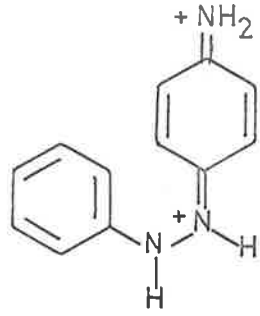
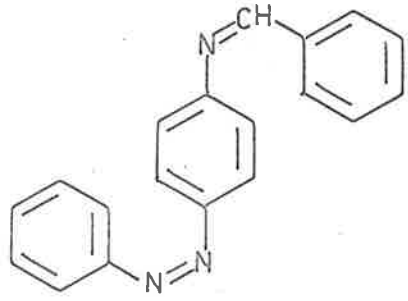


(39)

The powerful electron attracting effect of the protonated amino group would substantially reduce the bond order of the azo linkage and this would be reduced still further by isomerisation to the p-quinonoid dication (39). As it seems reasonable to assume that cyclisation occurs from the cis form, any effects reducing the stability of this form by lowering the double bond character of the azo linkage will considerably hinder cyclisation. It was thought probable[40] that the benzal derivative of 4-aminoazobenzene would so alter the electronic structure that cyclisation might occur. Accordingly, 4-benzalamino-azobenzene (40) was irradiated in 98% Analar sulphuric acid (to prevent hydrolysis of the Schiff base). There are two potential sites of cyclisation in such a molecule but cyclisation was found to occur

exclusively between the nuclei joined to the azo linkage. 2-Amino-benzo[c]cinnoline was obtained in 90% yield. This high yield is of



(40)

interest as previous cyclisations of azo compounds in more dilute acid produced benzo[c]cinnolines in approximately 50% yield along with some benzidine - rearrangement products. However, sulphur dioxide was evolved during the cyclisation in 98% Analar sulphuric acid and it was suggested that the hydrogen atoms liberated in the cyclisation were oxidised by the sulphuric acid.

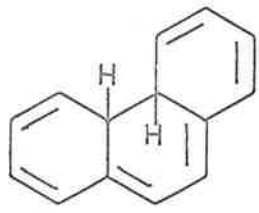
Other azobenzenes substituted with strongly electron-withdrawing groups, e.g. nitro and acetyl, were found to cyclise slowly, but in good yield in 98% Analar sulphuric acid. Again, no benzidine-type products were isolated from these cyclisations.

1.2. Mechanistic Considerations

The photochemically induced cis-trans isomerisation of stilbenes has been studied in some detail.[41] That the isomerisation can proceed via triplet states is shown by the fact that it will occur in the presence of known triplet excitation donors under conditions such that virtually all exciting light is absorbed by the donors.[42]

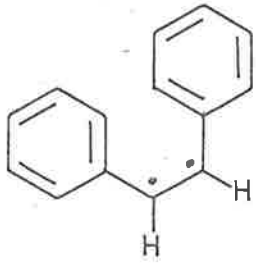
This result does not demand that the unsensitised isomerisation proceeds *via* triplet states but a comparison of the stationary state composition following direct and sensitised excitation makes this probable.[42]

The photochemical cyclisation of stilbene to phenanthrene has been postulated by Mallory[12] to proceed *via* an unorthodox dihydrophenanthrene intermediate (41).

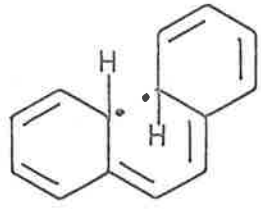


(41)

Initial suggestions by Schaffner[13] that photolysis of either *cis*- or *trans*- stilbene gives rise to a common excited state (42) which in turn gives rise to the excited state (43), followed by cyclisation to (41) have been disproved. Stegemeyer[43] found that although the



(42)



(43)

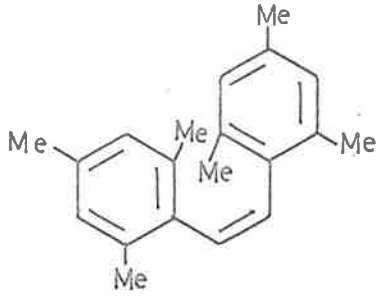
initial rate of phenanthrene formation was finite when oxygenated solutions of cis-stilbene were irradiated, the initial rate was zero following irradiation of solutions of trans-stilbene. Therefore the dihydrophenanthrene is formed from an excited state available only to cis-stilbene.

Irradiation of solutions of cis- or trans- stilbene in the absence of oxygen fails to produce phenanthrene but results in cis-trans isomerisation with no loss in the total amount of stilbene.[10] Thus the dihydrophenanthrene must undergo ring opening under these conditions at such a rate that the steady state concentration of this intermediate is low relative to that of stilbene. An exception to the normal non-cyclisation of stilbenes under anaerobic conditions has been mentioned previously. When the substrate has two strongly electron-attracting groups on the α-positions, a 1,3-prototropic shift occurs in the dihydrophenanthrene intermediate to produce a 9,10-dihydrophenanthrene.[14]

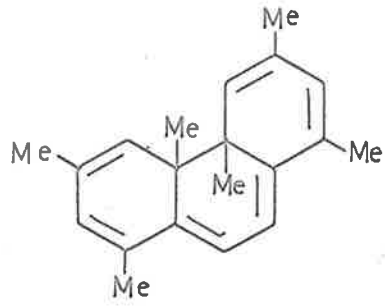
In the presence of oxygen, the dihydrophenanthrene (41) is believed to undergo two successive abstractions of the doubly-allylic 4a- and 4b-hydrogens and hydrogen peroxide has been detected in irradiated solutions exposed to air.[44]

Evidence for the structure of the dihydrophenanthrene is that irradiation of degassed solutions of stilbene produces a yellow colour.[4,41,44] Subsequent exposure of this yellow solution to the air caused decolourisation and the production of phenanthrene.[44] More recent evidence both for the structure of the dihydrophenanthrene

and the role of the oxygen has been reported by Muszkat.[45] Irradiation of solutions of 2,2':4,4':6,6'-hexamethylstilbene (44) in the presence or absence of air produced a red compound assumed to be 1,3,4a,4b,6,8-hexamethyl-4a,4b-dihydrophenanthrene (45). The stability of this



(44)



(45)

compound to oxidation is explained by the absence of the 4a- and 4b-hydrogens.

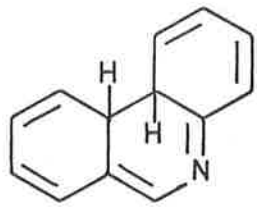
The trans-configuration for the dihydrophenanthrene (41) is defended by Mallory[12] on steric grounds and by the expectation that a cis-configuration would undergo spontaneous dehydrogenation. Also the analogous photochemical cyclisation of 2,4,6-octatriene (3, R = Me) has been shown[6] to give trans-1,2-dimethyl-3,5-cyclohexadiene (4, R = Me). The stereochemistry of such "electrocyclic reactions" has been rationalised recently by Woodward and Hoffman.[46]

The photocyclisation of stilbene to phenanthrene is not quenched by oxygen which suggests that the excited state undergoing ring closure is not a triplet. More convincing evidence is the report that dihydrophenanthrene formation does not occur when the

triplet state of stilbene is produced directly from a wide variety of triplet state photosensitiser molecules.[47]

The photochemical cis-trans isomerisation of azo compounds has so far received less attention than that of the stilbenes. The photostationary composition is independent of initial composition or light intensity but depends strongly on wavelength.[48] It appears that there cannot be a common excited state irrespective of which isomer is excited as the sum of the quantum yields for cis-trans and trans-cis isomerisation is less than unity.[49] Zimmerman has suggested[49] that the isomerisation is a thermal one occurring between excited cis- and trans- states and studies of the isomerisation at low temperatures support this.[50] The lower the temperature, the more the trans-isomer predominates indicating that it is of lower energy than the cis-isomer — a situation which, of course, parallels the ground state. More recent work by Hammond[51] on the photosensitised isomerisation of azobenzene has shown that the non-sensitised isomerisation does not proceed via the triplet state.

The photochemical cyclodehydrogenation of Schiff bases can apparently occur by two different mechanisms. Cyclisations in organic solvents[21,22] require an oxidant to convert the intermediate dihydrophenanthridine (46), to phenanthridine. However, the cyclisation reported to occur in sulphuric acid[26] produces, in addition to phenanthridine, some benzylaniline and is therefore mechanistically related to the cyclisation of azo compounds in acidic solution now to be discussed.

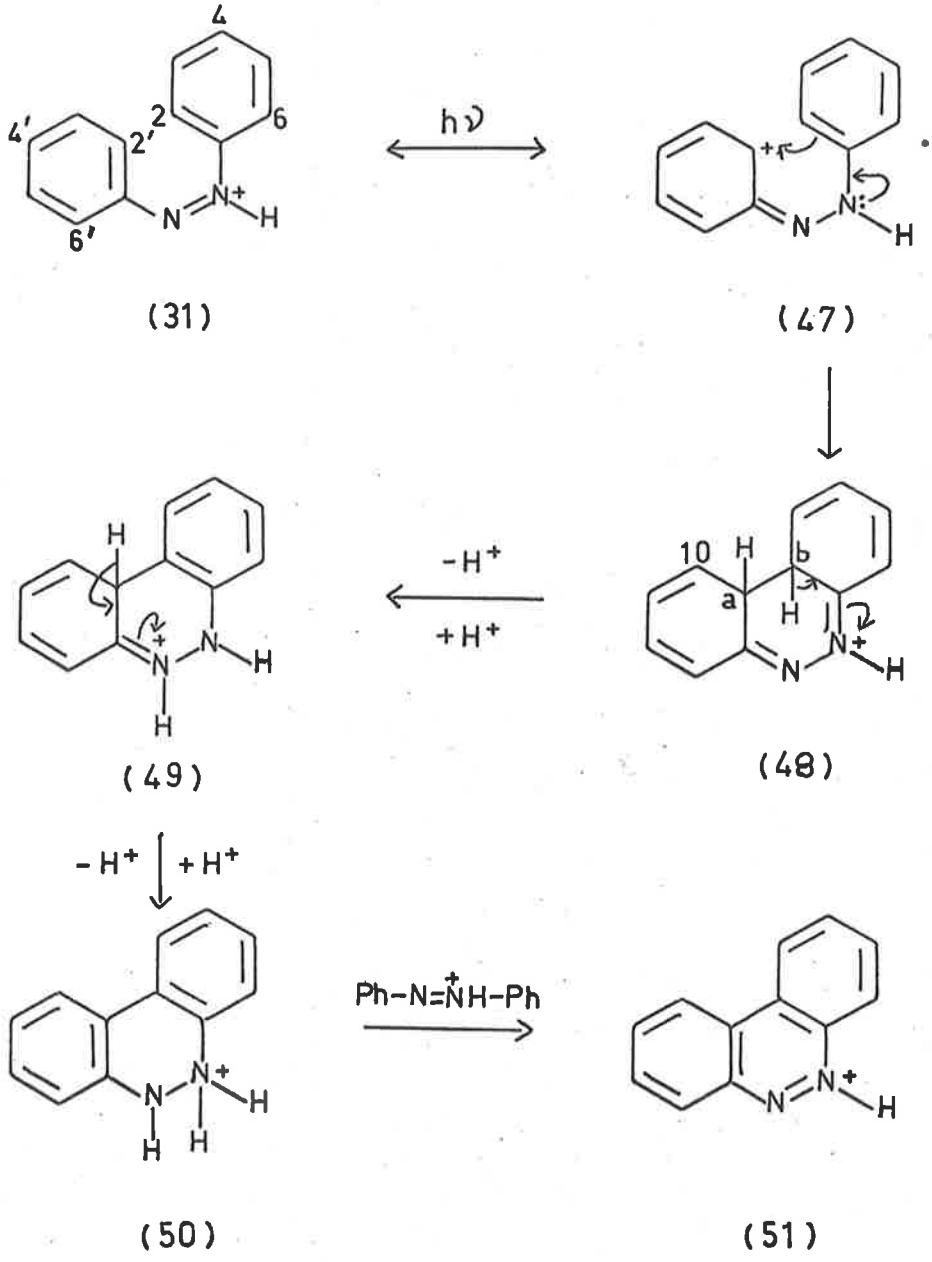


(46)

Jaffé[52] has examined the spectrum of azobenzene in organic solvents and has assigned the longest wavelength band, at 420 mμ, to an $n \rightarrow \pi^*$ transition. The failure of azobenzene, p-acetylstilbene and m- and p-nitrostilbenes to undergo cyclisation has been attributed by Mallory[10] to the lowest excited state being of the $n\pi^*$ rather than the $\pi\pi^*$ type which is apparently necessary for cyclisation. However, the longest wavelength absorption band of azobenzene in acidic solutions has been assigned[52] to a $\pi \rightarrow \pi^*$ transition and this has been shown[53] to be associated with an increased basicity of excited azobenzene compared with the ground-state molecule. These two factors, the lowest excited singlet state of protonated azobenzene being of the $\pi\pi^*$ type and the enhanced basicity of the excited state of azobenzene, form the basis for the mechanism of cyclisation of acidic solutions of azobenzene postulated by Badger, Drewer and Lewis[54] and detailed in Scheme I.

Because of the enhanced basicity of excited azobenzene, structure (47) may be considered as an important resonance form. This photoexcited cis-conjugate acid is considered to undergo ring closure to give the conjugate acid of 10a,10b-dihydrobenzo[c]cinnoline (48)

SCHEME I


4
2
6
4'
2'
6'
N
N+
H
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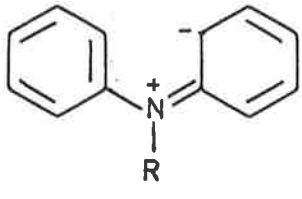
+r
N
N:
H
(31)
(47)
10
H
b
a
H
N
N+
H
-H+
+H+
H
N
N
H
H
(48)
(49)
-H+
+H+
N
N+
H
N
H
H
Ph-N=N+H-Ph
N
N+
H
(50)
(51)

which experiences two fast prototropic rearrangements to form the conjugate acid of 5,6-dihydrobenzo[c]cinnoline (50). This is readily oxidised by the powerful dehydrogenating agent, protonated azobenzene[35] to give benzo[c]cinnoline and hydrazobenzene. The latter, of course, would immediately rearrange under the acidic conditions to give benzidine.

Unlike the cyclisation of stilbene to phenanthrene, the initial ring-closure step is thought to be irreversible and, of course, no oxygen is required. In fact attempts to increase the yield of benzo[c]cinnoline by adding such oxidants as nitrobenzene, p-nitrobenzaldehyde, chloranil and benzil were unsuccessful[39] as these additives could not compete with protonated azobenzene as a dehydrogenating agent. It has been suggested[55] that the thermal cyclisation of azo compounds in the presence of the Lewis acid aluminium chloride also proceeds through an intermediate similar to (47).

The mechanism of Badger, Drewer and Lewis is reminiscent of that proposed for the cyclisation of diphenylamines to carbazoles.[56] An ionic mechanism was suggested for such transformations involving intermediates (52) and (53).



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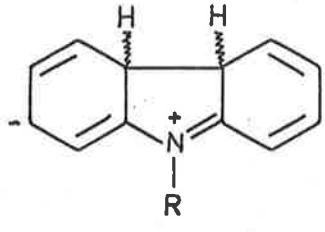


(53)

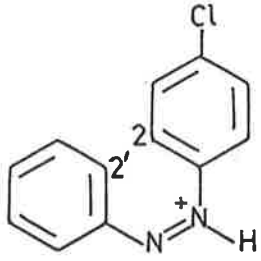
R= H, Me or Ph

More recent work[57] has shown that (53) is formed from a triplet state of diphenylamine. It was considered unlikely that a triplet state was involved in the cyclisation of azobenzene however as its relatively long lifetime would allow greater opportunity for cis-trans isomerisation and also secondary protonation to occur.[54] Both these effects would result in hinderance to ring closure.

The effect of acidity changes on the cylisation of azobenzene was also investigated.[54] It was found that an increase in acidity increased the yield fraction of the products but decreased the quantum yield. This decrease in quantum yield was attributed to the formation of a second conjugate acid. If the sp^2 hybridised nitrogen of structure (47) were protonated, ring closure would be inhibited while protonation of the sp^3 hybridised nitrogen would completely prevent cyclisation.

It was not found possible to completely explain the effects of substituents upon quantum yields and attempts to correlate them with Hammett substituent constants were unsuccessful. However, the authors were able, to a certain extent, to rationalise the differences in quantum yields found for azobenzene, 4-chloroazobenzene and 4-methylazobenzene which decreased in that order.

In structure (54), the -I effect of the chloro substituent would tend to inhibit development of a negative charge at the 2-position which is assumed to be necessary for cyclisation. On the other hand, the +M effect in structure (55) would reduce the charge on the protonated nitrogen and hence at the 2'-position and ring closure would again be



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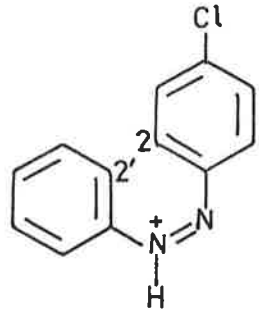

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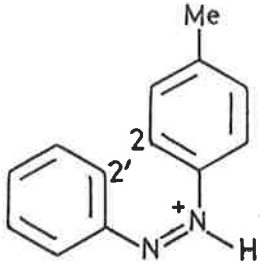

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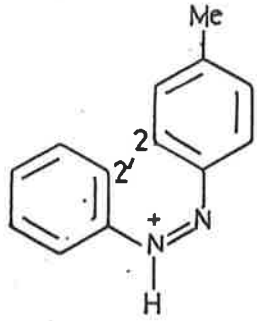


(57)

hindered.

Similar reasoning was applied to 4-methylazobenzene. In structure (56) the electron density at position 2 would be slightly increased by the +I effect of the methyl group and an enhancement of the rate of cyclisation should result. However, the hyperconjugative effect of the methyl group in structure (57) would clearly hinder cyclisation. It is reasonable to assume that protonation of 4-methylazobenzene gives rise mainly to tautomer (57) and this might account for the lower quantum yields observed for this compound.

CHAPTER II

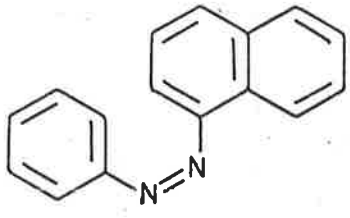
THE PHOTOCHEMISTRY OF SOME AZO COMPOUNDS IN 22N SULPHURIC ACID.

2.1 Azonaphthalenes.

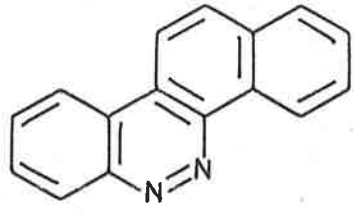
From the preceding review it is seen that the photochemical cyclodehydrogenation of azobenzenes is a general reaction which occurs with all substituted azobenzenes so far examined, with the exception of 4-amino- and 4-dimethylaminoazobenzene. It was decided therefore, to attempt to extend such cyclisation reactions to the azonaphthalenes.

The irradiations were carried out in a water-cooled Pyrex apparatus with a Philips HPK 125W mercury-quartz lamp. The radiation passed through a water-jacket before it entered the solution of the azo compound. The solution was not stirred but previous work had shown[39] that the small amount of heat from the lamp which reached the solution was sufficient to produce mixing due to convection currents.

1-Phenylazonaphthalene (58) was found to undergo ready cyclisation to give a good yield of naptho[1,2-c]cinnoline (59). The structure assigned to this product is supported by the fact that its ultra-

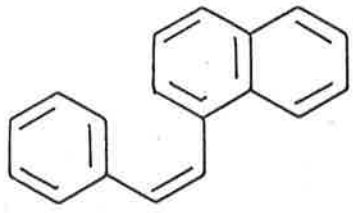


(58)



(59)

violet absorption spectrum resembles that of chrysene (8), the carbocyclic analogue (Fig. 1). This reaction has a parallel in the stilbene series where it has been shown[8] that irradiation of 1-styrylnaphthalene (60) in hexane solution, and in the presence of iodine, produces chrysene (8). The naphtho[1,2-c]cinnoline was isolated in 42% yield and although



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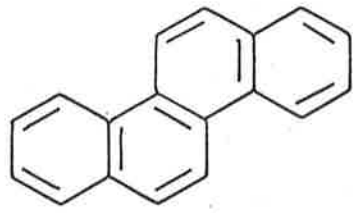
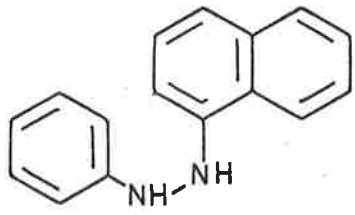


(8)

the other products were not positively identified, it appears that some of the 1-phenylazonaphthalene was reduced to N-1-naphthyl-N'-phenylhydrazine (61), which immediately underwent rearrangement. The by-



(61)

products were obtained as a grey-black solid whose infrared spectrum showed a band at 3300 cm^{-1} (NH). Also, a diazotised solution of the solid gave a red dye when coupled with 2-naphthol. The normal benzidine rearrangement products of N-1-naphthyl-N'-phenylhydrazine have been investigated.[58] However, attempts to separate the components of the

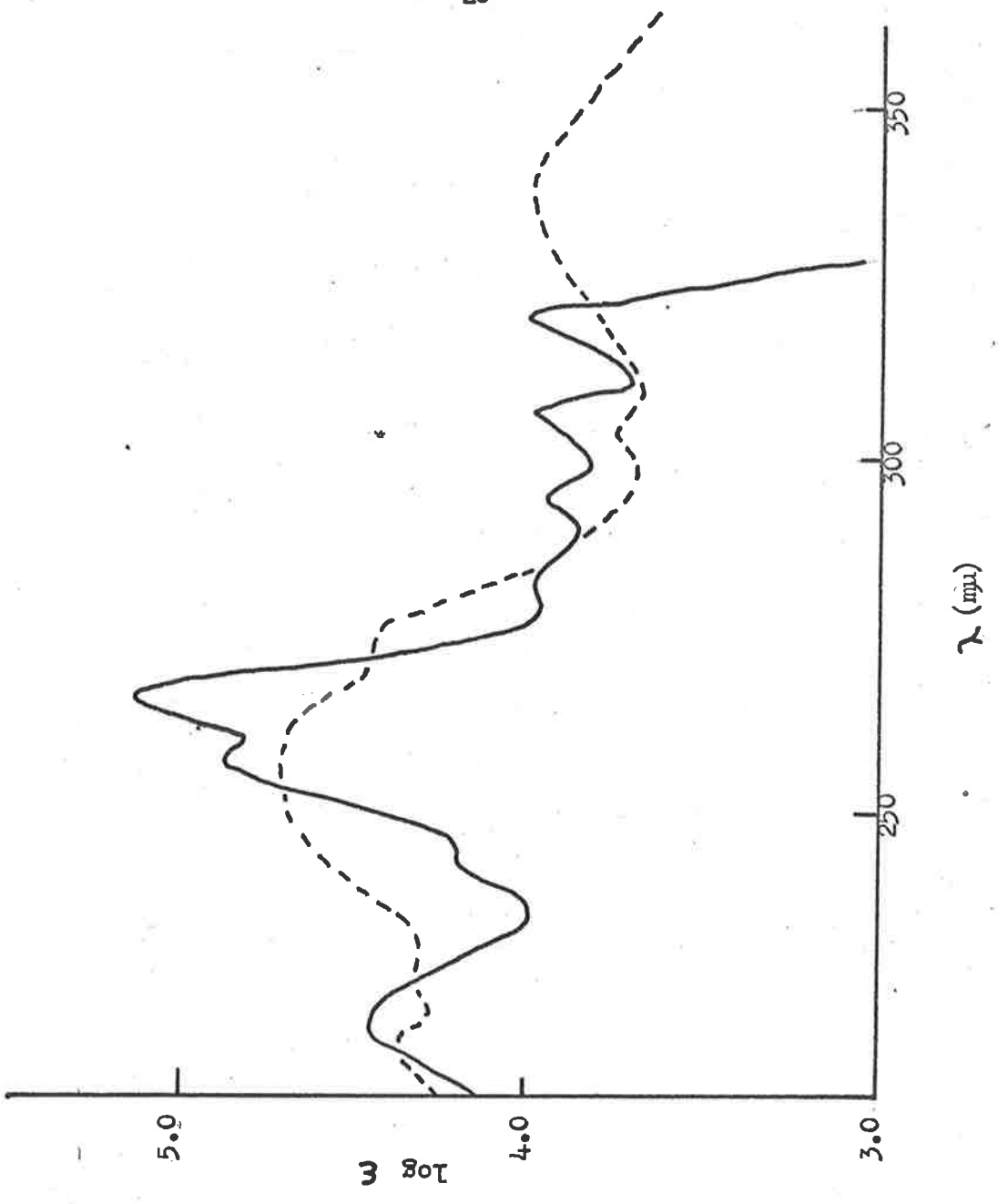


Fig. 1. - Absorption spectra of chrysene (8) (———) and of naphtho[1,2-c]cinnoline (59) (- - - -), in 95% ethanol.

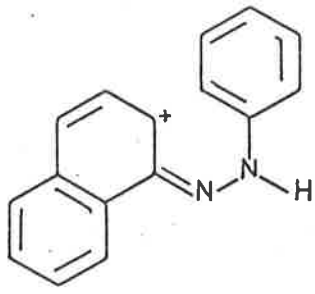
present rearrangement by the same methods were unsuccessful. Finally, an authentic sample of N-1-naphthyl-N'-phenylhydrazine was prepared by the zinc and ammonium chloride reduction of 1-phenylazonaphthalene. This was treated with acid and the products were compared, by thin-layer chromatography, with those obtained from the photolysis of 1-phenylazonaphthalene. Only one spot in both chromatograms showed identical R_F values. It would appear therefore, that the hydrazo compound has undergone an abnormal benzidine rearrangement under the photolysis conditions — a phenomenon which has been observed previously with substituted azobenzenes.[37]

Although 1-phenylazonaphthalene readily underwent cyclodehydrogenation, none of the other azonaphthalenes could be induced to do so. Irradiations were carried out on dilute solutions (c. 2×10^{-5} M) both at room temperature and at less than minus 30°, but no evidence of cyclisation was obtained, although the solutions showed some fading in colour. For low-temperature irradiations, the entire photolysis apparatus was placed in a Dewar bowl containing ethanol and solid carbon dioxide.

It is not fully understood why these azonaphthalenes resist photochemical cyclodehydrogenation. Of course, absorption of radiation by a molecule does not necessarily lead to a photochemical reaction. The energy absorbed can be dissipated by such non-productive processes as internal conversion, intersystem crossing, self quenching, fluorescence or phosphorescence. Some of these general processes may be important in the case of the azonaphthalenes but it is interesting to

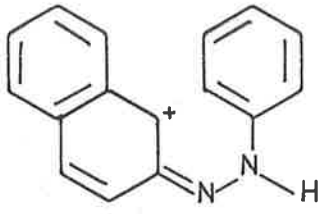
speculate on other factors peculiar to these compounds. Although cis-azobenzene was first isolated in 1937,[28] early attempts to isolate the cis-forms of the azonaphthalenes apparently failed.[59] However, in 1955, Frankel, Wolovsky and Fischer[60] isolated the cis-isomers of 1,2'- and 2,2'- azonaphthalene by working in a dimly lit room at 0°. They also showed that cis-1,1'-azonaphthalene was formed on irradiation of solutions of the trans-isomer, but considered that the isolation of this cis-isomer might be possible only by working at temperatures considerably below 0°. It is obvious then, that the cis-forms of the azonaphthalenes are considerably less stable than those of the azobenzenes.

If we now consider the postulated mechanism of cyclisation as discussed in the preceding chapter, then the more basic nitrogen of the azo linkage will be preferentially protonated. It has been calculated[61,62,63] that the conjugating ability of the 1-position in naphthalene is greater than that of the 2-position, which in turn is slightly greater than the conjugating ability of a phenyl ring. This is reflected in the basicities of 1-naphthylamine, 2-naphthylamine and aniline, and is borne out by experiments on the oxidation of aromatic azo compounds with perbenzoic acid.[64] If these results are applied to the photochemical cyclodehydrogenation of 1-phenylazonaphthalene, then protonation will presumably occur almost exclusively on the nitrogen adjacent to the phenyl ring. Thus cyclisation will proceed via (62), in which the aromaticity of the unsubstituted ring of the naphthalene nucleus remains undisturbed.



(62)

In the case of 2-phenylazonaphthalene, again there will be a slight preference for protonation to occur on the nitrogen adjacent to the phenyl ring. One can now visualise two possible excited states, (63) and (64). Cyclisation of (63) will be inhibited by steric



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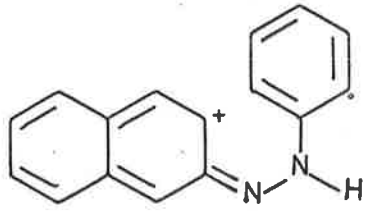
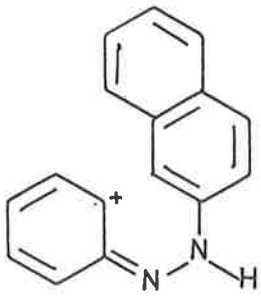


(64)

hinderance as the product which would be formed, dibenzo[c,f]cinnoline, is known[65] to possess considerable ring strain. On the other hand, the existence of an excited state such as (64) is unlikely as the 2,3-bond in naphthalene has little double bond character, and structure (64) involves the destruction of aromaticity in both rings of the naphthalene nucleus.

As the conjugating ability of the 2-position in naphthalene is only very slightly greater than that of a phenyl ring, it is possible

to envisage excited states (65) and (66) where protonation has occurred



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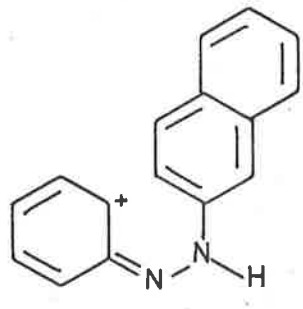
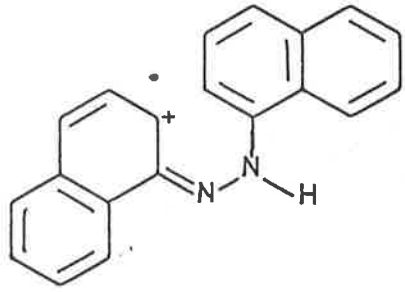


(66)

on the nitrogen adjacent to the naphthalene nucleus. Cyclisation from (65) would again produce dibenzo[c,f]cinnoline whose formation is unfavourable for reasons mentioned above. Cyclisation from (66) is also unlikely, again because of the low double bond character of the 2,3-bond in naphthalene, and also because ring closure would necessitate the loss of aromaticity of both phenyl rings of the naphthalene moiety. Application of the same principles to 1,2'- and 2,2'- azonaphthalene shows that there are no excited states favourable for cyclisation. However, the observed non-cyclisation of 1,1'-azonaphthalene cannot be explained in a similar way. It is possible to represent an excited state (67) which should be able to cyclise without undue loss of aromaticity to give benzo[h]naphtho[1,2-c]cinnoline, a compound known[65] to be free from ring strain. Two factors could contribute to the photochemical stability of 1,1'-azonaphthalene. As mentioned previously, Frankel, Wolovsky and Fischer[60] were able to isolate cis-isomers of 1,2'- and 2,2'- azonaphthalenes by working at temperatures near 0°. However no cis-1,1'-azonaphthalene could be isolated at this temperature and a

later paper by Fischer[50] states that temperatures less than minus 20° are necessary to stop the thermal cis trans isomerisation of 1,1'-azonaphthalene. This extreme lability of the cis-form of 1,1'-



(67)

azonaphthalene would account for the observed lack of cyclisation at room temperature. However, in the present work, irradiations were also carried out at minus 30° and still no cyclisation was observed. This could also be explained on the basis of Fischer's work[50] in which it was found that the proportion of cis-isomers of azo compounds, following irradiation, was a function both of temperature and wavelength of irradiating light. Irradiation of solutions, in organic solvents, of 1,1'-azonaphthalene at minus 30° with 313 mμ light produced approximately 80% trans-isomer, and irradiation with 546 mμ light, about 60% trans-isomer. The lamp used in the present work had an emission line at 313 mμ and at least part of this radiation would be transmitted through the Pyrex walls of the reactor. The lamp also had a strong emission line at 546 mμ. Thus the majority of the 1,1'-azonaphthalene present, even at minus 30°, would be in the trans-form which, of course, cannot undergo cyclisation. Related experiments with 2,2'-azonaphthalene[50]

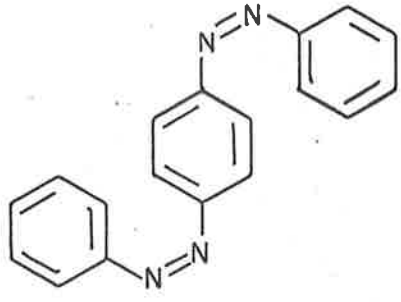
suggest that it too would exist mainly in the trans-form unsuitable for cyclisation. Although no cyclisation could be detected with 2-phenylazonaphthalene, 1,1'-, 1,2'-, nor 2,2'- azonaphthalene, some fading in colour of the solutions was observed so that acidic solutions of the azonaphthalenes are not entirely stable to light.

Polycyclic cinnolines are usually prepared by reducing the appropriate 2,2'-dinitrobiaryl, but the yield is often low both in reduction, and in the Ullmann reaction by which the dinitrobiaryl is formed. Holt and Went[30] have therefore studied the cyclisation of azo compounds in aluminium chloride/sodium chloride melts, and also by heating them with aluminium chloride in refluxing methylene chloride, with a view to developing an improved synthesis of polycyclic cinnolines. Benzo[f]naphtho[2,1-c]cinnoline was obtained from 2,2'-azonaphthalene in 70% yield by means of a melt and in 90% yield using aluminium chloride in refluxing methylene chloride. 1,1'-Azonaphthalene, 1,2'-azonaphthalene and 2-phenylazonaphthalene were also cyclised but in much poorer yield. However, 1-phenylazonaphthalene could not be cyclised under either of these conditions. The present work then, may be considered as being complementary to that of Holt and Went as it constitutes the first example of the cyclisation of 1-phenylazonaphthalene to naphtho[1,2-c]cinnoline. This cinnoline has been prepared previously[66] by the lithium aluminium hydride reduction of 1-nitro-2-o-nitrophenylnaphthalene. It is stated[66] that 1g of the dinitrobiaryl yielded, on reduction, 2.4 g of the cinnoline which is a 300% yield. It seems likely that a decimal point has been misplaced and that the yield is

in fact 30%. As the preparation of 1-nitro-2-o-nitrophenylnaphthalene was achieved in a crude yield of only 25%, the synthesis, in over 40% yield of naphtho[1,2-c]naphthalene by the photochemical cyclodehydrogenation of 1-phenylazonaphthalene offers some advantages. The photochemically produced sample is also purer as shown by its melting point of 195° compared with 190° for the sample produced by reduction of the dinitrobiaryl.

2.2 Bisazo Compounds.

It was considered of interest to examine the photochemical behaviour of acidic solutions of compounds containing two azo linkages in the same molecule i.e. bisazo compounds. 4-Phenylazoazobenzene (68) is the simplest such compound, and there appeared to be the possibility



(68)

that a double cyclisation may occur to give a pentacyclic product.

The photocyclisation of azo compounds to benzo[c]cinnolines is very readily followed spectrophotometrically. For instance, the intense broad absorption band at 420 mμ of azobenzene itself in 22N sulphuric acid is replaced by peaks at 252 and 365 mμ typical of benzo[c]cinnoline in acidic solution (Fig. 2). The bleaching of dilute

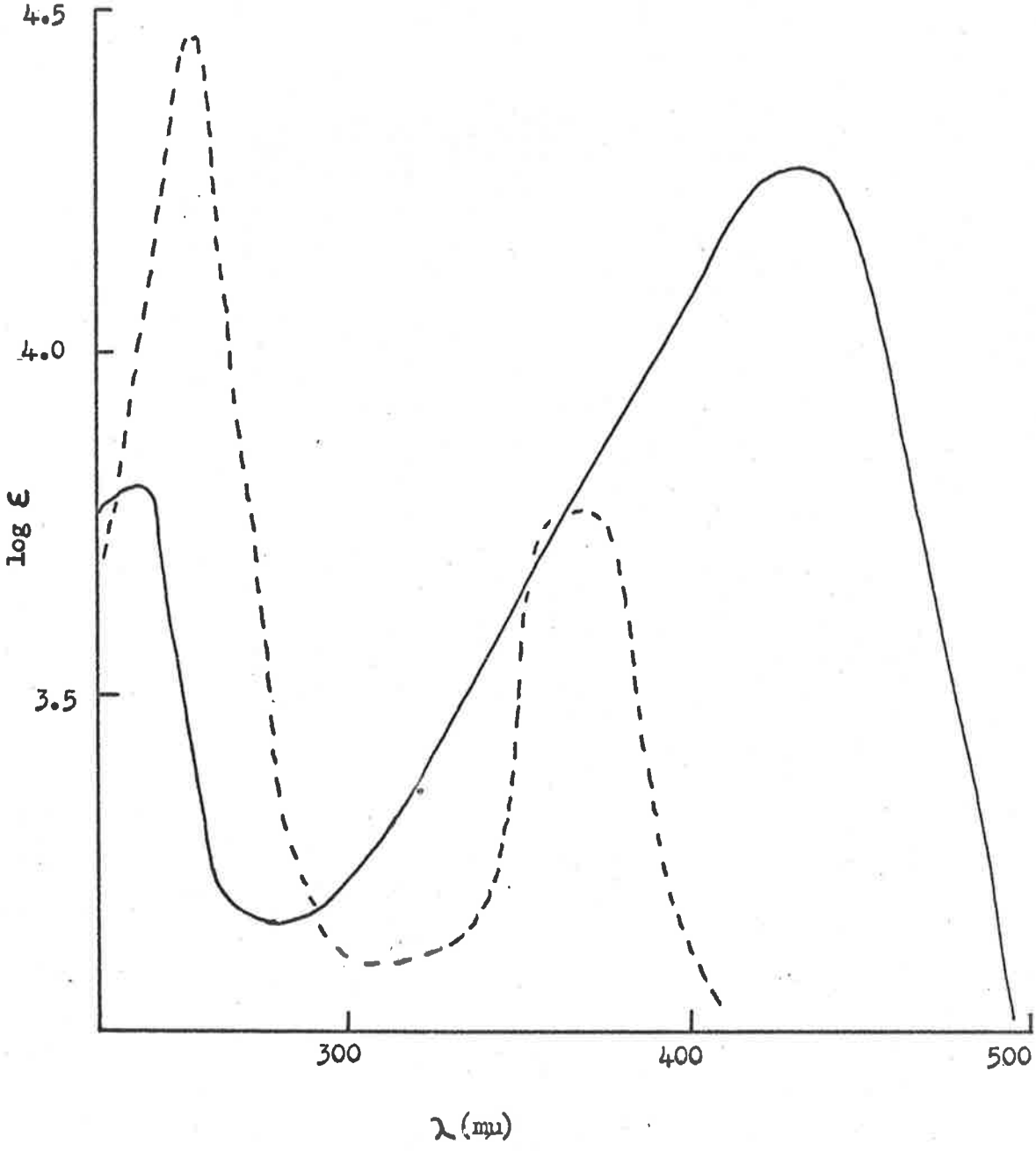
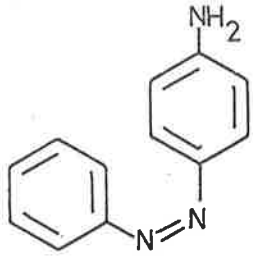


Fig. 2. - Absorption spectra of azobenzene (———) and of benzo[c]cinnoline (- - - -), in 22N sulphuric acid.

(c. 2×10^{-5} M) acidic solutions of azo compounds following irradiation is usually also indicative of cyclisation.

When dilute solutions of 4-phenylazoazobenzene in 22N sulphuric acid were exposed to sunlight, a rapid bleaching occurred. However, the ultraviolet absorption spectrum of the irradiated solution showed no absorption bands attributable to cyclised products. Similar results were obtained when dilute solutions were irradiated with either a mercury-quartz or a tungsten lamp. As the decolourisation was fastest with a tungsten lamp, this lamp was used for experiments on a preparative scale. Irradiations with such a lamp were carried out by immersing the lamp in the solution to be examined. The beaker containing the solution was placed within a larger beaker through which cold water was passed. Under these conditions, the temperature of the solution was maintained at about 40°.

4-Phenylazoazobenzene is readily soluble in 22N sulphuric acid and the resultant solution is dark red in colour. Irradiation of concentrated solutions caused the colour to change to green, and a considerable quantity of tar was produced. However, the isolable products were separated by chromatography on alumina and proved to be 4-aminoazobenzene (69) and 4-amino-3-(4'-aminophenyl)azobenzene (70). The structure of (69) was readily established by comparison with an authentic sample. The structure assigned to (70) is supported by the fact that its ultraviolet absorption spectrum in 22N sulphuric acid closely resembles that of 4-aminoazobenzene in the same solvent (Fig. 3). Its infrared spectrum showed the presence of NH, and a red dye was



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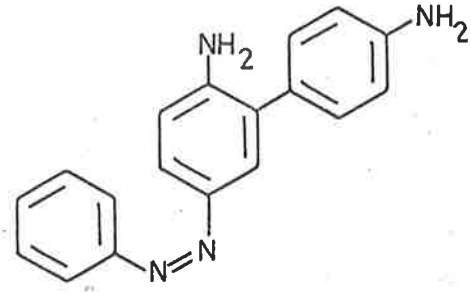


(70)

produced when a diazotised solution was added to 2-naphthol. The presence of two primary amino groups was shown by the fact that it formed a bis-salicylidene derivative.

The same two products were formed when 22N sulphuric acid solutions of 4-phenylazoazobenzene were left at room temperature in the dark, and it is obvious that the bisazo compound is unstable in 22N sulphuric acid. The formation of 4-aminoazobenzene could be explained by a simple hydrolysis of 4-phenylazoazobenzene. The other product of such a hydrolysis would be nitrosobenzene which is fairly unstable at room temperature and its decomposition would explain the tar formation. The 4-amino-3-(4'-aminophenyl)azobenzene (70) is apparently formed by a benzidine-type rearrangement of 4-phenylazohydrazobenzene (71). In view of Nesmeyanov and Golovnya's report[35] that azobenzene in sulphuric acid can abstract hydrogen from a variety of compounds, the formation of (71) is readily explained. The hydrogen in this case may be extracted from the nitrosobenzene although it could also be provided by the other substrates present.

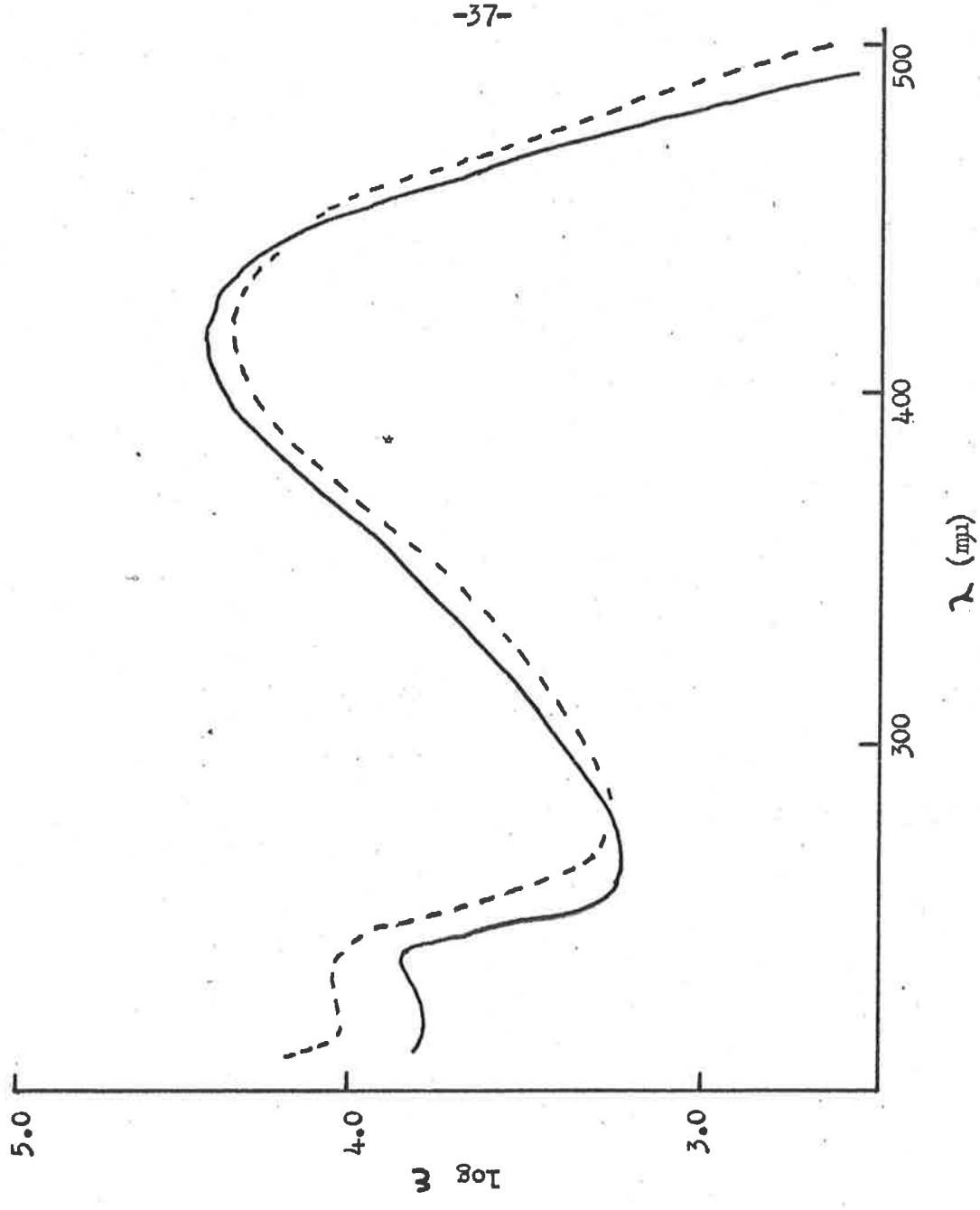
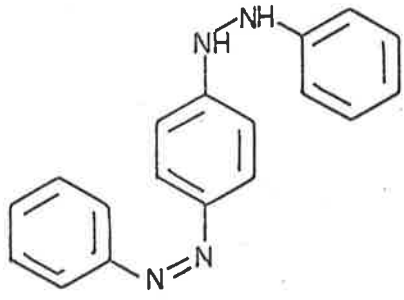


Fig. 3. - Absorption spectra of 4-aminoazobenzene (69) (———) and of 4-amino-3-(4'-aminophenyl)azobenzene (70) (- - - -), in 2$\underline{N}$ sulphuric acid.



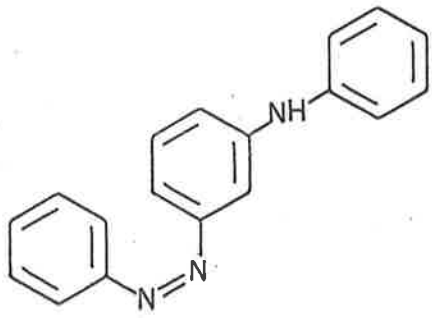
(71)

Prediction of the products to be expected following a benzidine rearrangement of (71) is possible only by consideration of the mechanism of such a reaction. As this rearrangement is important in explaining most of the products observed in this work, it will be discussed in some detail in a later chapter. However, at this point it is relevant to quote Ingolds summarising statement of the orientational principles so far observed in the benzidine rearrangement. This is as follows[67] : "A 4-substituent, if strongly electron donating, leads to 2,N'-linking, if not, to 2,4'-linking, and if both strongly donating and attracting (halogens) to both modes of linking; an electron donating substituent, if at 4, orients linking towards 2 and if at 2, towards 4, with a strength paralleling that of its electron donation."

The application of these rules to the rearrangement of (71) predicts the formation of the observed diphenyline, 4-amino-3-(4'-aminophenyl)azobenzene (70). For, under the strongly acidic conditions

used, there can be little doubt that the azo linkage will be protonated thus causing electron attraction and orientation to 2,4'-linking.

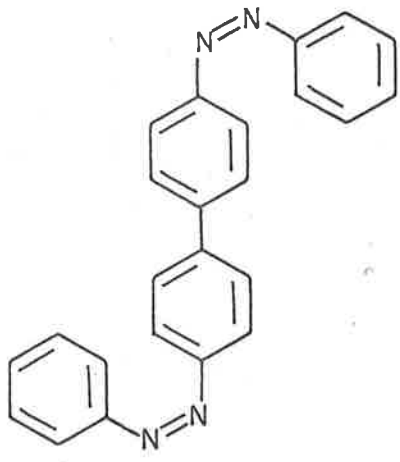
Two previous reports have been made on the acid catalysed rearrangement of (71). In one of these,[68] the only products detected were those of disproportionation i.e. 4-phenylazoazobenzene, 4-amino-azobenzene and aniline. However, in the earlier work,[69] a compound was isolated which had incorporated chlorine from the catalysing hydrochloric acid. Its structure was not rigorously determined although the authors suggest it was derived from the first formed o-semidine (72). It is possible that, under the mild acidic conditions used, the



(72)

azo linkage resisted protonation and thus guided the rearrangement along this alternative path leading to 2,N'-linking.

As 4-phenylazoazobenzene, then, is quite unstable in 22N sulphuric acid, it was decided to attempt to find a bisazo compound, stable in such a medium, whose photochemistry could therefore be examined. To this end, 4,4'-bis(phenylazo)biphenyl, (73), was prepared. The product was purified by chromatography prior to crystallisation.

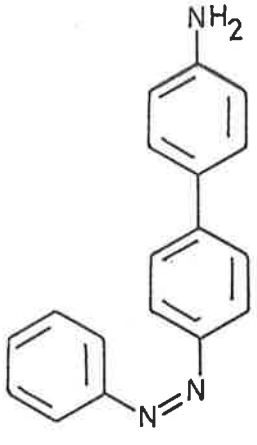


(73)

Initial experiments with dilute solutions showed that irradiation caused fairly rapid decolourisation and a change in the ultraviolet absorption spectrum attributable to cyclisation. A qualitative comparison of the rates of decolourisation produced by irradiation with a mercury-quartz lamp, sunlight, and a tungsten lamp was made. The last was the most rapid and tungsten irradiation was therefore used for the preparative work. Irradiation of concentrated solutions of 4,4'-bis(phenylazo)biphenyl in 22N sulphuric acid produced some tar, but the compound is considerably more stable in this medium than is 4-phenylazoazobenzene. Irradiation was continued until the ultraviolet absorption spectrum showed the reaction to be virtually complete. After neutralisation of the reaction mixture, the products were extracted and separated by chromatography on alumina.

Early fractions from the column yielded a red solid whose

ultraviolet absorption spectrum was that of an azo compound rather than a benzo[c]cinnoline. It melted over a range of temperature and was obviously impure. It showed two spots on examination by thin-layer chromatography on silica gel, and it was therefore subjected to rechromatography on silica gel. The two components isolated were 4-(4'-aminophenyl)azobenzene (74) and 4-[4'-amino-3'-(4''-aminophenyl)-phenyl]azobenzene (75). The structure of (74) was determined unambiguously by comparison with an authentic sample prepared by condensing one mole of nitrosobenzene with one mole of benzidine.[70] Benzylidene



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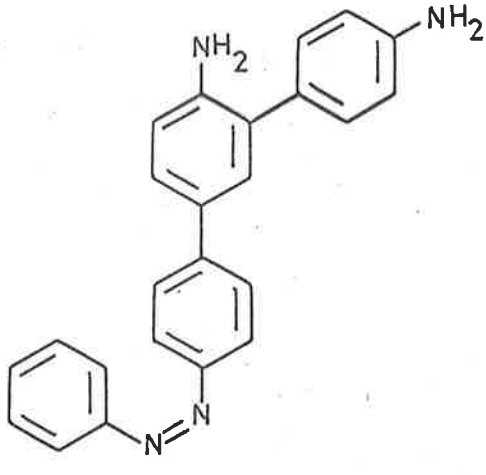

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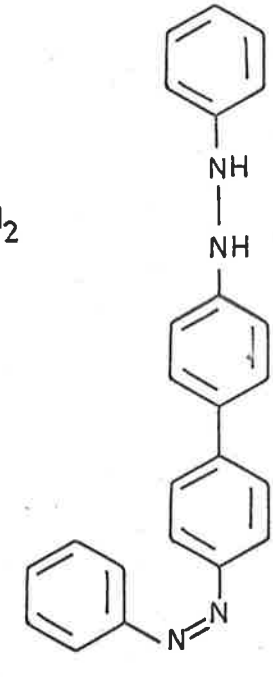
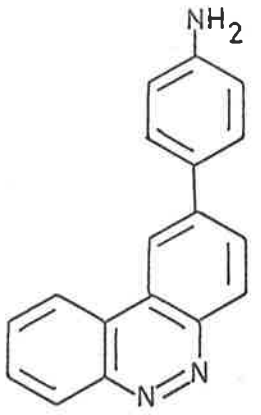


(76)

and anisylidene derivatives were also prepared and found to be identical with authentic samples. The structure assigned to (75) is supported by the fact that it formed a bis-salicylidene derivative, thus showing the presence of two primary amino groups. The presence of an azo linkage was evident from an examination of its absorption spectrum. 4-(4'-Aminophenyl)azobenzene (74) could arise either by hydrolysis of 4,4'-bis(phenylazo)biphenyl (73), in a manner analogous to that postulated for the decomposition of 4-phenylazoazobenzene, or by disproportionation of the assumed intermediate, 4-[4'-(2"-phenylhydrazino)]phenylazobenzene (76). The azo group of such an intermediate would be protonated under the reaction conditions and thus act as an electron attracting substituent. The application of Ingold's rules to such a system predicts the formation of the other observed product, 4-[4'-amino-3'-(4"-aminophenyl)phenyl]azobenzene (75). The action of hydrochloric acid on (76) has been studied previously[68] but only disproportionation products (73), (74) and aniline were observed.

The two major products from the photolysis of 4,4'-bis(phenylazo)biphenyl were two substituted benzo[c]cinnolines, 2-(4'-aminophenyl)-benzo[c]cinnoline, (77), and 2-[4'-amino-3'-(4"-aminophenyl)phenyl]benzo-[c]cinnoline (78).

The structure of (77) was unambiguously determined by its deamination to 2-phenylbenzo[c]cinnoline (81). This was shown to be identical with an authentic sample prepared by the photochemical



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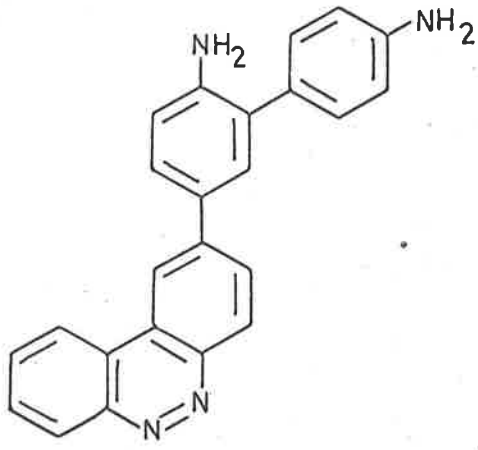
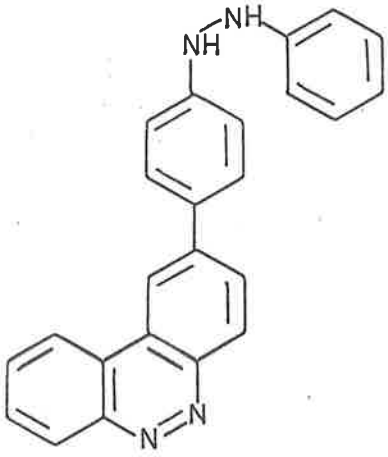


(78)



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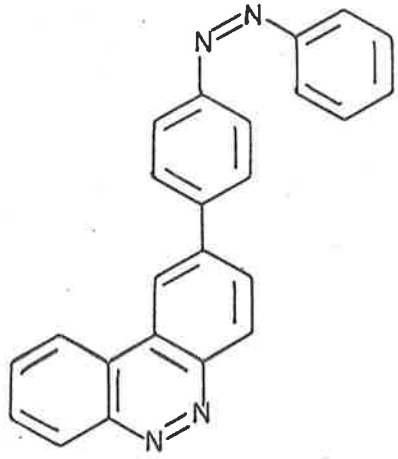
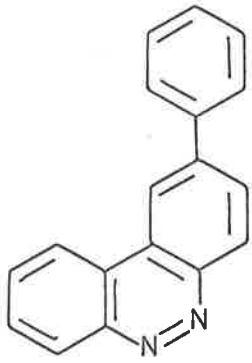


(80)

cyclodehydrogenation of 4-phenylazobenzene (82). This azo compound was prepared by condensing 4-aminobiphenyl with nitrosobenzene. The benzidine rearrangement products arising from the irradiation of 4-phenylazobenzene were not investigated. However, 4-phenylhydrazobenzene has been reported[71] to yield both a semidine and a diphenyline on treatment with acid. The formation of both products is in accordance with Ingold's rules.



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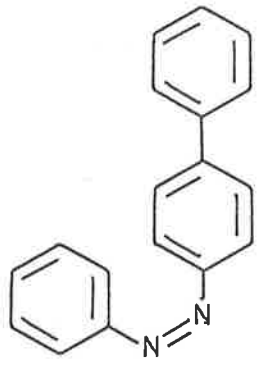


(82)

The structure of (78) was indicated by the close similarity of its ultraviolet absorption spectrum in 22N sulphuric acid to that of (77) in the same solvent (Fig. 4). The presence of two primary amino groups was shown by the fact that it formed a bis-salicylidene derivative.

Both (77) and (78) presumably arise from the first formed 2-[4'-(2"-phenylhydrazino)]phenylbenzo[c]cinnoline (79). Disproportionation of this compound would produce (77), aniline and 2-(4'-phenylazo)phenylbenzo[c]cinnoline (80). However, no trace of this azobenzo[c]cinnoline, (80), or of its cyclised product, 2,2'-bisbenzo-[c]cinnoline[72] was found. The compound must therefore undergo further reaction, either hydrolysis to give (77) and nitrosobenzene, in a manner similar to that postulated for the decomposition of 4-phenylazoazobenzene, or hydrogen abstraction, perhaps from the aniline already formed, to give (79).

The production of (78) by a benzidine rearrangement of (79) is to be expected on the basis of Ingold's rules. The cinnoline part

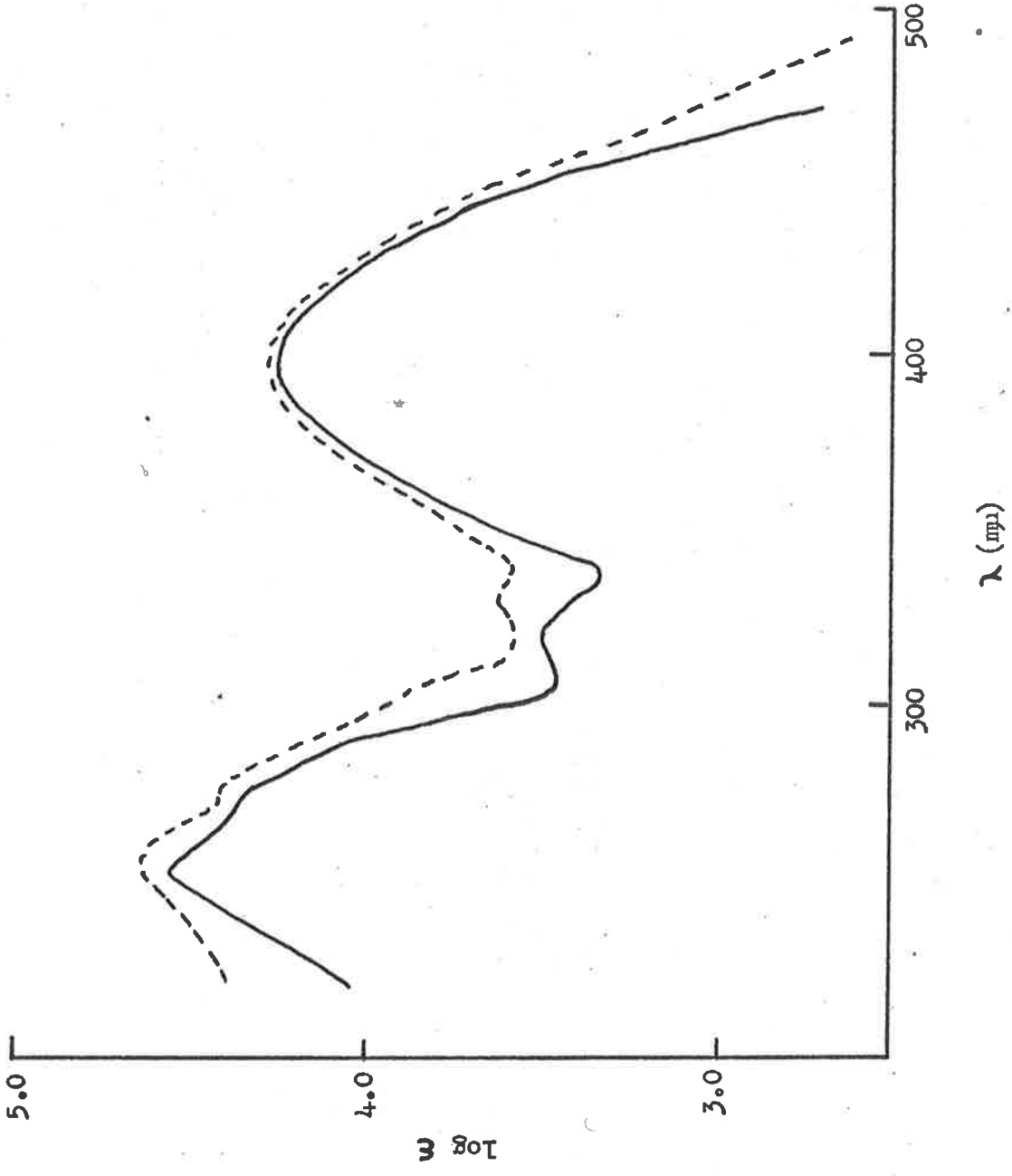
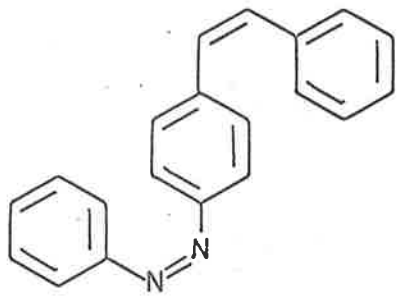


Fig. 4. - Absorption spectra of 2-(4'-aminophenyl)benzo[c]cinnoline (77) (———) and of 2-[4'-amino-3'-(4''-aminophenyl)phenyl]benzo[c]-cinnoline (78) (– – – –), in 22N sulphuric acid.

of the molecule will be protonated under the conditions of the reaction and the electron attracting effect of this will be readily transmitted to the hydrazo part of the molecule.

2.3 Other Azo Compounds

It was also thought important to study the photolysis of 4-styrylazobenzene (83) because of its structural relationship to

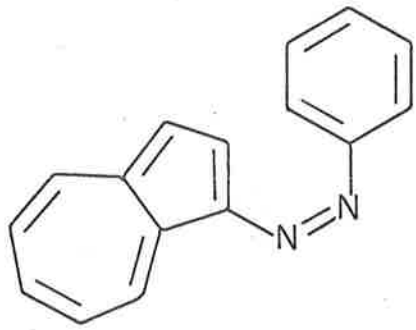


(83)

4-phenylazoazobenzene. There is the possibility that cyclisation may occur either around the azo or around the ethylenic linkage; or, it may occur at both. It was hoped that, by judicious choice of solvent and wavelength of irradiating light, each of these possibilities might be realised. Dilute (c. 10^{-5}M) solutions of (83) in 22N sulphuric acid were found to be slowly decolourised by irradiation with sunlight, tungsten or mercury-quartz lamps. However, the ultraviolet absorption spectrum of the irradiated solution showed only a very small peak at 255 mμ. It appears therefore that 4-styrylazobenzene is unstable under these conditions and this was borne out by experiments on a larger scale. The compound is only sparingly soluble in 22N sulphuric acid

and therefore preparative experiments were carried out in 10% ethanol in 22N sulphuric acid. Prolonged irradiation in this solvent with a mercury-quartz lamp gave mainly intractable tar and unchanged starting material. A very small yield of a yellow oil showing absorption at 255 and 370 mμ was obtained but it could not be purified. Irradiation of dilute solutions of 4-styrylazobenzene in 95% ethanol and also in cyclohexane were carried out but no evidence of cyclisation was obtained.

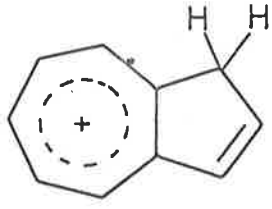
Finally, it was decided to examine the photochemical behaviour of acidic solutions of 1-phenylazoazulene (84). Dilute (c. 10^{-5}M)



(84)

solutions in 22N sulphuric acid were irradiated with sunlight, a tungsten lamp and a mercury-quartz lamp but in no case was there any change in the ultraviolet absorption spectrum. It has already been mentioned, in connection with the azonaphthalenes, that absorption of radiation by a molecule does not necessarily lead to photochemical reaction, and there are a number of non-productive processes which may occur. There is however, an additional factor to be considered in the present case. It is known[73] that in strong acid the 1-position

of azulene is protonated to give the ion (85). Contributions from forms such as this may inhibit the cyclisation of 1-phenylazoazulene in 22N sulphuric acid.



(85)

CHAPTER III

THE PHOTOCHEMISTRY OF SOME AZO AND RELATED COMPOUNDS IN 98% ANALAR SULPHURIC ACID.

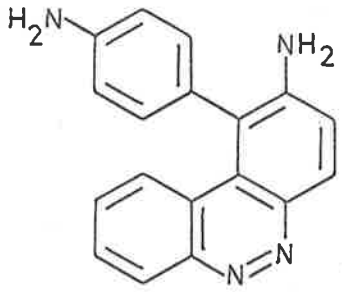
3.1 Bisazo Compounds.

The work described so far has shown that 4-phenylazoazobenzene (68) is unstable in 22N sulphuric acid. It has further been suggested that the bisazo compound is hydrolysed in this medium to 4-aminoazobenzene and nitrosobenzene. 4-Benzalaminoazobenzene and benzalaniline are also readily hydrolysed by aqueous acid, but work in this laboratory has shown that they are sufficiently stable in 98% Analar sulphuric acid to be photochemically cyclodehydrogenated to 2-aminobenzo[c]cinnoline[40] and phenanthridine[26] respectively. It was decided therefore, to investigate the photochemistry of 4-phenylazoazobenzene in the same solvent. If the initial step in the decomposition of 4-phenylazoazobenzene in 22N sulphuric acid is, in fact, a hydrolysis, then it should be possible to prevent its occurrence, or at least reduce it considerably, by using the more anhydrous medium.

When dilute (c. 10^{-5}M) solutions of 4-phenylazoazobenzene in 98% Analar sulphuric acid were irradiated, either with sunlight or with a mercury-quartz lamp, the colour of the solution was fairly rapidly discharged. Moreover, and in contrast to previous irradiations in 22N acid, the ultraviolet absorption spectrum showed changes attributable to cyclisation. No comparisons were made as to the efficiency of a tungsten lamp *versus* a mercury-quartz lamp for bringing about these changes. The previously described tungsten irradiation apparatus had

no provision for maintaining the irradiated solution under anhydrous conditions, and the cyclisation was considered to be sufficiently fast when a mercury-quartz lamp was employed.

Irradiation on a preparative scale was continued until the ultraviolet absorption spectrum showed the reaction to be virtually complete. Although the reaction was considerably cleaner than when performed in 22N sulphuric acid, some tar production was still evident. The reaction mixture was worked up in the usual way by making it slightly alkaline, extracting all the organic material, and chromatographing this on alumina. Initial fractions from the chromatogram yielded unchanged 4-phenylazoazobenzene and this was followed by the decomposition products 4-aminoazobenzene (69) and 4-amino-3-(4'-aminophenyl)azobenzene (70). However, the two major products obtained from this irradiation were the cyclised compounds, 2-amino-1-(4'-aminophenyl)benzo[c]cinnoline (86) and 2-(4'-aminophenyl)aminobenzo-[c]cinnoline (87). The structure of (86) was elucidated as follows. Its infrared spectrum (nujol) showed absorption at 3310, 3190 and 3470 cm^{-1} (NH). Furthermore its ultraviolet absorption spectrum, in dilute sulphuric acid, closely resembled that of 2-aminobenzo[c]-cinnoline in the same solvent (Fig. 5). The presence of a 2-amino-benzo[c]cinnoline moiety was therefore considered to be likely. That two primary amino groups were present was shown by the fact that it formed a bis-salicylidene derivative. Conclusive proof of the skeletal



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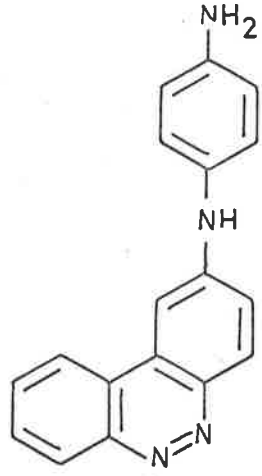
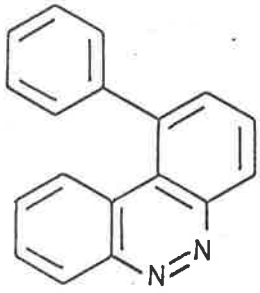
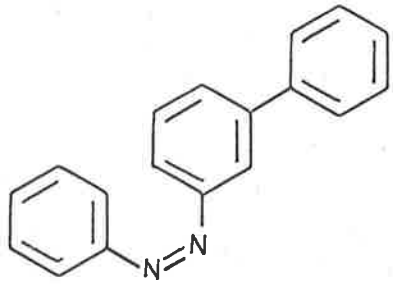


(87)

structure of (86) was obtained by deaminating it to 1-phenylbenzo[c]-cinnoline (88). This was shown to be identical with an authentic specimen prepared by the photochemical cyclodehydrogenation of 3-phenylazobenzene (89). This azo compound can, of course, cyclise in one of two ways to give either 1-phenylbenzo[c]cinnoline (88), or 3-phenylbenzo[c]cinnoline (90). Both these possibilities were



(88)



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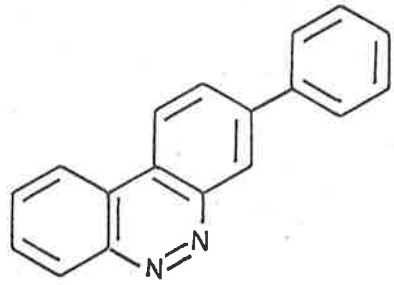


(90)

realised and this cyclisation will be considered in more detail in Section 3.2.

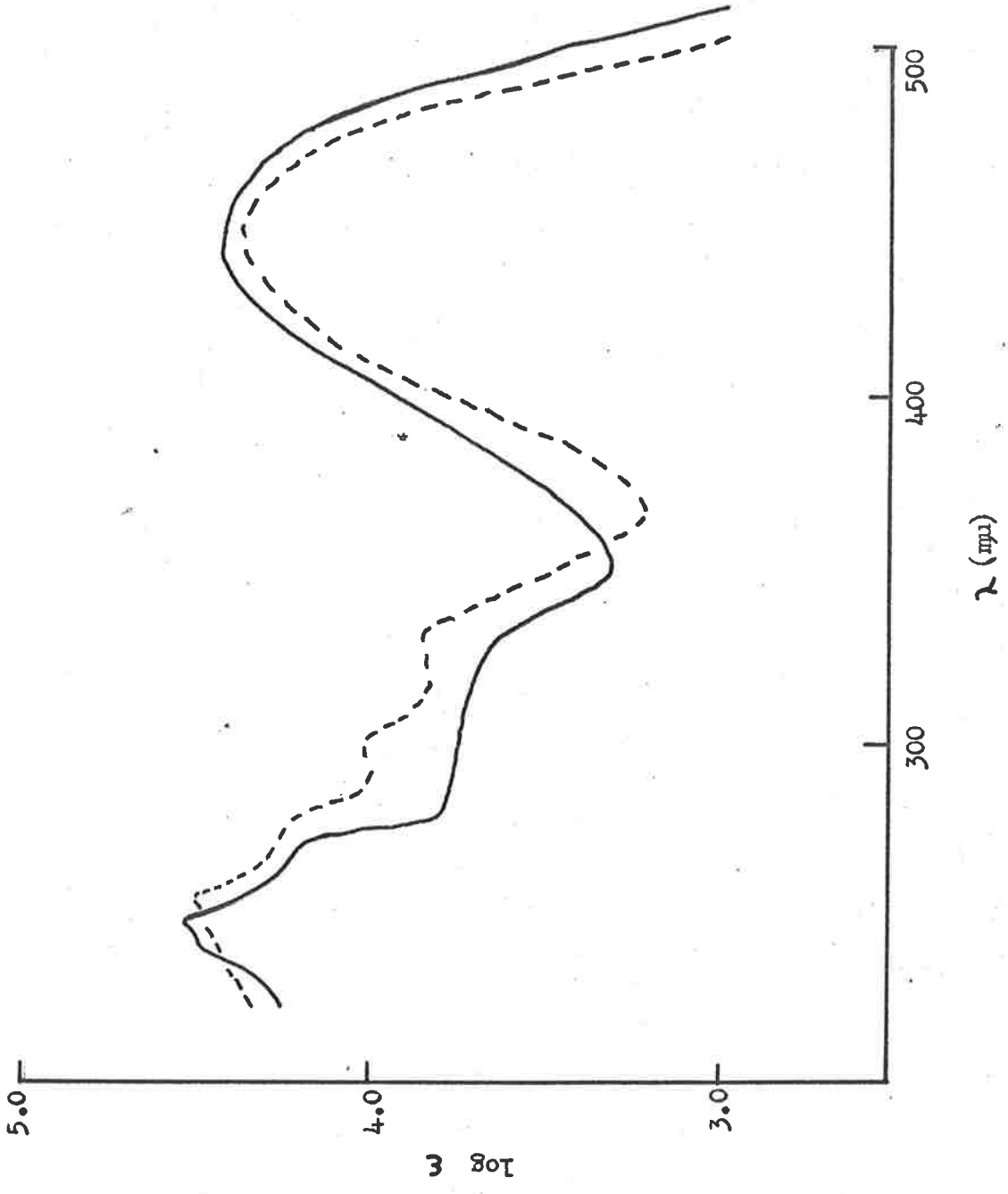
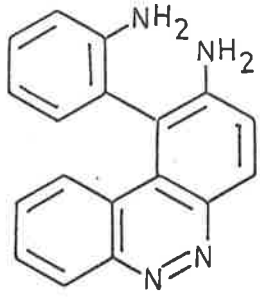


Fig. 5. - Absorption spectra of 2-aminobenzo[c]cinnoline (93, R = H) (———) and of 2-amino-1-(4'-aminophenyl)benzo[c]cinnoline (86) (- - - -), in 6N sulphuric acid.

For the final structural determination of (86), it remained to ascertain the position of the second primary amino group. The possibility existed that the two amino groups might be present in an o-benzidine structure (91). Such o-diamines are known to eliminate ammonia readily to form the appropriate carbazole which in this case would be (92). The compound isolated from the photolysis of 4-phenyl-



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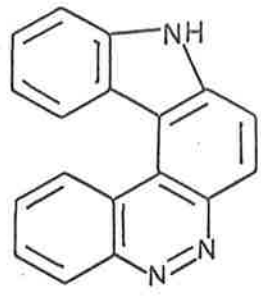


(92)

azoazobenzene was therefore treated in two ways previously found to cause such carbazole formation in related compounds — by heating to 220° with a little concentrated hydrochloric acid[74] and by boiling for 50 hours with 5N sulphuric acid.[75] However, in both cases, only unchanged starting material was recovered. The structure of the photolysis product was thus shown unambiguously to be 2-amino-1-(4'-aminophenyl)benzo[c]cinnoline (86).

The final structural determination of the other photolysis product, (87), proved to be more difficult. As may be seen from Fig. 6, the ultraviolet absorption spectrum of (87) in dilute sulphuric acid closely resembles that of 2-dimethylaminobenzo[c]cinnoline, (93, R = Me), in the same solvent. The latter compound has been prepared

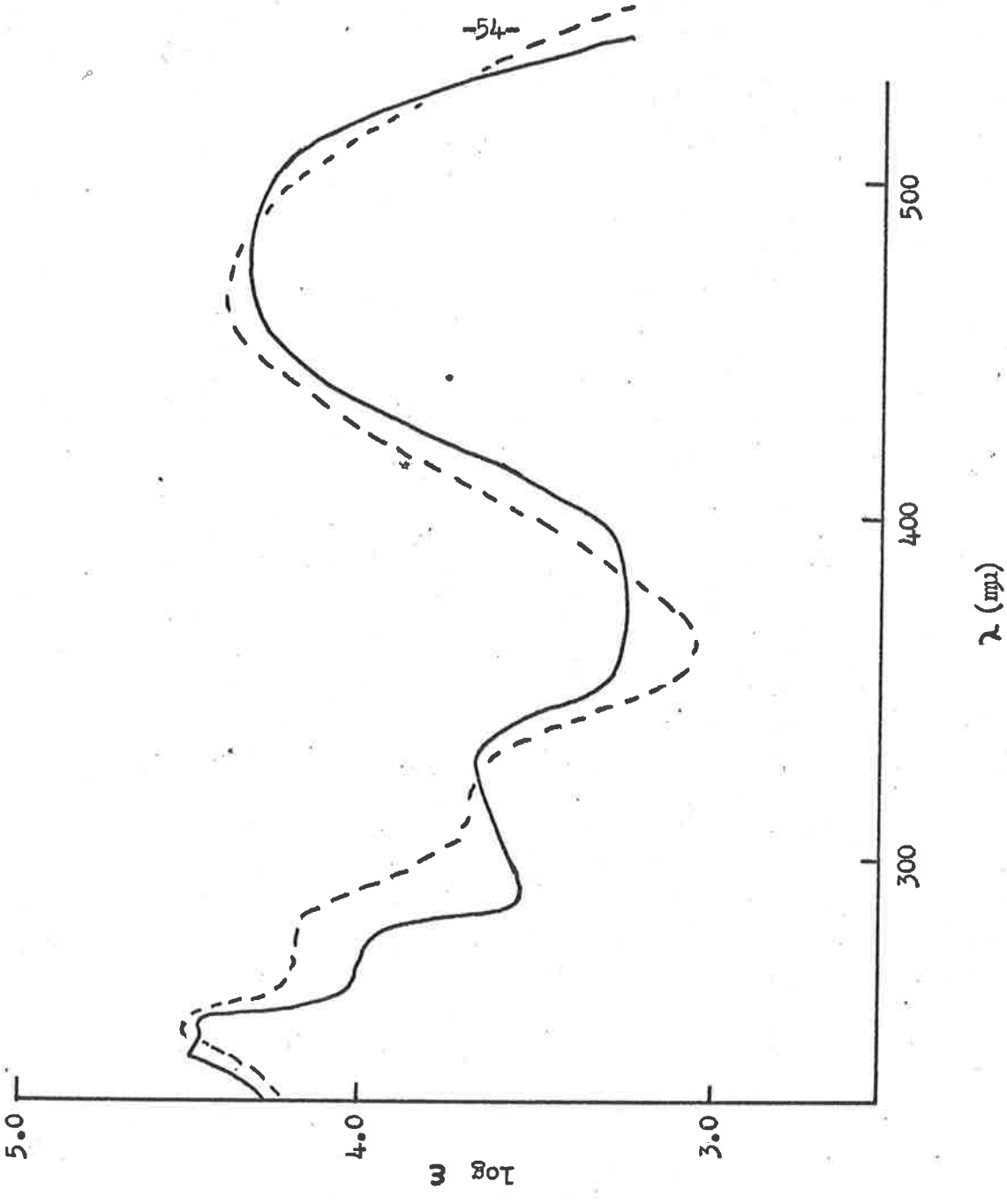
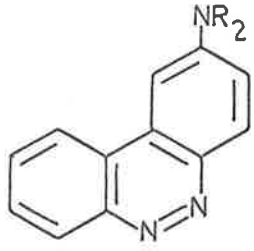


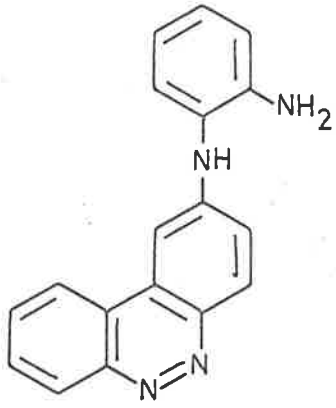
Fig. 6. - Absorption spectra of 2-dimethylaminobenzo[c]cinnoline (93, R = Me) (———) and of 2-(4'-aminophenyl)aminobenzo[c]cinnoline (87) (- - - -), in 6N sulphuric acid.

in this laboratory by the photochemical cyclisation of the N-oxide of 4-dimethylaminoazobenzene.[76] Moreover, the longest wavelength absorption

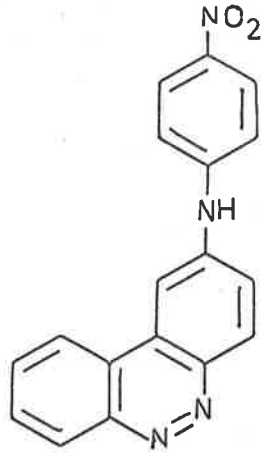


(93)

band of both of these compounds has been bathochromically shifted by about 30 mμ relative to 2-aminobenzo[c]cinnoline, (93, R = H). It has been shown,[77] that in the case of 4-aminoazobenzene, such a bathochromic shift can be caused by N-substitution. For instance, the long wavelength absorption bands of the mono-acid salts of 4-aminoazobenzene and of 4-dimethylaminoazobenzene occur at 500 and 520 mμ respectively. It seems likely that a similar phenomenon might be observed in the case of 2-aminobenzo[c]cinnoline and it was therefore thought probable that the photolysis product (87) was an N-substituted 2-aminobenzo[c]-cinnoline. The infrared spectrum of the photolysis product indicated the presence of a second amino substituent. The experimental data presented so far are equally in accord with the formulation of the photolysis product as the p-semidine, (87), or as the o-semidine, (94). However, the nuclear magnetic resonance spectrum showed — in addition to several complex multiplets between τ c.1.41 and τ c. 2.63, assigned to the benzo[c]cinnoline protons — a well defined quartet,



(94)

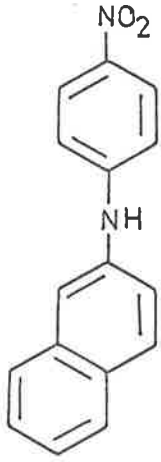


(95)

centred at τ c. 3.02, which integrated for four protons. This was assigned to the A_2B_2 system of the p-disubstituted phenyl ring of (87), and structure (94) was therefore excluded.

As final structural proof of the photolysis product, (87), it was decided to attempt an unequivocal synthesis by first preparing 2-(4'-nitrophenyl)aminobenzo[c]cinnoline (95). Reduction of the nitro group of this compound would produce the desired 2-(4'-aminophenyl)-aminobenzo[c]cinnoline.

Lantz and Obellianne[78] have prepared a similar compound, 2-(4'-nitrophenyl)aminonaphthalene (96), by heating 2-naphthylamine, p-fluoronitrobenzene, magnesium carbonate and water in a sealed tube, and it was decided to apply this method in the present instance. 2-Aminobenzo[c]cinnoline was prepared by the photochemical cyclodehydrogenation of 4-benzalaminoazobenzene in 98% Analar sulphuric acid.[40]



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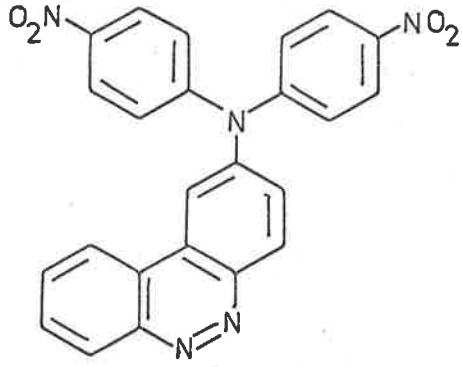


(97)

However, when this amine was heated with p-fluoronitrobenzene under the conditions of Lantz and Obellianne, only starting materials were recovered. The temperature of the reaction was then raised, but complete decomposition occurred.

Similar reactions between amines and nitrohaloaromatic compounds are known to be catalysed by the presence of excess amine.[79] However, heating excess 2-aminobenzo[c]cinnoline with p-fluoronitrobenzene in a variety of refluxing solvents yielded only unchanged starting materials.

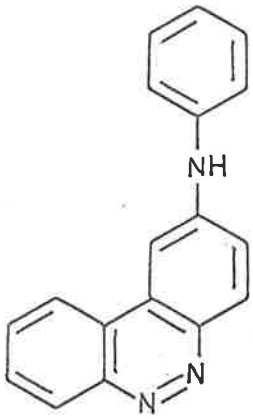
A common way of preparing secondary amines is by heating together a primary amine and a nitrohaloaromatic compound in the presence of potassium carbonate.[80] When this method was applied to the synthesis of 2-(4'-nitrophenyl)aminobenzo[c]cinnoline (95), excess p-fluoronitrobenzene being used as the solvent, a good yield of the

tertiary amine, 2-(di-4'-nitrophenyl)aminobenzo[c]cinnoline, (97), was obtained. The structure of this compound was deduced from its elementary analysis, ultraviolet absorption spectrum, and the absence of absorption in its infrared spectrum in the region 4000-3000 cm^{-1} (NH). This reaction was repeated in several other solvents using a slight molar excess of 2-aminobenzo[c]cinnoline to p-fluoronitrobenzene. When the reaction was carried out in nitrobenzene at 200°, the major product was the tertiary amine, (97). When refluxing diethyl ketone (b.p. 103°) was used as a solvent, only unchanged 2-aminobenzo[c]cinnoline was recovered. In dimethylformamide (b.p. 153°), approximately equal quantities of (97) and 2-aminobenzo[c]cinnoline were recovered. Similar results were obtained when p-bromonitrobenzene was substituted for p-fluoronitrobenzene. It is far from clear why this tertiary amine, (97), should form so readily. The mechanism presumably involves a nucleophilic attack by the amine on p-fluoronitrobenzene. Once the secondary amine is formed, the electron withdrawing effect of the nitro group should considerably reduce the amine's nucleophilicity relative to that of 2-aminobenzo[c]cinnoline. In addition to this, steric factors should hinder the production of the tertiary amine.

A modification of the above method of synthesis of secondary amines involves the acetylation of the primary amine prior to treatment with the haloaromatic compound and potassium carbonate.[81] This modified method was applied in the present instance but again, the tertiary amine, (97), was formed.

A different approach towards the confirmation of the struc-

ture of 2-(4'-aminophenyl)aminobenzo[c]cinnoline (87) was now adopted. The compound was deaminated to 2-phenylaminobenzo[c]cinnoline (98), which bears an obvious relationship to 4-phenylazodiphenylamine (99, R = H). It was decided, therefore, to attempt to prepare (98) by the photochemical cyclodehydrogenation of (99, R = H). 4-Phenylazodiphenylamine dissolves readily in sulphuric acid to give a dark, blue-purple



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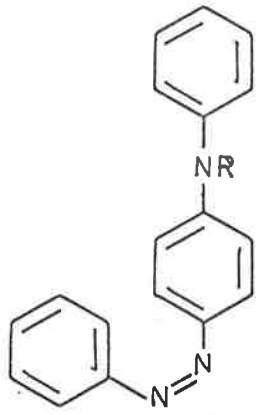
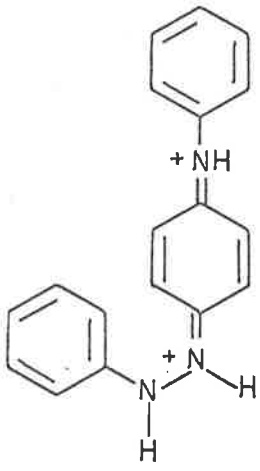


(99)

solution. Dilute (c. 10^{-5} M) acidic solutions of 4-phenylazodiphenylamine were irradiated with sunlight and with a mercury-quartz lamp but in neither case was there any change in the ultraviolet absorption spectrum. This result was not unexpected in view of the close similarity of (99, R = H) to the photochemically stable 4-amino- and 4-dimethylaminoazobenzene.[39] In concentrated sulphuric acid, 4-phenylazodiphenylamine presumably exists, at least partly, as the dication (100). Contributions from such a structure will substantially reduce the bond order of the azo linkage, and thus the stability of



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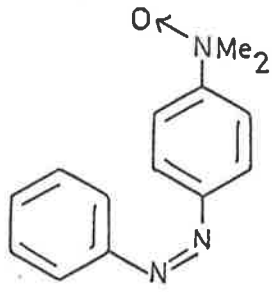
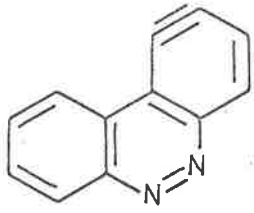


(101)

the cis-isomer, which rationalises the stability of this compound. However, it has been found in this laboratory that 4-benzalaminoazobenzene will undergo cyclisation around the azo linkage.[40] The preparation of the benzylidene derivative so alters the electronic effect of the amino group that cyclisation occurs. Moreover, more recent work[76] has shown that the N-oxide of 4-dimethylaminoazobenzene (101) can be photochemically cyclodehydrogenated to 2-dimethylaminobenzo[c]cinnoline. It was thought, therefore, that acylation of 4-phenylazodiphenylamine might produce similar electronic effects and thus allow cyclisation to occur. The acetate of 4-phenylazodiphenylamine, (99, R = Ac), was therefore prepared and it was found to give a yellow solution when dissolved in 98% Analar sulphuric acid. A bleaching of this colour was observed when dilute solutions were irradiated and changes in the ultraviolet absorption spectrum occurred which could be attributed to cyclisation. However, in experiments on

a preparative scale, the original dark yellow solution became blue-purple fairly rapidly and it was obvious that hydrolysis was proceeding more quickly than cyclisation. Irradiations were carried out with a mercury-quartz lamp and with sunlight but in both cases, only 4-phenylazodiphenylamine was isolated. The benzoate of 4-phenylazodiphenylamine, (99, R = Bz), was then prepared. It could not be obtained pure, but experiments on a slightly impure sample showed its behaviour to resemble that of the acetate. The yellow colour of dilute solutions was discharged on irradiation and spectral changes characteristic of cyclisation were observed. However, following irradiation on a preparative scale, only 4-phenylazodiphenylamine was isolated.

2-Phenylaminobenzo[c]cinnoline (98) was finally prepared, in excellent yield, by heating 2-chlorobenzo[c]cinnoline[38] and sodium anilide in excess aniline. The product obtained had a sharp melting point and moved as a single spot when examined by thin-layer chromatography. It was therefore concluded to be a pure compound. The 2-phenylazobenzo[c]cinnoline may have arisen by a straightforward displacement of the chloride ion which, of course, could only give rise to a single product. However, such reactions as this frequently proceed *via* aryne intermediates,[82] which normally give rise to a mixture of isomers. The formation of only one isomer in the present case could be incorporated into a mechanism involving an aryne intermediate if the 1,2-aryne (102) were preferentially formed. The anilide ion must then be assumed to attack the 2-position, rather than the sterically hindered 1-position, to give the observed product. No work



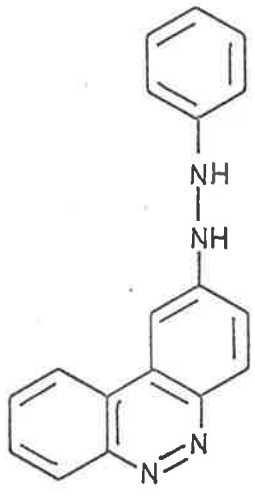
(102)

(103)

appears to have been done with 3-chlorophenanthrene, the carbocyclic analogue of 2-chlorobenzo[c]cinnoline. However, the exclusive production of a 1,2-naphthyne, (103), on treatment of several 2-halonaphthalenes with lithium piperidide has been reported.[83]

That the phenylaminobenzo[c]cinnoline produced in this way was indeed the 2-isomer was confirmed by a study of its ultraviolet absorption spectrum in dilute acid. This showed its longest wavelength band at 479 mμ, i.e. bathochromically shifted by about 30 mμ from that of 2-aminobenzo[c]cinnoline. The synthetic product was shown to be identical with that obtained by the deamination of 2-(4'-aminophenyl)aminobenzo[c]cinnoline.

The two cyclised products obtained from the irradiation of acidic solutions of 4-phenylazoazobenzene, then, have been shown to be 2-amino-1-(4'-aminophenyl)benzo[c]cinnoline (86) and 2-(4'-aminophenyl)aminobenzo[c]cinnoline (87). It seems likely that both these products arise from the first formed 2-(2'-phenylhydrazino)benzo[c]-cinnoline, (104), by way of a benzidine rearrangement. The mechanism of such a rearrangement will be discussed in a later chapter but it is pertinent at this stage to mention that the formation of the diphenyline (86) by the benzidine rearrangement of the hydrazo compound (104) is in



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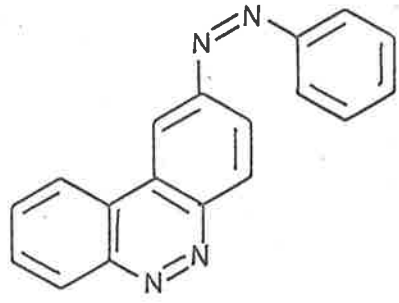


(105)

accord with Ingold's rules. Also, although specifically excluded by Ingold when formulating his rules, the production of p-semidines, such as (87), has been found to occur during the benzidine rearrangement of 4-aminohydrazobenzene.[84]

As evidence of the possible occurrence of 2-(2'-phenylhydrazino)benzo[c]cinnoline (104) as an intermediate in the photolysis of 4-phenylazoazobenzene, it was decided to synthesise the hydrazo compound and subject it to benzidine rearrangement conditions. 2-Aminobenzo[c]cinnoline was prepared by the photochemical cyclodehydrogenation of 4-benzalaminoazobenzene.[40] Condensation of this amine with nitrosobenzene gave a poor yield, (10%), of 2-phenylazobenzo[c]cinnoline (105). This method of preparing azo compounds does not seem to give good results when applied to polycyclic amines; for instance, the azonaphthalenes cannot be synthesised in this way. However, when

2-aminobenzo[c]cinnoline was heated with nitrobenzene in the presence of sodium hydroxide, the desired azo compound was obtained in almost 40% yield. 2-Phenylazobenzo[c]cinnoline was reduced to 2-(2'-phenylhydrazino)benzo[c]cinnoline (104) with zinc and ammonium chloride. The structure of this compound was indicated by its ultraviolet absorption spectrum, which was typically that of a benzo[c]cinnoline, and by its infrared spectrum, which showed the presence of the hydrazo group. 2-(2'-Phenylhydrazino)benzo[c]cinnoline was dissolved in 98% Analar sulphuric acid and the resulting solution was allowed to stand for several hours. The reaction was then worked up as would be a photolysis reaction mixture and the products were separated by chromatography. Initial fractions from the column yielded 2-phenylazobenzo[c]cinnoline. This may have arisen by disproportionation but is more likely to have been produced by aerial oxidation of the hydrazo compound during the latter's preparation. Although the preparation and purification of (104) were carried out as quickly as possible, they were not performed under an atmosphere of nitrogen so that some oxidation is to be expected. Later fractions yielded 2-amino-1-(4'-aminophenyl)benzo[c]cinnoline (86) and 2-(4'-aminophenyl)aminobenzo[c]cinnoline (87). These observations are consistent with the postulation of 2-(2'-phenylhydrazino)-benzo[c]cinnoline as an intermediate in the photolysis of 4-phenylazoazobenzene.

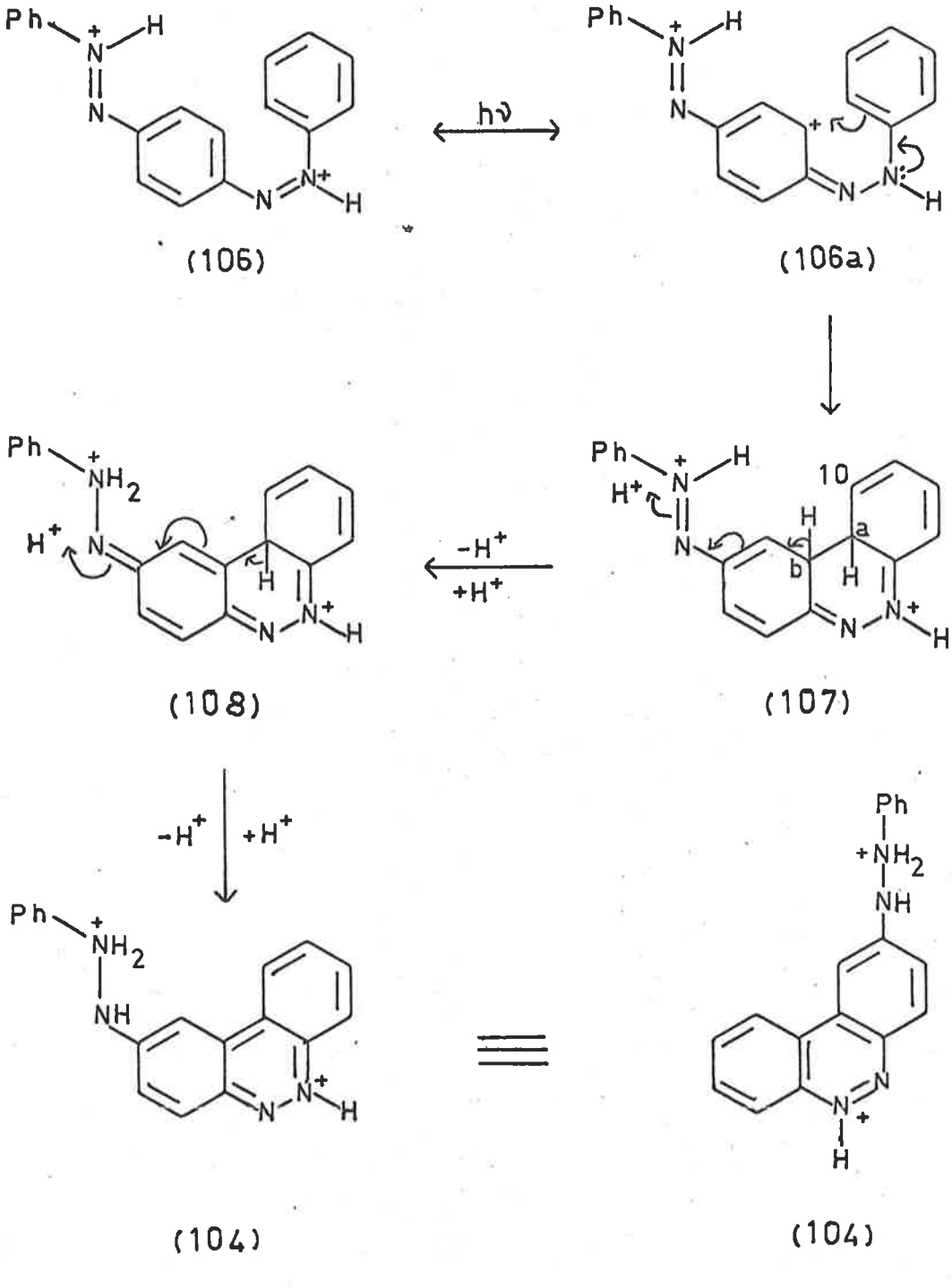
It was considered of interest to examine the photochemistry of 4,4'-bis(phenylazo)biphenyl (73) in 98% Analar sulphuric acid. Attempts to carry out this reaction on a preparative scale using a

mercury-quartz lamp were unsuccessful. On a 3g scale, no change in the ultraviolet absorption spectrum was observed after 10 days irradiation. The photochemical reactor was therefore immersed in a beaker of running water and surrounded by five 100W tungsten lamps. However, there was still no detectable change in the ultraviolet absorption spectrum after one weeks irradiation. Finally, the photolysis was completed on a 50 mg scale with mercury-quartz irradiation. Even on this small scale, it was found necessary to irradiate the solution for four days. The products were shown to be identical (thin-layer chromatography) with those previously obtained by the irradiation of 4,4'-bis(phenylazo)biphenyl in 22N sulphuric acid.

It is obvious, then, that the irradiation of 4-phenylazoazobenzene and of 4,4'-bis(phenylazo)biphenyl, whether in 22N or in 98% Analar sulphuric acid, does not result in the formation of doubly cyclised products. The question now arises as to why this should be so. It is of course possible that the second azo group is reduced because of its relatively close proximity to the azo linkage undergoing cyclisation. There is, however, another possibility.

Mention has already been made of the postulated mechanism of cyclisation of azobenzene and this route is detailed in Scheme 1 of the Introduction. A similar mechanism can be written for the photocyclisation of 4-phenylazoazobenzene (Scheme 2). The positive charge originally on the protonated nitrogen in the ground state (106), is considered to be shared in the excited state with carbon atoms 2 and 6 (106a). Ring closure of (106a) leads to the formation of the

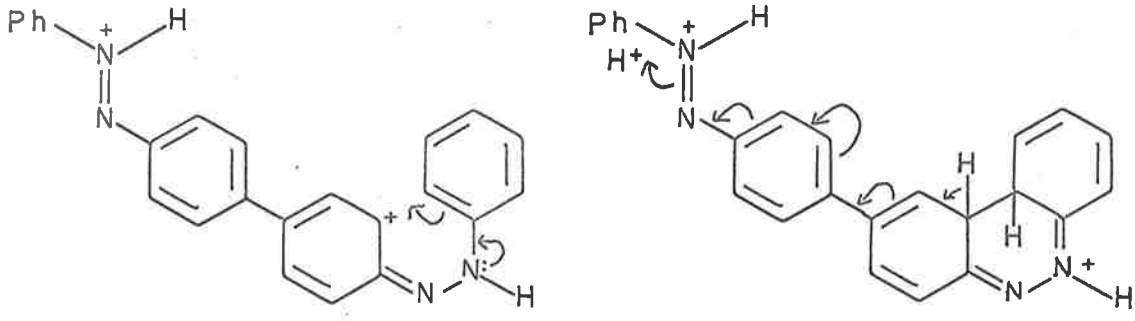
SCHEME 2.



dihydrobenzo[c]cinnoline (107). This is assumed to undergo a fast prototropic shift to give (108), which then experiences a further prototropic shift to yield the diprotonated 2-(2'-phenylhydrazino)-benzo[c]cinnoline (104). This final compound is, of course, the postulated intermediate in the formation of the observed photolysis products, 2-amino-1-(4'-aminophenyl)benzo[c]cinnoline (86) and 2-(4'-aminophenyl)aminobenzo[c]cinnoline, (87).

Similar arguments will apply to the case of 4,4'-bis(phenylazo)biphenyl (73). The positive charge initially residing on the protonated azo nitrogen in the ground state is again visualised as being delocalised as illustrated in Scheme 3. Cyclisation is then

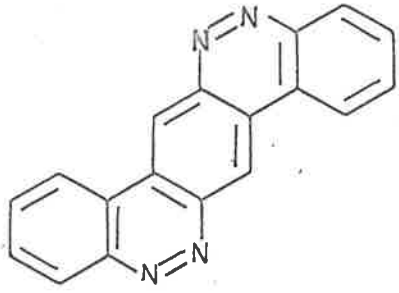
SCHEME 3.



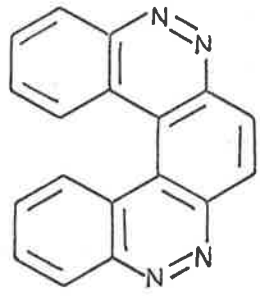
assumed to occur as in Scheme 2 and, as the effect of the second azo linkage is readily transmitted through the conjugated system, the observed concomitant cyclisation and reduction can be rationalised.

Finally, it was decided to investigate the photochemistry

of 2-phenylazobenzo[c]cinnoline (105) in acidic solution, from which reaction it was hoped to obtain a pentacyclic product. There are two possible sites of cyclisation in such a molecule and either benzo[1,2-c:4,5-c']dicinnoline (109) or benzo[1,2-c:4,3-c']dicinnoline (110) may be formed. A mixture of (109) and (110) might also result.



(109)



(110)

Irradiation of 98% Analar sulphuric acid solutions of 2-phenylazobenzo[c]cinnoline produced some 2-amino-1-(4'-aminophenyl)benzo[c]cinnoline (86), and some 2-(4'-aminophenyl)aminobenzo[c]cinnoline (87). However, in addition to these products, there was isolated a small yield of a pentacyclic compound. It seems likely that the non-strained benzo[1,2-c:4,5-c']dicinnoline, (109) would be formed in preference to the highly sterically strained benzo[1,2-c:4,3-c']dicinnoline (110). The "overcrowding" of the carbocyclic analogue of (110), viz. dibenzo[c,g]phenanthrene, is shown by the mutarotation of solutions of the morphine salt of the 3,4-dicarboxylic acid,[85] and has been confirmed by X-ray crystallographic studies.[86] A comparison of the ultraviolet absorption spectrum of the photolysis product with those of the two possible carbocyclic analogues, dibenz[a,h]anthracene, and

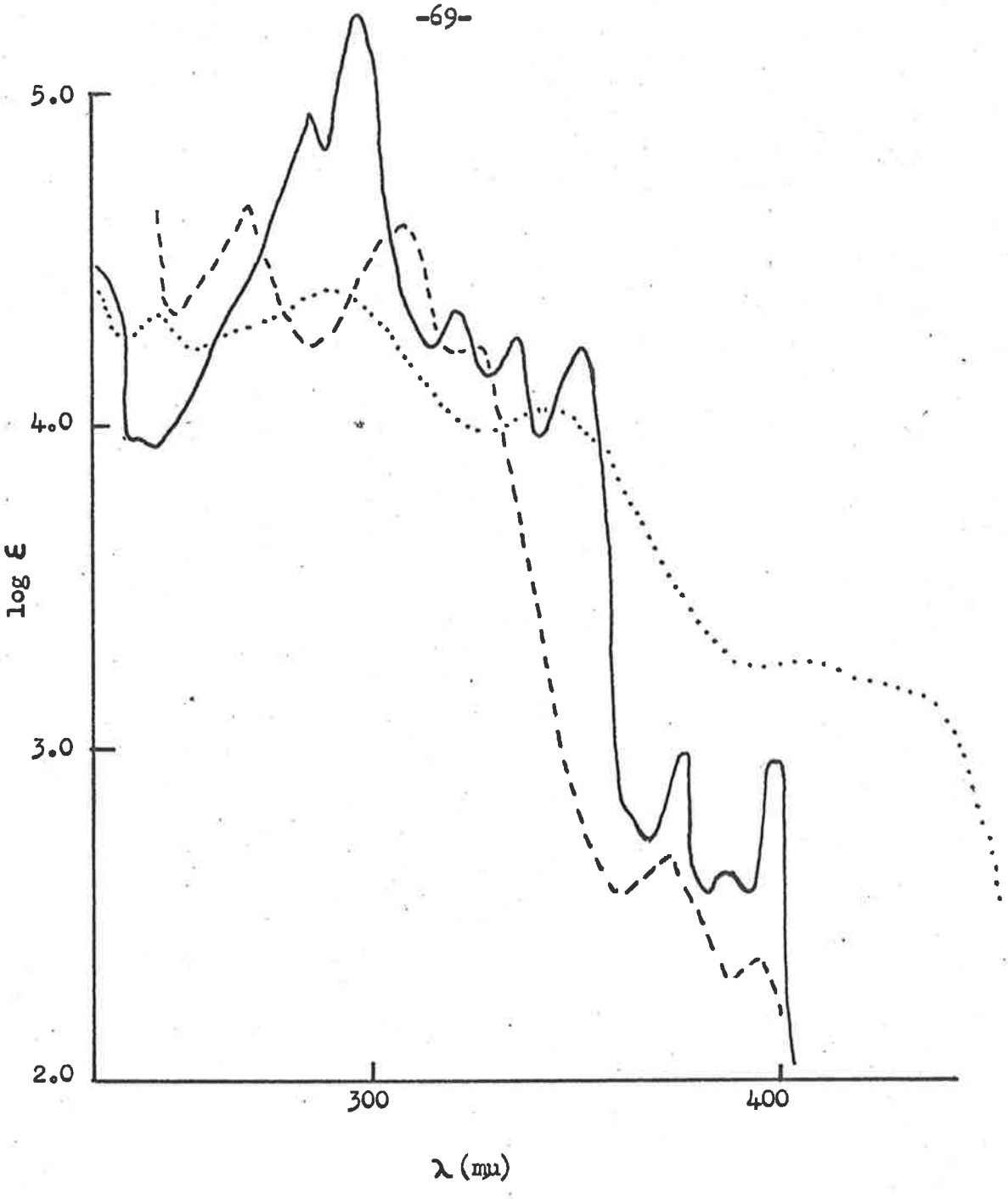


Fig. 7. - Absorption spectra of dibenz[a,h]anthracene (———), dibenzo[c,g]phenanthrene (- - - -) and of benzodicinnoline (109 or 110) (·····), in 95% ethanol.

dibenzo[c,g]phenanthrene, (Fig. 7), is in accord with its formulation as benzo[1,2-c:4,5-c']dicinnoline, (109), although this does not constitute conclusive structural proof.

This explanation, on steric grounds, of cyclisation occurring at the 3- rather than the 1- position of the benzo[c]cinnoline nucleus may seem to conflict with the previously observed production of 2-amino-1-(4'-aminophenyl)benzo[c]cinnoline (86) by a benzidine rearrangement of 2-(2'-phenylhydrazino)benzo[c]cinnoline, (104). The formation of (86), of course, involves preferential attack at the 1- rather than the 3- position of the benzo[c]cinnoline nucleus. However, in this latter case, the steric strain can be relieved considerably by the phenyl ring adopting a plane at right angles to that of the benzo[c]-cinnoline nucleus. There are good reasons, based on electronic theory, why attack in this case should occur at the 1-position and these will be discussed in Chapter 5.

3.2. Other Azo Compounds.

Mention has already been made of the photolysis of 3-phenylazobenzene (89). No reference to this compound could be found in the literature but it was synthesised, in good yield, by the condensation of 3-aminobiphenyl with nitrosobenzene. Initial irradiations were carried out in 98% Analar sulphuric acid as this solvent has been reported[40] to give high yields of cyclised products. In addition to this, the azo compound was found to be readily and completely soluble in this medium. However, although the ultraviolet

absorption spectrum showed changes normally associated with cyclisation, no products were obtained when the reaction mixture was worked up in the usual way of basification followed by extraction. It was thought that sulphonation may have occurred, catalysed by the heat of neutralisation of the acid. The working up procedure was therefore modified and the dilution and basification were carried out very slowly and with efficient cooling. In addition to this, the reaction mixture was vigorously stirred with a mechanical stirrer, to avoid localised heating, and the temperature of the solution was maintained below 20°. However, still no products could be isolated. It was therefore decided to carry out the cyclisation in 22N sulphuric acid.

3-Phenylazobenzene is very sparingly soluble in 22N sulphuric acid and it was found necessary to add 10% ethanol to increase its solubility. Even so, the solubility is not high and, perhaps because of this, the cyclisation was found to be extremely slow. As mentioned earlier, both the possible cyclised products, 1-phenylbenzo[c]cinnoline, (88), and 3-phenylbenzo[c]cinnoline, (90), were isolated. In some previous work in this laboratory,[40] several 3-substituted azobenzenes were found to give only one cyclised product, the 3-substituted benzo[c]cinnoline. However, in other work,[37,38] both possible isomers were formed. In this latter case, the isomers were separated by counter current distribution. However, in the present work it was found that pure samples of each of the isomers could be obtained by chromatography on alumina. The two compounds moved on the column as a broad yellow band, initial fractions from which yielded pure 1-

phenylbenzo[c]cinnoline. A fairly large proportion of mixed 1- and 3-isomers followed but final fractions yielded pure 3-phenylbenzo[c]-cinnoline. As would be expected, the 3-isomer was formed in greater yield than the hindered 1-isomer. The structures were assigned to these isomers on the basis of their ultraviolet absorption spectra (Fig. 8). 3-Phenylbenzo[c]cinnoline exhibited its $\lambda_{max.}$ at 275 mμ in ethanol. This is to be expected as its basic skeletal structure is that of a p-terphenyl, and the parent compound is known[89] to absorb at 278 mμ in the same solvent. 1-Phenylbenzo[c]cinnoline was found to have a $\lambda_{max.}$ at 253 mμ (ethanol). This is almost identical with that of benzo[c]cinnoline itself,[90] which is reasonable as the 1-phenyl group will be in a plane at right angles to that of the benzo[c]cinnoline moiety and will therefore have little effect on the latter's absorption spectrum.

The photochemistry of 4-styrylazobenzene, (83), was now examined in 98% Analar sulphuric acid. The results were similar to those obtained in 22N acid, and although spectral changes attributable to cyclisation were observed, no products could be isolated.

Dilute solutions of 1-phenylazoazulene, (84), in 98% Analar sulphuric acid were also irradiated but no detectable change in the ultraviolet absorption spectrum occurred.

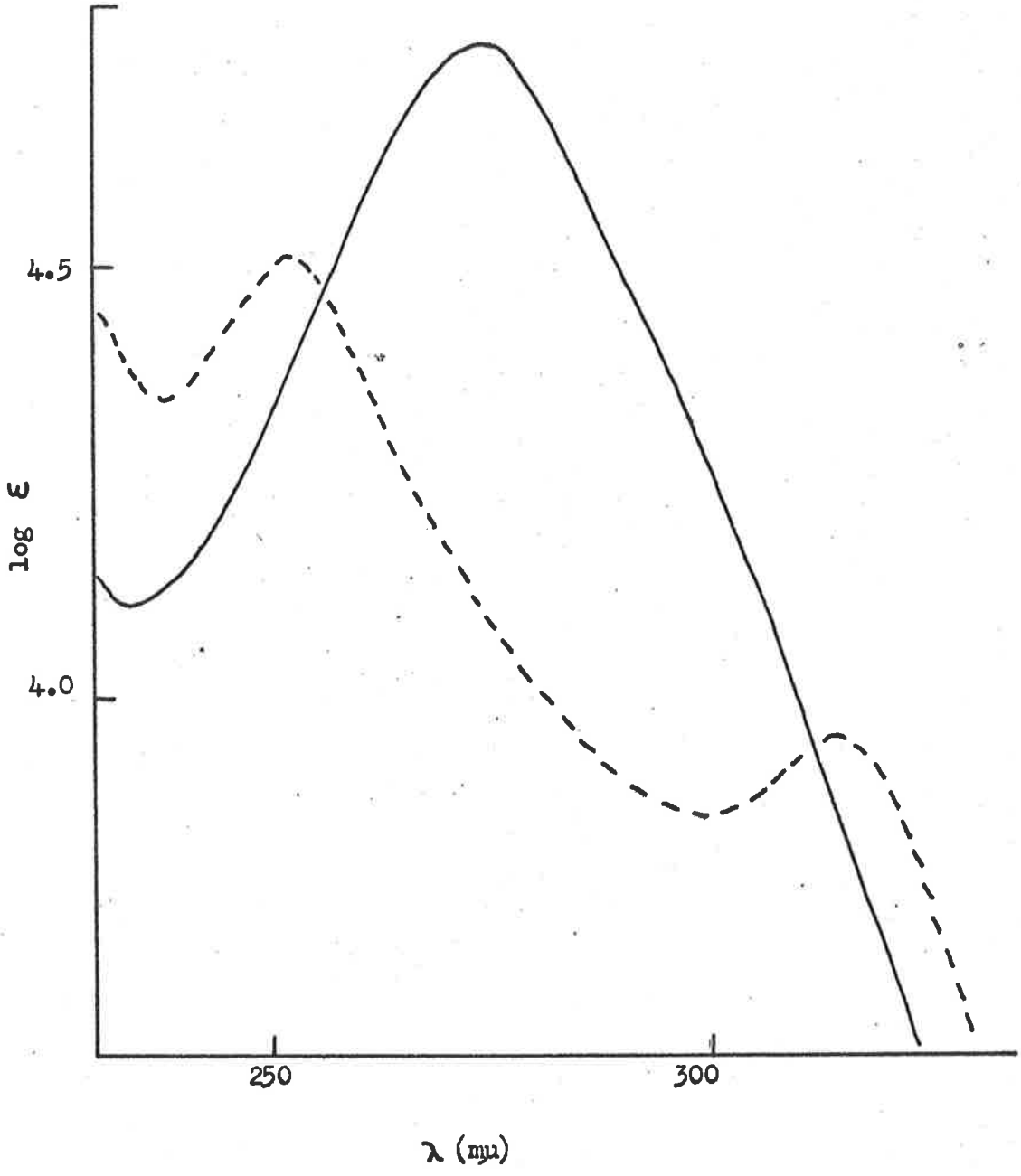
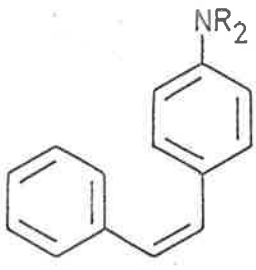


Fig. 8. - Absorption spectra of 1-phenylbenzo[c]cinnoline (88) (- - - -) and of 3-phenylbenzo[c]cinnoline (90) (———), in 95% ethanol.

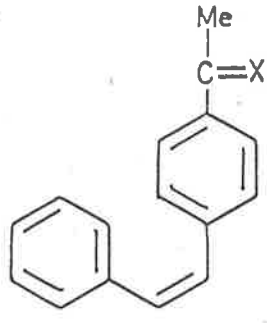
3.3. Related Compounds.

Mention was made in the Introduction of Mallory's suggestion[10] that certain stilbenes, substituted with such groups as amino, dimethylamino or acetyl, resist photocyclisation because their lowest excited state is of the $n\pi^*$ rather than the $\pi\pi^*$ type. It was decided, therefore, to examine the photochemistry of some of these compounds, and their Schiff bases, in acidic solution. In strong acid, the $n \rightarrow \pi^*$ excitation will presumably be inhibited.

Dilute solutions of 4-aminostilbene, (111, R = H), and of 4-benzalaminostilbene, (111, R_2 = PhCH) in 98% Analar sulphuric acid



(111)



(112)

were therefore irradiated. In neither case was there any appreciable change in their ultraviolet absorption spectra.

The behaviour of acidic solutions of 4-acetylstilbene, (112, X = O), was now examined. The compound is readily soluble in 98% Analar sulphuric acid and yields a yellow-green solution with a strong green fluorescence. Irradiation of dilute solutions caused the slow growth of a peak at 260 mμ. However, when the reaction was repeated

on a preparative scale, no products could be isolated.

Finally, the Schiff base formed from 4-acetylstilbene and aniline, (112, X = PhN), was examined. This compound has not been reported previously, but was synthesised by the method used to prepare the corresponding Schiff base of acetophenone.[91] Irradiation of dilute solutions of (112, X = PhN) in 98% Analar sulphuric acid produced a peak at about 240 mμ. Again no material could be isolated when the irradiation was carried out on a larger scale.

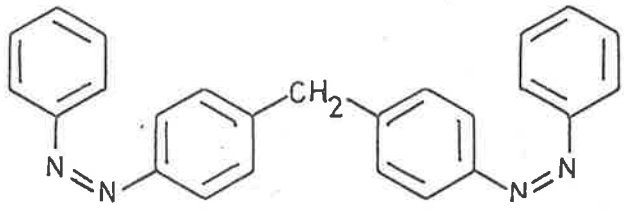
CHAPTER IV

FURTHER PHOTOCHEMICAL STUDIES IN 98% ANALAR SULPHURIC ACID.

4.1 Non-Conjugated Bisazo Compounds.

In the preceding chapter, the concomitant cyclisation and reduction which occurs during the irradiation of acidic solutions of 4-phenylazoazobenzene and of 4,4'-bis(phenylazo)biphenyl was discussed. The mechanism proposed to explain this phenomenon incorporated two prototropic shifts from the 10a- and 10b- positions of the first formed 10a,10b-dihydrobenzo[c]cinnoline, to the nitrogen atoms of the attached azo group. Such shifts are possible only if the two halves of the molecule are conjugatively linked. To shed further light on the matter, it seemed important to extend the investigations to bisazo compounds in which the two halves of the molecule are no longer linked by conjugation. It was thought possible that cyclisation might occur independently round each of the azo linkages.

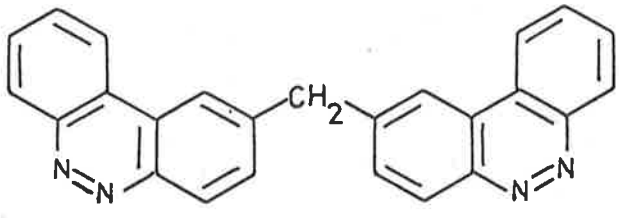
The simplest such non-conjugated bisazo compound is 4,4'-bis(phenylazo)diphenylmethane (113).



(113)

This compound does not appear to have been made previously but it was synthesised in the standard manner by condensing nitrosobenzene with 4,4'-diaminodiphenylmethane. As the yield fraction of cyclised products has been shown to increase with increasing acid strength,[54] it was decided to carry out this irradiation in 98% Analar sulphuric acid.

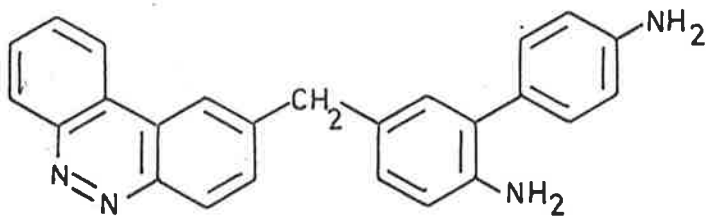
Initial experiments on dilute (c. 10^{-5}M) solutions showed spectral changes attributable to cyclisation and an experiment on a preparative scale was therefore carried out. As is common with these photochemical reactions, some tar formation was evident. However, when the ultraviolet absorption spectrum indicated that the cyclisation was complete, the reaction mixture was worked up in the usual way, and the extracted organic material was chromatographed on alumina. No evidence of the doubly cyclised product di-(2-benzo[c]cinnolinyl)methane (114)[72] was obtained. In fact, only one major product appeared to be formed



(114)

and this was eluted from the column with ether. Evaporation of the solvent left a yellow solid which could be precipitated from benzene with light petroleum, but which melted over a range of temperature and was obviously impure. Thin-layer chromatography showed it to consist

of a major component contaminated with a small amount of impurity. Its ultraviolet absorption spectrum showed the presence of a benzo[c]cinnoline nucleus, and the presence of NH was evident from its infrared spectrum. Although the compound itself could not be purified by recrystallisation, it readily formed a salicylidene anil. This derivative was easily purified by recrystallisation, and its elementary analysis suggested that it was formed from the diamine 2-[4'-amino-3'-(4"-aminophenyl)benzyl]benzo-[c]cinnoline (115). A purified sample of the anil was subjected to acid hydrolysis and the base so liberated was found to crystallise easily from

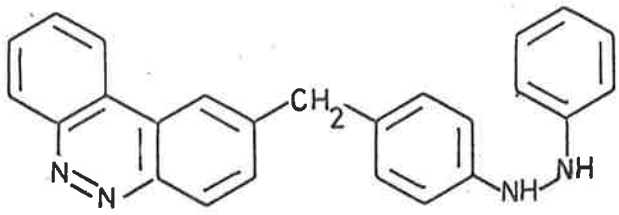


(115)

benzene. An elementary analysis was in accord with the formulation of this amine as (115). Although the nuclear magnetic resonance spectrum was too complex for all the peaks to be assigned, the presence of two primary amino groups was confirmed.

It is obvious, then, that the irradiation of the non-conjugated bisazo compound, 4,4'-bis(phenylazo)diphenylmethane, as with the conjugated bisazo compounds, 4-phenylazoazobenzene and 4,4'-bis(phenylazo)-biphenyl, leads to concomitant cyclisation and reduction. The explanation of this phenomenon offered in the preceding chapter is not applicable to

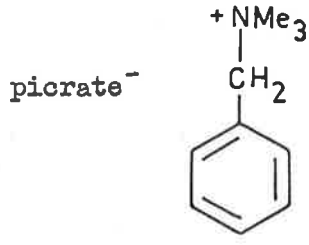
the case of the non-conjugated 4,4'-bis(phenylazo) diphenylmethane. Of course this does not invalidate the mechanism for the conjugated bisazo compounds. However, in the case of 4,4'-bis(phenylazo)diphenylmethane, it seems that the second azo linkage is reduced because of its relatively close proximity to the 10a- and 10b- hydrogens of the first formed 10a,10b-dihydrobenzo[c]cinnoline. The intermediate which would be produced by such a reduction is 2-[4'-(2"-phenyl)hydrazinobenzyl]benzo-[c]cinnoline (116), and this is obviously the precursor of the isolated



(116)

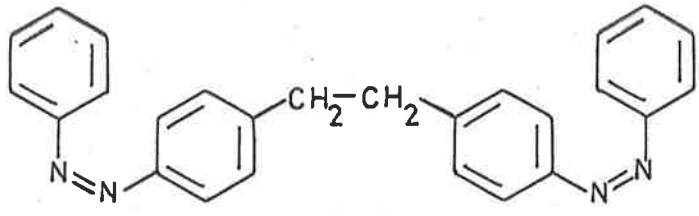
2-[4'-amino-3'-(4"-aminophenyl)benzyl]benzo[c]cinnoline (115). According to Ingold's Rules (p.38), such diphenyline formation occurs when the hydrazo molecule undergoing rearrangement is substituted in the 4-position with an electron-attracting group. There can be little doubt that in 98% sulphuric acid, the benzo[c]cinnoline moiety of (116) will be protonated. The electron-attracting effect of such a positively charged group must be transmitted through the methylene bridge to the hydrazo part of the molecule. Analogies for such an electron-attracting effect to be transmitted through a methylene group are to be found in the literature. For instance Ingold et al[92] have shown that nitration

of trimethylbenzylammonium picrate, (117), yields 88% of the m-nitro isomer. Thus the formation of 2-[4'-amino-3'-(4"-aminophenyl)benzyl]-benzo[c]cinnoline (115) during the irradiation of 4,4'-bis(phenylazo)-diphenylmethane, (113), can be rationalised.



(117)

Finally, it was decided to investigate the photochemistry of another non-conjugated bisazo compound, 4,4'-bis(phenylazo)bibenzyl (118),

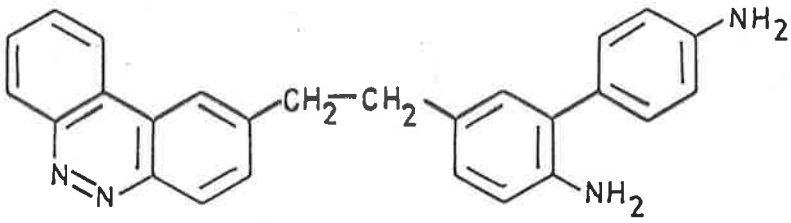


(118)

and to examine the products for evidence of the occurrence of a double cyclisation.

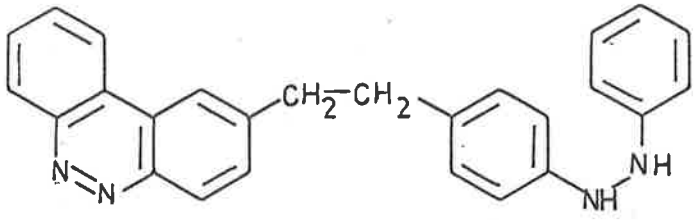
Once again, no reference to this compound could be found in the literature, but it was synthesised, by the same general method as was used for 4,4'-bis(phenylazo)diphenylmethane, by condensing nitroso-

benzene with 4,4'-diaminobibenzyl. The photochemical reaction was carried out, and the products were extracted and chromatographed on alumina in the usual way. As in the previous case, no doubly cyclised products could be detected. A small yield of a brown oil was obtained, and this gave an ultraviolet absorption spectrum which indicated the presence of a benzo[c]cinnoline moiety. The infrared spectrum showed the presence of NH. Although this could not be purified, it was readily converted into a crystalline salicylidene derivative. An elementary analysis of this anil suggested that it was derived from 1-(2'-benzo-[c]cinnolinyl)-2-[4"-amino-3"-(4"-aminophenyl)phenyl]ethane (119). Unfortunately, an insufficient quantity of this anil was obtained to allow its hydrolysis to the free base (119). The formation of such a



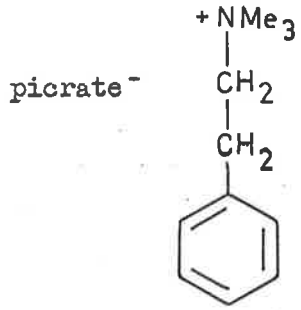
(119)

diphenyline from the presumedintermediate 1-(2'-benzo[c]cinnolinyl)-2-[4"-(2"-phenylhydrazino)phenyl]ethane, (120), requires that the electron-attracting effect of the protonated benzo[c]cinnoline nucleus be transmitted, through the bridging methylene groups, to the hydrazo part of the molecule. The transmission of such an electronic effect through two saturated carbon atoms is known to occur. It is illustrated by the



(120)

isolation of 19% of the m-nitro isomer following nitration of trimethyl-β-phenylethylammonium picrate (121).[92] Of course the electronic effect

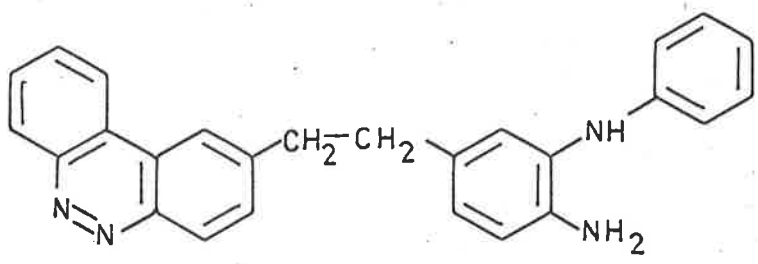


(121)

of the positively-charged nitrogen is considerably reduced, and this is reflected in the present case by the small yield of (119) which was obtained.

The major product from the irradiation of 4,4'-bis(phenylazo)-bibenzyl was not positively identified. It was a red solid which was strongly adsorbed on the alumina column and could only be eluted with the aid of methanol. This also had the effect of removing some of the tar, and the compound was not obtained pure. However, its ultra-violet absorption spectrum showed the presence of a benzo[c]cinnoline

nucleus, and the presence of NH was indicated by its infrared spectrum. It would not form a salicylidene derivative. It too is presumably formed from the intermediate (120) and its most probable structure, if Ingold's rules are applied, is the o-semidine (122).



(122)

4.2. Azobenzene

In the early experiments on the irradiation of acidic solutions of azobenzene carried out in this laboratory,[37] benzo[c]cinnoline was found to be produced in about 50% yield. The other product, formed in slightly lower yield, was benzidine. However, in later work,[54] it was shown that the yield of benzo[c]cinnoline was dependent on the acidity of the medium. As the acidity was increased, the quantum yield decreased, but the yield fraction of benzo[c]cinnoline increased. In other work with substituted azobenzenes,[40] yields of approximately 90% have been claimed when the irradiations were carried out in 98% Analar sulphuric acid. It is obvious, then, that in concentrated acid, the hydrazobenzene first formed does not undergo a normal benzidine

rearrangement. The acid-catalysed rearrangement of hydrazobenzene normally gives rise to benzidine and diphenyline in the approximate ration of 70:30. Furthermore, it has been stated by Carlin et al,[93] that this ratio of products is independent of the strength of the catalysing acid. This may well be the case for the low range of acidities studied by these workers, but more recent investigations with concentrated acids have shown that as the acidity of the medium is increased, the proportion of benzidine produced decreases.[94] It has been suggested,[54] that for irradiations of azobenzene carried out in strong acid, the hydrazobenzene first formed undergoes disproportionation to form aniline and azobenzene. The azobenzene so produced then re-enters the cycle to yield more benzo[c]cinnoline and hydrazobenzene, as illustrated in Scheme 4.

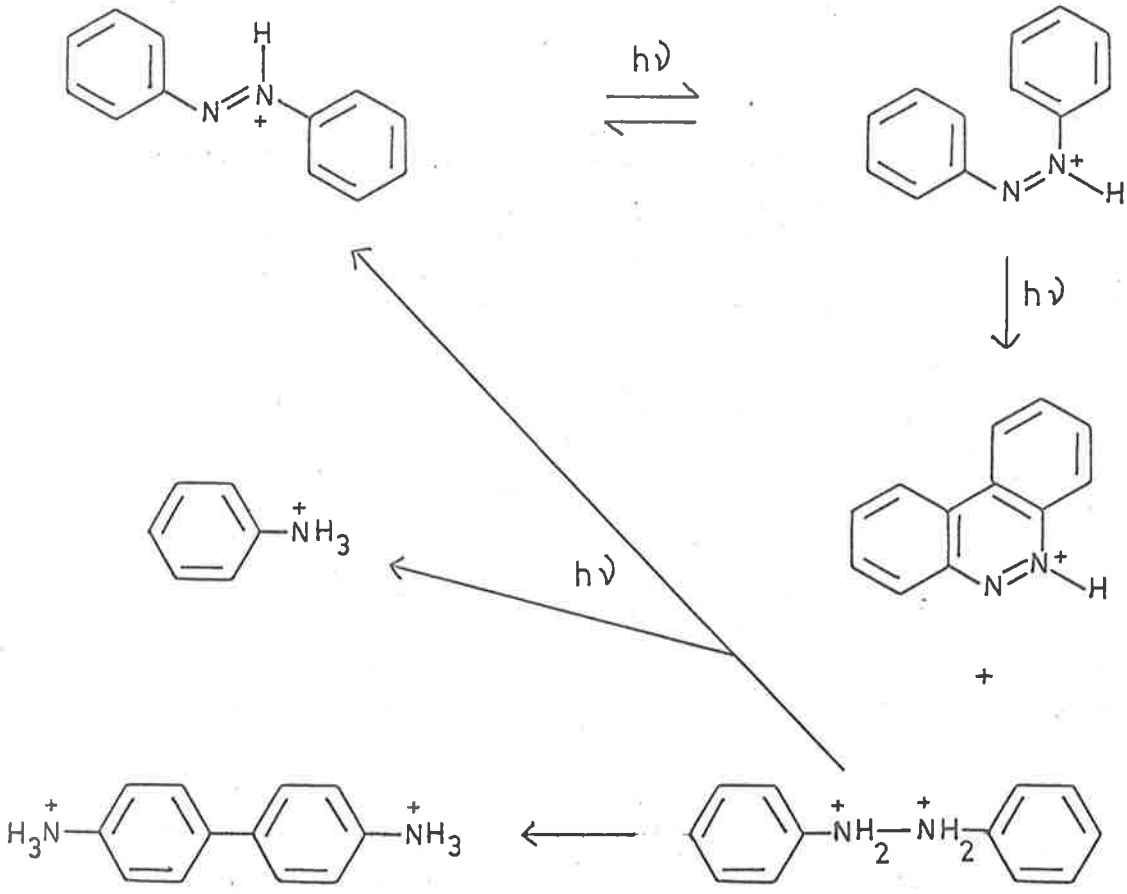
It can be seen from such a scheme that the maximum amount of benzo[c]cinnoline which can be produced from such a cycle is 66.2/3%. This is made clearer in Scheme 5. Continuation of such a scheme predicts a yield of benzo[c]cinnoline of

$$\frac{1}{2} + \frac{1}{8} + \frac{1}{32} + \frac{1}{128} + - - - - -$$

$$= \frac{1}{2}\left(1 + \frac{1}{4} + \frac{1}{16} + \frac{1}{64} + - - - - -\right.$$

$$= \frac{1}{2}\left(\frac{1}{1 - \frac{1}{4}}\right) = \frac{2}{3} \text{ i.e. } 66\frac{2}{3}\%$$

It was decided therefore, to study the photochemistry of azobenzene in 98% Analar sulphuric acid with a view to comparing the experimentally determined yield of benzo[c]cinnoline with the limiting



SCHEME 4

Azobenzene ⟶ Benzo[c]cinnoline + Hydrazobenzene

1 → $\frac{1}{2}$ + $\frac{1}{2}$

Hydrazobenzene ⟶ Azobenzene + Aniline

$\frac{1}{2}$ → $\frac{1}{4}$ + $\frac{1}{4}$

Azobenzene ⟶ Benzo[c]cinnoline + Hydrazobenzene

$\frac{1}{4}$ → $\frac{1}{8}$ + $\frac{1}{8}$

etc.

SCHEME 5

value of 66.2/3%, predicted by Scheme 5.

In experiments on a preparative scale, benzo[c]cinnoline was found to be formed in a crude yield of 60% (55% after recrystallisation), following the irradiation of azobenzene in 98% Analar sulphuric acid. Spectrophotometric determinations of the yield of benzo[c]cinnoline gave a value of 59%. These results are quite close to the predicted value of 66.2/3%, and it should be stated that some loss of hydrazobenzene to benzidine will probably occur, as indicated in Scheme 4, so that the limiting yield is not likely to be reached. It does, however, seem significant that this limiting yield was not exceeded.

When azobenzene is irradiated in 22N acid, the benzidine produced appears in the reactor as crystals of the insoluble sulphate. However, when the reaction was carried out in concentrated sulphuric acid, no benzidine sulphate was observed, even on dilution to c. 22N. Another obvious difference between the two reactions was that sulphur dioxide was evolved only in the more concentrated acid. The evolution of sulphur dioxide during the irradiation of several substituted azobenzenes in 98% Analar sulphuric acid has been noticed previously.[40]

It has already been mentioned, that as the strength of the rearranging acid is increased, the amount of benzidine formed from hydrazobenzene decreases. It was thought possible that, with the extremely strong 98% sulphuric acid, benzidine might not be formed at all. A sample of hydrazobenzene was therefore prepared and it was found to dissolve readily in 98% sulphuric acid. However, on dilution of the resulting solution to about 22N, benzidine sulphate was precipitated. It would appear, then, that if hydrazobenzene is produced during the

irradiation of azobenzene in 98% sulphuric acid, it does not undergo a normal benzidine rearrangement. The diluted solution was made alkaline and extracted in the usual way, and the products were chromatographed on alumina. No trace of azobenzene was found. The postulated formation of azobenzene from hydrazobenzene as illustrated in Scheme 4, then, must only occur when the solution is irradiated. Scheme 4 predicts the formation of aniline, and it seemed important, therefore, to search for aniline, or its decomposition products, in the irradiated solution.

Another irradiation, on a preparative scale, of azobenzene in concentrated sulphuric acid was carried out. When the cyclisation was complete, the solution was made slightly alkaline and the precipitated solids were removed by filtration. The filtrate was steam distilled and the distillate extracted with ether to give a small yield of a brown oil, the infrared spectrum of which showed absorption at c. 3400 and 3500 cm^{-1} (NH). The oil was treated with bromine water and the solid so obtained was compared, by thin-layer chromatography, with an authentic sample of tribromoaniline. Only a very faint spot of R_F identical with that of the standard was produced. It would appear then, that if aniline is produced during the irradiation, it must undergo some subsequent change.

A further irradiation of azobenzene was carried out and the products, isolated in the usual way, were chromatographed on alumina. Elution with benzene and evaporation of the solvent yielded benzo[c]-cinnoline. When the eluant was changed to ether, a reddish solution with a blue fluorescence was obtained. Evaporation of the solvent gave

a brown oil, the infrared spectrum of which showed strong absorption at 3450 cm^{-1}, and a shoulder at 3300 cm^{-1} (NH). Elution with methanol and evaporation gave a black oil, the infrared spectrum of which showed a peak at 3500 cm^{-1} (NH).

It seemed important to examine the behaviour of aniline on irradiation. A solution of redistilled aniline in 98% Analar sulphuric acid was therefore irradiated, and it is significant that sulphur dioxide was evolved. The reaction mixture was worked up and chromatographed in the usual way. Elution with benzene yielded unchanged aniline. However, elution with ether, and then with methanol, followed by evaporation of the solvents, gave two black oils. The infrared spectra of these two products closely resembled those of the similarly isolated products from the irradiation of azobenzene.

It would appear then, that the representation of the irradiation of azobenzene in 98% Analar sulphuric acid by Scheme 4 is in accord with the experimental facts so far determined. The maximum predicted yield of 66.2/3% benzo[c]cinnoline is not quite attained but this could be explained by the loss of small quantities of hydrazobenzene through a normal benzidine rearrangement. Although aniline itself was not detected, products containing amino groups were isolated and these may have arisen from the first-formed aniline. The evolution of sulphur dioxide during the irradiation of azobenzene in concentrated acid could also be explained by the decomposition of the first-formed aniline.

CHAPTER V

THE BENZIDINE REARRANGEMENT.

Most of the irradiations discussed in this dissertation have involved a benzidine rearrangement in the final product formation. It seems essential, then, to review briefly the present state of knowledge of this reaction, and to see whether the products formed in the present work can be rationalised on the basis of past experience of the benzidine rearrangement. It should be emphasised at this point, however, that although the mechanism of the benzidine rearrangement has become better understood in recent years, the problem is by no means completely solved. In addition to this, the conditions of the rearrangements in the present work are quite unlike any of those on which the suggested mechanistic schemes have been based. The hydrazo compound which arises during irradiation is possibly produced in an electronically excited state, and the medium in which it is formed is considerably more acidic than the vast majority of those studied previously.

The term "benzidine rearrangement" is a general one for the acid - catalysed* conversion of hydrazobenzene (33) into one or more of the following rearrangement products; benzidine (34), diphenyline (123), o-benzidine (124), o-semidine (125) or p-semidine (126). Disproportionation to the azo compound and amine can also occur (127). Although

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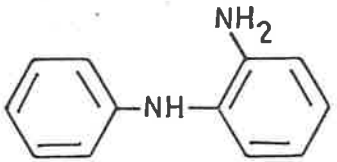
* Such rearrangements can also be brought about non-catalytically, but this is beyond the scope of the present discussion.



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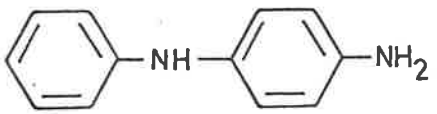

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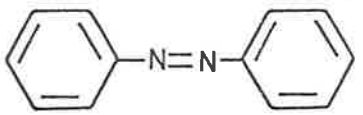

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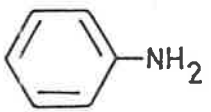

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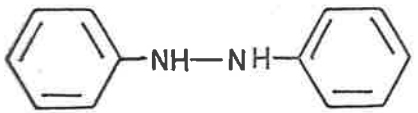

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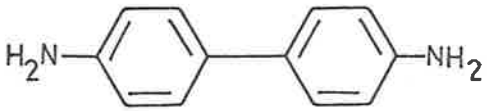

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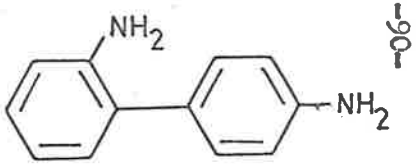

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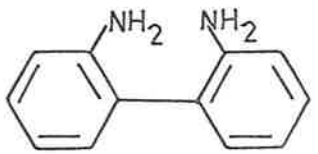
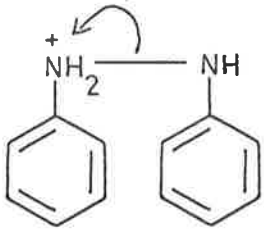


(124)

the rearrangement has been studied for over 60 years, the mechanism by which it occurs is still uncertain and the subject of much debate. Early theories, such as that of Stieglitz,[95] adopted the concept of dissociation to overcome the considerable stereochemical difficulties. However, Ingold and Kidd[96] found no products of the type AB when AA- and BB- type hydrazobenzenes were rearranged in the same solvent, which excludes an intermolecular process. Smith, Schwartz and Wheland,[97] have confirmed this using a more refined technique, with radioactively labelled molecules, and it is now generally accepted that the benzidine rearrangement proceeds intramolecularly.

It is this condition of intramolecularity which imposes considerable stereochemical difficulties. Even in the cis-form of hydrazobenzene, the para positions are 4.3A° apart, and yet a bond must be formed between these two positions without the two nuclei drifting apart. It has been suggested[98] that the doubly protonated hydrazo molecule cleaves homolytically into two radical ions, which are held together in a solvent cage. However, no reports have been made of products arising from the attack of such radicals on the walls of the cage. Further evidence against this hypothesis is that sensitive methods for the detection of radicals have failed to disclose their presence.[67] Only two theories remain which explain the benzidine rearrangement on an intramolecular basis. These are the π-complex mechanism of Dewar,[99] and the polar-transition-state mechanism of Ingold.[67]

Dewars theory, as postulated in 1945,[100] assumes the initial monoprotonation of the hydrazo molecule to give (128), which then



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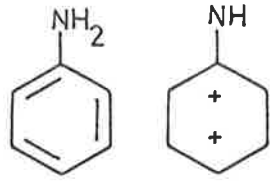
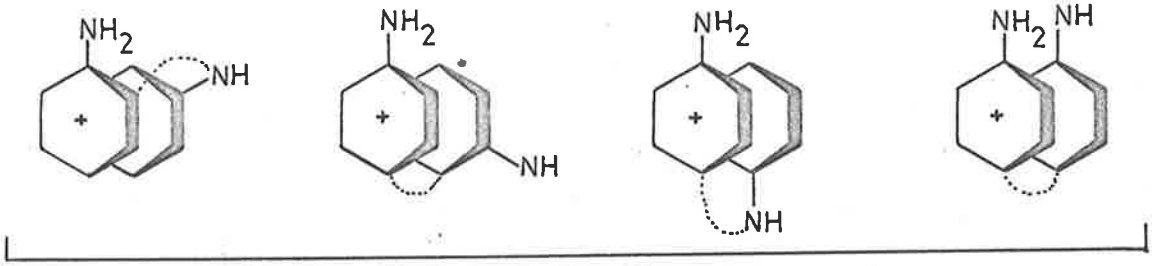


(129) (130)

heterolyses to aniline (129), and a positive ion (130). A π-complex is then assumed to be formed between (129) and (130), the two components being held together by a dative bond in which the highest filled molecular orbital of aniline acts as a donor, and the corresponding empty orbital of (130) acts as an acceptor. It is assumed that the aromatic rings can rotate relative to each other, and unfolding of the species so produced, (131), gives rise to the observed products. The

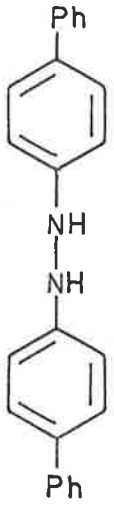


(131)

confirmation by Hammond and Shine[101] of an earlier report[102] that the rearrangement was quadratic in hydrogen ions, was incorporated by Dewar into his mechanism by assuming that the function of the second proton was to convert the π-complex to products.

As support for his mechanism, Dewar has quoted Friebel and

Rassow's report[103] that the rearrangement of 4,4'-diphenylhydrazobenzene, (132), gives only the disproportionation products, 4,4'-diphenylazobenzene (133) and 4-aminobiphenyl (134). However, more recent work has



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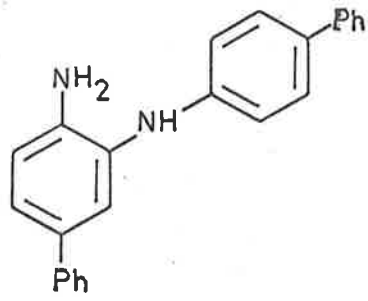
(133)

(134)



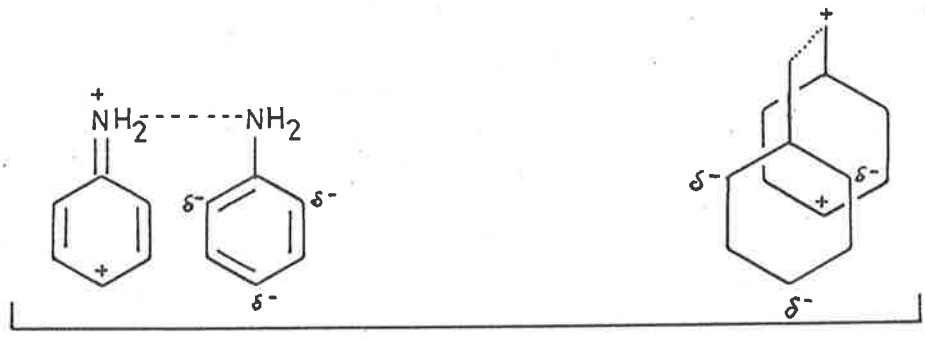
(135)

shown[104] that in addition to disproportionation products, about 25% of the o-semidine (135) is produced.

It is known that the acid catalysed rearrangement of hydrazonaphthalenes leads to 4,4'- and 2,2'-, but never to 2,4'-linked products. This has been explained by Dewar on the lack of axial symmetry of the π-complex, which no longer has freedom of rotation, and which is therefore prevented from forming the intermediate in the production of a 2,4'-diphenyline. However, it has recently been shown that the rearrangement of N-1-naphthyl-N'-phenylhydrazine (61),[58] and of N-2-naphthyl-N'-phenylhydrazine,[75] leads to hydrazonaphthalene-type, rather

than hydrazobenzene-type products. This could not be predicted by Dewar's mechanism as the removal of one benzene ring should permit rotation of the π-complex to recur and thus result in the production of some 2,4'-linked products. These two experimental observations, the products obtained by the rearrangement of 4,4'-diphenylhydrazobenzene, and by the rearrangement of the phenylhydrazonaphthalenes, are at variance with the π-complex mechanism but are readily incorporated into the polar-transition-state theory of Ingold.[67]

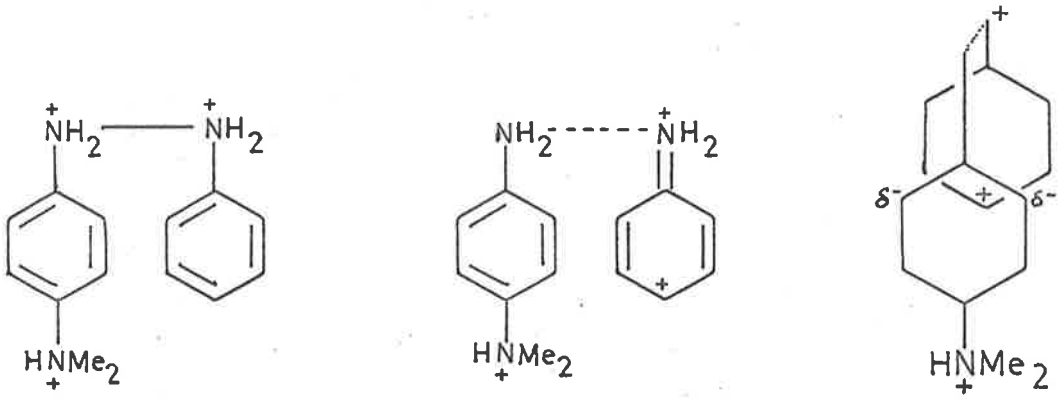
The mechanisms envisaged by Ingold for the rearrangement of the hydrazobenzenes and the hydrazonaphthalenes differ slightly, and the former will be considered first. Ingold postulates the rearrangement of hydrazobenzenes to involve diprotonation of the substrate, followed by considerable heterolysis of the N-N bond to give a transition state (136).



(136)

The components are considered to be held together by largely electrostatic bonds which can retain enough strength to maintain the unity of the particle at up to 7A°. Also, the weak directing properties of such polar bonds allow changes in molecular geometry to occur easily, and the positive charge at the <u>para</u> position of the cation will be attracted

to the centroid of the partial negative charges on the quasi-aniline moiety. It follows that only 2,2'- and 4,4'- linking can occur. The effect of a <u>para</u> substituent can also be rationalised; for instance that of the electron-attracting group, $^{+}NMe_2H$, as in Scheme 6. Such



SCHEME 6.

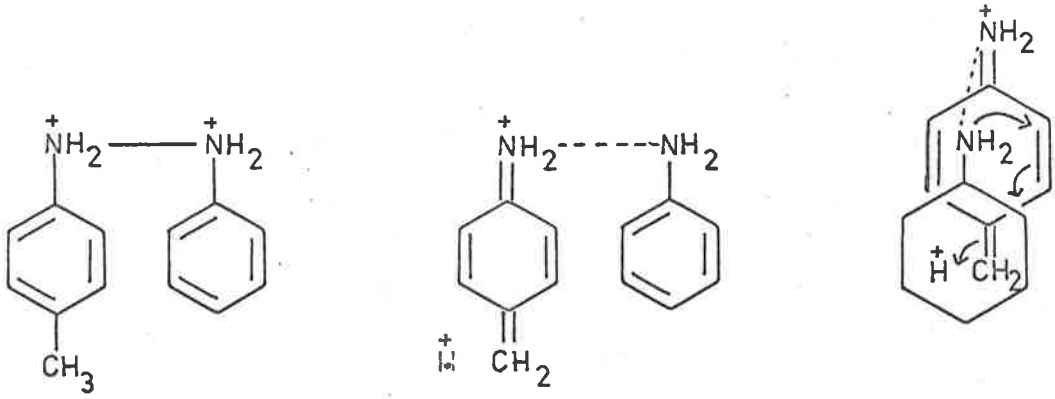
an example is not discussed in detail by Ingold but, by the application of his principles, it is seen that the initial effect of the substituent is to determine the direction of the N-N bond heterolysis. The two parts so produced will again be held together by an electrostatic-type bond, but the positive <u>para</u> charge of the <u>p</u>-quinonoid structure will be attracted to the centre of highest electron density as illustrated. Moreover, 4,4'-linking is precluded by the <u>p</u>-substituent, and therefore only a 2,4'-diphenyline can result.

The example just discussed bears an obvious relationship to many of those encountered in the present work, where the electron-attracting <u>p</u>-substituent was either a protonated azo group, or a protonated benzo[<u>c</u>]cinnoline moiety. Thus the formation of 4-amino-3-

(4'-aminophenyl)azobenzene (70) on irradiation of 4-phenylazoazobenzene (68) can be rationalised on the basis of Ingold's mechanism. Also explicable by this mechanism is the production of 4-[4'-amino-3'-(4"-aminophenyl)phenyl]azobenzene (75), and of 2-[4'-amino-3'-(4"-aminophenyl)phenyl]benzo[c]cinnoline (78) following irradiation of 4,4'-bis(phenylazo)biphenyl (73). The formation of 2-[4'-amino-3'-(4"-aminophenyl)benzyl]benzo[c]cinnoline (115) during the irradiation of 4,4'-bis(phenylazo)diphenylmethane (113) is also in accord with this mechanism. For, as discussed in the preceding chapter, the electron-attracting properties of a positively-charged nitrogen can be transmitted through a methylene bridge. This also explains the formation of the minor product, 1-(2'-benzo[c]cinnolinyl)-2-[4"-amino-3"-(4"'-aminophenyl)phenyl]ethane (119) on irradiation of 4,4'-bis(phenylazo)-bibenzyl (118). However, although some electron-attracting effect can be transmitted through two saturated carbons, it is considerably weakened in the process. The rearrangement of the supposed intermediate, 1-(2'-benzo[c]cinnolinyl)-2-[4"-(2"'-phenylhydrazino)phenyl]ethane (120), produced during this irradiation will therefore mainly follow a path resembling that taken by 4-methylhydrazobenzene. This is illustrated in Scheme 7. Again, the initial effect of the substituent is to determine the direction of heterolysis of the N-N bond. When the two parts come together, they will be displaced, relative to each other, more than in the case of hydrazobenzene. In the quasi cationic moiety, bond-forming electron-acceptance is possible only at the 2-position. Because of the displacement, this position can be reached most easily

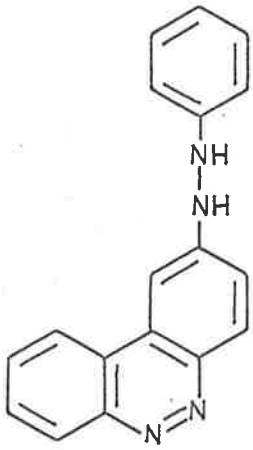
by the electrons of the nitrogen of the aniline-like moiety, and hence a 2-N'-semidine results. The major product to be expected following the irradiation of 4,4'-bis(phenylazo)biphenyl, (118), is therefore the o-semidine, (122).

The products formed during the irradiation of 4-phenylazoazobenzene (68) in 98% Analar sulphuric acid require separate consideration. As was mentioned in Chapter III, the presumed intermediate in the formation of the two cyclised products is 2-(2'-phenylhydrazino)benzo[c]cinnoline (104). This hydrazo compound bears some resemblance to N-2-naphthyl-N'-phenylhydrazine (137). The rearrangement of this latter compound has been studied[75] and it has been shown to give mainly the



SCHEME 7.

hydrazonaphthalene-type product, 2-amino-1-(2'-aminophenyl)naphthalene (138); the only other product being a small amount of the carbazole (139). However, in the present work, rearrangement of (104) has been found to lead to hydrazobenzene-type products, the diphenyline (86),



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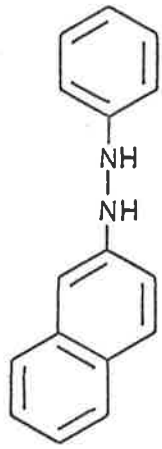
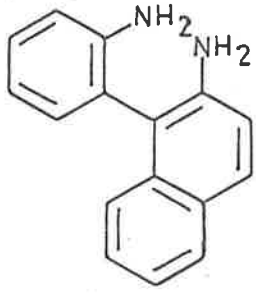


(137)

and the p-semidine (87). It seems essential then to attempt to explain why two superficially similar hydrazo compounds (104) and (137) should give rise to such different products.

It is known[101,102] that the rearrangement of unsubstituted hydrazobenzene is second-order in hydrogen ions. However, Carlin and Odioso[105] have found that the rearrangement of 2,2'-dimethylhydrazobenzene has a 1.6-order dependence on hydrogen ion concentration. This was interpreted by Blackadder and Hinshelwood,[106] as showing the existence of another rearrangement mechanism which was linear in hydrogen ions. Ingold et al[67] considered that the anomalous behaviour of 2,2'-dimethylhydrazobenzene was due to the peculiar property of the o-methyl substituent of both weakening an aniline base and donating electrons to the ring. These effects should also be shown by the 2-naphthyl, and even more by the 1-naphthyl groups. Ingold has, in fact, verified that the benzidine rearrangements of 1,1'-hydrazonaphthalene,[107] 1,2'-hydrazonaphthalene[108] and N-1-naphthyl-N'-phenylhydrazine[58] can proceed via



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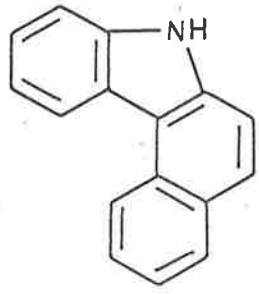
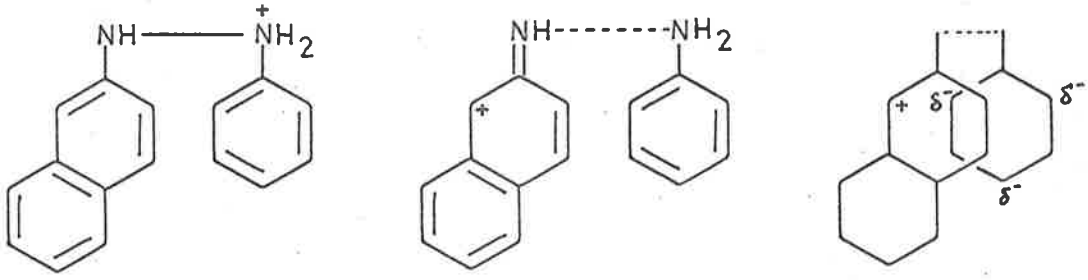


(139)

a mechanism which is first-order in hydrogen ions. The lowest order in hydrogen ions observed for 2,2'-hydrazonaphthalene[109] was 1.15, and for N-2-naphthyl-N'-phenylhydrazine[75] was 1.1.

The rearrangement of N-2-naphthyl-N'-phenylhydrazine (137) is explained by Ingold using the mechanism, first-order in hydrogen ions, illustrated in Scheme 8. The direction of N-N heterolysis will be as

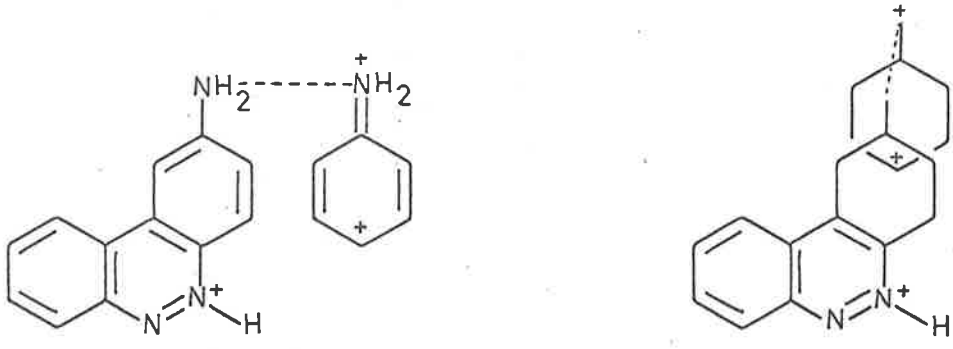


SCHEME 8

shown, guided both by the greater basicity of the phenylamine nitrogen, and the facile electron release of the naphthalene moiety. The two components will converge, without longitudinal displacement, and so produce the observed 2-amino-1-(2'-aminophenyl)naphthalene (138).

The reason that the superficially similar 2-(2'-phenyl-hydrazino)benzo[c]cinnoline (104) does not follow the same rearrangement

route is now apparent. The rearrangement occurred in 98% sulphuric acid and it seems certain that in this medium, the benzo[c]cinnoline moiety will be protonated. The presumed strongly electron-attracting effect of this protonation would easily override any electron release from the condensed ring system as postulated in the case of N-2-naphthyl-N'-phenylhydrazine. The rearrangement of 2-(2'-phenylhydrazino)benzo[c]-cinnoline is therefore assumed to occur by a hydrazobenzene-type, rather than a hydrazonaphthalene-type route, and this is illustrated in Scheme 9.



SCHEME 9.

The effect of the protonated benzo[c]cinnoline moiety will be to determine the direction of N-N heterolysis. This will occur as shown, and when the two parts come together, they will be slightly displaced due to the repulsion between the positive charges on the benzo[c]-cinnoline nitrogen, and on the para-position of the quinonoid dication. The para-position of the dication will therefore be close to positions

1 and 3 of the benzo[c]cinnoline nucleus. It is now necessary to explain why the 1-substituted benzo[c]cinnoline was formed exclusively, although the 1-position is considerably more sterically hindered than is the 3-position.

In phenanthrene, the carbocyclic analogue of benzo[c]cinnoline, the 3,4-bond (corresponding to the 1,2-bond in benzo[c]cinnoline) is known to have greater double-bond character than the 2,3-bond.[110] Also the free valence number of the 4-position in phenanthrene (1-position in benzo[c]cinnoline) is greater than that of the 2-position[110] (3-position in benzo[c]cinnoline). Moreover, a molecular orbital treatment of benzo[c]cinnoline itself,[111] has shown that the 1-position should be more susceptible to electrophilic attack than should the 3-position. A more refined treatment, making allowance for protonation, has confirmed this.[112] These conclusions have been borne out experimentally and benzo[c]cinnoline has been found to undergo nitration[113] and bromination[114] preferentially in the 1-position. No 3-isomer was detected in either of these investigations.

The final collapse of the polar-transition-state represented in Scheme 9, could be approximately described as an electrophilic attack by the *para* positive charge of the *p*-quinonoid dication, on the benzo[c]-cinnoline nucleus. In view of the preceding discussion, it seems reasonable that this would occur preferentially at position 1.

CHAPTER VI

EXPERIMENTAL

6.1. General

Melting points were determined in capillaries in a stirred paraffin bath, or on a Reichert micro-hot stage, and are uncorrected.

Infrared spectra were determined with Perkin-Elmer 137 and 237 spectrophotometers.

Ultraviolet absorption spectra were determined with an Optica CF4 recording spectrophotometer, or a Perkin-Elmer 137 ultraviolet spectrophotometer.

Nuclear magnetic resonance spectra were recorded by Dr. T.M. Spotswood and Mr. L. Paltridge with a Varian D.P.60 spectrometer operated at 60 Mc/s. Chemical shifts were measured relative to tetramethylsilane or dimethylsulphoxide as internal standards; and the solvent used was either deuterochloroform or dimethylsulphoxide.

Thin-layer chromatography was carried out on an adsorbent layer of Kieselgel G, 0.2 mm thick.

Unless otherwise stated, the light petroleum used had a boiling range of 60-80°.

All organic solvent extracts were dried over anhydrous magnesium sulphate.

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

6.2 Photochemical Reactors.

Irradiations with Mercury-Quartz Lamp.

Irradiations with a Philips 125W mercury-quartz lamp were carried out in a water-cooled Pyrex apparatus. The lamp was surrounded by a cylindrical water-jacket which was in turn surrounded by a jacket containing the solution. The capacity of the reactor was about 120 ml. For irradiations at low temperatures, the apparatus was placed in a Dewar bowl containing ethanol and solid carbon dioxide. Under these conditions, the solution was maintained at less than -30°.

Irradiations with Tungsten Lamp.

These were carried out by immersing the tungsten lamp in the solution to be examined in a beaker. This beaker was placed within a larger beaker containing running water. Under these conditions, the solution was maintained at c. 40°.

Irradiations with Sunlight.

These were carried out in a stoppered Pyrex culture dish. Sufficient solution to produce a thin layer c. $\frac{1}{4}$" thick was used (c. 250 ml).

6.3 Preparation of Azo Compounds.

Azobenzene.

Commercially available azobenzene was purified by distillation, followed by recrystallisation from aqueous ethanol. It had m.p. 68° (lit.[115] 68°).

3-Phenylazobenzene.

1-(m-Nitrophenyl)-3,3-triazine was prepared from dimethylamine

and a diazotised solution of 3-nitroaniline.[116] The triazine was decomposed with hydrogen chloride, in the presence of benzene, to give 3-nitrobiphenyl.[117] This was reduced to 3-aminobiphenyl by the action of hydrazine hydrate and Raney nickel,[118] the product being isolated as the hydrochloride.

3-Aminobiphenyl hydrochloride (1.9 g) was converted to the free base with aqueous sodium hydroxide. The amine was extracted with ether, and the ethereal solution, after being washed and dried, was evaporated to dryness. The residual amine was then dissolved in glacial acetic acid (3 ml), and to this solution was added a solution of nitrosobenzene (1 g) in glacial acetic acid (3 ml). The reaction mixture was warmed on a water-bath for 1 hr, and then allowed to stand overnight at room temperature. In the working-up process, the reaction mixture was first diluted with a large volume of water, and the acetic acid was neutralised with sodium hydroxide. The oil which had separated was then extracted with ether. After the ethereal solution had been washed and dried, it was evaporated to dryness. The crude product, which remained as a brown oil, was redissolved in light petroleum and subjected to chromatography on alumina. The main orange band was eluted with the same solvent, and the eluate, after evaporation, yielded an orange solid which was recrystallised from light petroleum. 3-Phenylazobenzene (1.5 g, 70%) was thereby obtained as orange-red plates, m.p. 51-52° -

(Found: C, 83.6; H, 5.4; N, 10.5. $C_{18}H_{14}N_2$ requires C, 83.7; H, 5.5; N, 10.85%).

4-Phenylazobenzene.

4-Aminobiphenyl (8.5 g) in acetic acid (50 ml) was added to nitrosobenzene (6.5 g) in acetic acid (25 ml), and the solution was heated on the water-bath for 15 min, then cooled. The solid was collected, washed, and chromatographed in light petroleum on alumina. The first orange fraction was evaporated to leave an orange-red solid. This was recrystallised from ethanol to yield 4-phenylazobenzene (10 g, 77%) as orange-yellow plates, m.p. 153-154° (lit.[119] 152°).

4-Benzalaminoazobenzene.

A clear solution of 4-aminoazobenzene (5 g) in boiling ethanol was mixed with an equimolar quantity (2.7 g) of benzaldehyde. After 30 min, the crystalline product was collected. Recrystallisation from benzene/ethanol (1:1) gave 4-benzalaminoazobenzene as shining red-brown plates m.p. 130-131° (lit.[120] 130.5°).

4-Phenylazoazobenzene.

This was prepared by condensing 4-aminoazobenzene with nitrosobenzene in acetic acid.[69] After chromatography on alumina, the 4-phenylazoazobenzene was recrystallised from ethanol and formed red-brown plates, m.p. 167-168° (lit. 167°).

4,4'-Bis(phenylazo)biphenyl.

This was prepared by condensing benzidine and nitrosobenzene in acetic acid.[59] Chromatography on alumina and recrystallisation from benzene gave 4,4'-bis(phenylazo)biphenyl as yellow-red plates, m.p. 231-232° (lit. 226°).

4-(4'-Aminophenyl)azobenzene.

This was prepared by condensing benzidine with one mole of nitrosobenzene in acetic acid.[70] The product was purified by chromatography on alumina. Elution with light petroleum gave a small amount of 4,4'-bis(phenylazo)biphenyl. Elution with benzene gave the major product, 4-(4'-aminophenyl)azobenzene. This crystallised from light petroleum as red plates, m.p. 151-152° (lit. 151-152°).

4,4'-Bis(phenylazo)diphenylmethane.

4,4'-diaminodiphenylmethane was prepared from aniline, hydrochloric acid and formaldehyde by the method of Scanlan.[121] When the reaction was complete, the excess aniline was removed by steam-distillation. The precipitate was dissolved in a slight excess of hydrochloric acid and the solution was cooled in an ice-bath. Dilute ammonium hydroxide was now added, the solution became milky and a sticky brown gum appeared. The addition of ammonium hydroxide was continued until a white solid began to be precipitated. At this point, the liquid was decanted from the resinous material which had settled to the bottom of the beaker. Continued addition of ammonium hydroxide to the decanted liquor precipitated the 4,4'-diaminodiphenylmethane as a white solid. This was removed by filtration but, as no satisfactory solvents have been reported for its crystallisation, it was not further purified.

4,4'-diaminodiphenylmethane (6 g) was dissolved in acetic acid (25 ml), with warming, and added to a solution of nitrosobenzene (7.5 g) in acetic acid (25 ml). The mixture was warmed on the water-

bath and there was an almost immediate precipitation of a brown solid. Warming was continued for 30 min, then the mixture was cooled and the solid collected. It was washed, dried and chromatographed in benzene on alumina. The first orange fraction was evaporated to leave a red-orange solid (8.9 g, 78%). Recrystallisation from light petroleum gave 4,4'-bis(phenylazo)diphenylmethane (8.1 g) as flat orange needles, m.p. 190-191° -

(Found: C, 80.1; H, 5.55; N, 14.5. $C_{25}H_{20}N_4$ requires C, 79.8; H, 5.4; N, 14.9%).

4,4'-Bis(phenylazo)bibenzyl.

4,4'-dinitrobibenzyl was prepared by the action of air and methanolic potassium hydroxide on 4-nitrotoluene.[122] The method was modified slightly as it proved impossible to filter the resulting pasty red-brown mass without first pouring it into hot water. The resulting suspension was filtered, and the residue was washed with boiling water, and then with ethanol. The residual solid was recrystallised from benzene to give 4,4'-dinitrobibenzyl as yellow needles, m.p. 183-185° (lit. 179-180°).

4,4'-Diaminobibenzyl was prepared by reducing 4,4'-dinitrobibenzyl with iron and hydrochloric acid.[122] 4,4'-Diaminobibenzyl was recrystallised from aqueous ethanol to give white plates, m.p. 141-143° (lit. 135-137°).

4,4'-Diaminobibenzyl (6.4 g) and acetic acid (50 ml) were heated together on the water-bath to c. 70°. To this yellow-brown opalescent mixture was added a solution of nitrosobenzene (7.5 g) in

acetic acid (25 ml), also at 70°. The mixture immediately darkened, and within a few minutes a brown solid was precipitated, and the temperature rose to c. 85°. The flask was removed from the water-bath and left for 1 hr at room temperature. The brown solid was collected, washed free from acetic acid, dried, and chromatographed in benzene on alumina. The first orange-red fraction to be eluted was evaporated to leave an orange-red solid (8 g, 68%). This was recrystallised from light petroleum to give 4,4'-bis(phenylazo)bibenzyl as orange-red plates, m.p. 187-188° -

(Found: C, 80.25; H, 5.7; N, 14.4. $C_{26}H_{22}N_4$ requires C, 80.0; H, 5.7; N, 14.35%).

2-Phenylazobenzo[c]cinnoline.

(i) 2-Aminobenzo[c]cinnoline (200 mg) was dissolved, with gentle heating, in acetic acid (1 ml). To this solution was added a solution of nitrosobenzene (130 mg) in acetic acid (0.5 ml), whereupon the mixture became dark brown. The brown solution was warmed on the water-bath for 1 hr, and then left overnight at room temperature. The reaction mixture was then poured into water, neutralised with sodium hydroxide solution, and extracted with benzene. Some black solid which did not dissolve was re-extracted with boiling benzene. The combined benzene extracts were washed and evaporated to leave a brown oil (230 mg), which was chromatographed in benzene on alumina. The light yellow fraction which was eluted very quickly was discarded. The following red fraction was evaporated to leave a red solid (30 mg, 10%). Recrystallisation from light petroleum yielded 2-phenylazobenzo[c]cinnoline as

orange needles, m.p. 218-219°.

(ii) 2-Aminobenzo[c]cinnoline (1.5 g) and nitrobenzene (2 ml) were mixed and heated to 190° (oil bath). Powdered sodium hydroxide (1 g) was added portion-wise to this mixture, and the temperature was raised to 200°. The colour of the reaction mixture then darkened, and a vigorous exothermic reaction took place with the temperature rising spontaneously to 230°. On being cooled, the reaction mixture set to a black solid. This was powdered and extracted with boiling benzene until no more red material could be removed. The benzene extract was washed well with water and evaporated to a small volume. The concentrated extract was then passed through a column of alumina. A small yellow band was the first to be eluted. This material was discarded. The main (red) band followed and this, after elution and evaporation of the solvent, yielded a red solid which was further purified by recrystallisation from light petroleum. 2-Phenylazobenzo[c]cinnoline (0.8 g, 37%) was thereby obtained as orange needles, m.p. 218-219° -

(Found: C, 76.2; H, 4.2; N, 19.8. $C_{18}H_{12}N_4$ requires C, 76.1; H, 4.25; N, 19.7%).

4-Styrylazobenzene.

Benzyl cyanide was nitrated, and then hydrolysed to 4-nitrophenylacetic acid, by the method of Robertson.[123] 4-Nitrostilbene was prepared by heating the 4-nitrophenylacetic acid with benzaldehyde in the present of piperidine.[124] The 4-nitrostilbene was reduced with ethanol, ferrous sulphate and ammonia to yield 4-aminostilbene.[125]

Finally, the 4-aminostilbene was condensed with nitrosobenzene in acetic acid to yield 4-styrylazobenzene.[125] The method of purification of this compound was improved by chromatographing it on alumina prior to recrystallising it from acetic acid. In this way, 4-styrylazobenzene was obtained as red-brown plates m.p. 196-197° (lit. 191°).

1-Phenylazoazulene.

This was prepared from azulene and phenyldiazonium chloride.[127] The product was purified by chromatography and the 1-phenylazoazulene so obtained had m.p. 120-121° (lit. 120-121°).

1-Phenylazonaphthalene.

This was prepared by condensing 1-naphthylamine with nitrobenzene in the presence of powdered sodium hydroxide.[128] However, the dark red oil, obtained by ether extraction and evaporation, was not distilled but was purified by chromatography in light petroleum on alumina. Recrystallisation of the product from ethanol gave 1-phenylazonaphthalene as red prisms m.p. 68-69° (lit. 69°).

Other azonaphthalenes.

1,1'-, 1,2'-, and 2,2'- Azonaphthalenes were available from earlier work[64] as also was 2-phenylazonaphthalene.

6.4 Other Preparations.

Nitrosobenzene.

This was prepared by reducing nitrobenzene with zinc and ammonium chloride, and then oxidising the β-phenylhydroxylamine so produced with acid dichromate.[129] Although nitrosobenzene may be kept for only one or two days at room temperature, it was found possible to store it, without decomposition, for at least a year in the freezing compartment of a refrigerator.

2-Aminobenzo[c]cinnoline.

This was prepared by the photochemical cyclodehydrogenation of 4-benzalaminoazobenzene.[40] However, the working-up procedure was modified slightly. When the cyclisation was complete, as judged by the ultraviolet absorption spectrum, the acidic solution was poured into about an equal volume of water, with cooling, and the benzaldehyde so liberated was extracted with ether. The acidic solution was made slightly alkaline with sodium hydroxide solution (cooling), and the floculent yellow precipitate of 2-aminobenzo[c]cinnoline which resulted was filtered off and washed with water. Recrystallisation from aqueous ethanol yielded 2-aminobenzo[c]cinnoline as yellow needles m.p. 246-247° (lit. 247°).

2-Acetamidobenzo[c]cinnoline.

2-Aminobenzo[c]cinnoline was acetylated by refluxing with acetic acid and acetic anhydride. 2-Acetamidobenzo[c]cinnoline crystallised from ethanol as pale yellow needles, m.p. 239-240° (lit.[40] 240°).

Attempted Syntheses of 2-(4'-Nitrophenyl)aminobenzo[c]cinnoline.

(i) Sealed Tube Reaction.

2-Aminobenzo[c]cinnoline (200 mg), p-fluoronitrobenzene (175 mg), magnesium carbonate (100 mg) and water (1 ml) were heated together in a Carius tube at 200° for 10 hr. The reaction mixture was steam-distilled to remove the p-fluoronitrobenzene and the yellow solid remaining proved to be unchanged 2-aminobenzo[c]cinnoline.

The reaction was repeated in a steel bomb at 230° and a black solid was obtained which was insoluble in all common organic solvents.

(ii) Using Excess Amine.

2-Aminobenzo[c]cinnoline (200 mg) and p-fluoronitrobenzene (60 mg) were heated together in nitrobenzene (5 ml) at 205° for 15 hr. The reaction mixture was steam-distilled and the residual black solid was dissolved in tetrahydrofuran and adsorbed on a column of alumina. Elution with benzene caused the separation of a pink band. This was eluted with benzene/ether (1:1) and on evaporation of the solvent yielded a pink substance (c. 2 mg). Its ultraviolet absorption spectrum was not that of a benzo[c]cinnoline and it was discarded. Elution with ether and evaporation of the solvent yielded only unchanged 2-aminobenzo[c]cinnoline.

This experiment was repeated in dimethyl sulphoxide, ethylene glycol and in dimethylformamide; but in all cases only unchanged starting material was recovered.

(iii) In the Presence of Potassium Carbonate.

2-Aminobenzo[c]cinnoline (200 mg), p-fluoronitrobenzene (2 ml), potassium carbonate (150 mg), and a little cuprous iodide were refluxed together for 16 hr. The resulting red-brown solution was steam-distilled, to remove excess p-fluoronitrobenzene, and the residual black solid was dissolved in tetrahydrofuran and adsorbed on a column of alumina.

Elution with ether/benzene (1:4) gave a pink and a yellow fraction. Evaporation of the solvent left very little material and it was discarded.

Elution with ether/benzene (1:2) and evaporation of the solvent yielded a yellow solid (280 mg). Recrystallisation from benzene/light petroleum gave 2-[di(4'-nitrophenyl)amino]benzo[c]cinnoline as yellow needles which changed their crystalline form at 146-148° and showed m.p. 220-221° -

(Found: C, 65.9; H, 3.7; N, 15.7; O, 15.0. $C_{24}H_{15}N_5O_4$ requires C, 65.9; H, 3.5; N, 16.0; O, 14.6%).

The infrared spectrum (Nujol and $CHCl_3$) showed no peaks attributable to N-H stretching in the 3500-3000 cm^{-1} region. The ultraviolet absorption spectrum ($6\underline{N}$ H_2SO_4) showed peaks at 255 and 340 mμ, typical of a benzo[c]cinnoline derivative in this solvent.

This experiment was repeated using p-bromonitrobenzene in place of p-fluoronitrobenzene. Only the same tertiary amine could be isolated.

2-Aminobenzo[c]cinnoline (200 mg), p-fluoronitrobenzene (140 mg), and potassium carbonate (150 mg) were heated for 16 hr in nitrobenzene (2 ml) at 190-200°. The reaction mixture was worked up as before. The major product was 2-[di(4'-nitrophenyl)amino]benzo[c]-cinnoline and the only other material isolated was a small amount of unreacted 2-aminobenzo[c]cinnoline.

A similar experiment was carried out using diethyl ketone (b.p. 103°) as solvent. The solid remaining after steam-distillation was examined by thin-layer chromatography. Only one spot, of R_F identical to 2-aminobenzo[c]cinnoline, was observed.

Finally, the same experiment was repeated using dimethyl-formamide (b.p. 153°) as solvent. The solid remaining after steam-distillation was again examined by thin-layer chromatography. Only two spots were obtained, one of identical R_F with that of 2-amino-benzo[c]cinnoline and the other of R_F identical with that of 2-[di-(4'-nitrophenyl)amino]benzo[c]cinnoline.

(iv) From 2-Acetamidobenzo[c]cinnoline.

2-Acetamidobenzo[c]cinnoline (200 mg), p-fluoronitrobenzene (3 ml), potassium carbonate (160 mg), and a little copper bronze were refluxed together overnight. The reaction mixture was worked up in the usual way by steam-distillation and the residual solid was dissolved in tetrahydrofuran and filtered free from the copper bronze. The resulting solution was examined by thin-layer chromatography but only two spots were observed; one of R_F identical with that of 2-acetamido-benzo[c]cinnoline, and the other of R_F identical with that of 2-[di-

(4'-nitrophenyl)amino]benzo[c]cinnoline.

4-Phenylazodiphenylamine.

A commercially available sample of this compound was recrystallised several times from light petroleum. It had m.p. 82° (lit.[130] 82°).

N-Acetyl-4-phenylazodiphenylamine.

To a solution of 4-phenylazodiphenylamine (2 g) in acetic anhydride (5 ml), was added one drop of perchloric acid. The solution, which became very dark, was heated to 100-105° for 15 min in an oil-bath. The solution was then allowed to cool to c. 50° and water was cautiously added to destroy the excess acetic anhydride. The yellow-brown solid which crystallised was collected, washed well with water, and recrystallised from light petroleum. N-Acetyl-4-phenylazodiphenylamine (2.02 g, 88%) was obtained as bright red prisms, m.p. 112-113° -

(Found: C, 76.35; H, 5.5; N, 13.3. $C_{20}H_{17}N_3O$ requires C, 76.2; H, 5.4; N, 13.3%).

N-Benzoyl-4-phenylazodiphenylamine.

4-Phenylazodiphenylamine (1 g) and benzoyl chloride (0.6 ml) were refluxed in benzene (15 ml) overnight. The benzene was evaporated to leave a brown oil which was then dissolved in ether. The ethereal solution was washed with sodium hydroxide, and then water, and dried. Evaporation of the solvent left a viscous red syrup which could not be induced to crystallise. The infrared spectrum ($CHCl_3$) showed strong

absorption at 1650 cm^{-1} (carbonyl), and only very weak absorption at 3450 cm^{-1} (NH).

2-Chlorobenzo[c]cinnoline.

This was available from previous work[38] when it had been prepared by the photochemical cyclodehydrogenation of 4-chloroazobenzene. It crystallised from toluene as yellow needles m.p. 215-216° (lit.[38] 215.5 - 216°).

2-Phenylaminobenzo[c]cinnoline.

Sodium (100 mg) was added in small pieces to freshly distilled aniline (5 ml), and the mixture was gently warmed until all the sodium had dissolved. 2-Chlorobenzo[c]cinnoline (200 mg) was added to this black solution, and the whole was refluxed for 1 hr. The reaction mixture was then subjected to steam-distillation until no more volatile material passed over. A dark yellow residue remained, and this was extracted with ether. After the ethereal extract had been washed and dried, the solvent was removed; and the residual solid was redissolved in benzene and chromatographed on a column of alumina.

Several minor coloured fractions were first eluted from the column with ether/benzene mixtures, the ether content being progressively raised. These fractions yielded insignificant amounts of material which were not examined further.

Elution with pure ether caused the main (yellow) band to be removed. After evaporation of the solvent, a yellow solid (260 mg) remained, and this was recrystallised from benzene/light petroleum.

2-Phenylaminobenzo[c]cinnoline was thereby obtained as yellow needles, m.p. 227-228° -

(Found: C, 79.4; H, 4.8; N, 15.2. $C_{18}H_{13}N_3$ requires C, 79.7; H, 4.8; N, 15.5%).

4-Acetylstilbene.

This was prepared by a Meerwein reaction between diazotised 4-aminoacetophenone and cinnamic acid.[131] 4-Acetylstilbene was obtained as colourless plates from benzene/light petroleum, m.p. 141-142° (lit. 141-142°).

Anil of 4-acetylstilbene.

This was prepared according to Reddelein's method for the preparation of acetophenone anil.[91] 4-Acetylstilbene and aniline were heated together to 190° in the presence of zinc chloride. The resultant anil recrystallised from light petroleum as flat yellow needles, m.p. 173-174° -

(Found: C, 88.1; H, 6.3; N, 4.8. $C_{22}H_{19}N$ requires C, 88.85; H, 6.4; N, 4.7%).

4-Aminostilbene.

This was available as an intermediate in the preparation of 4-styrylazobenzene(vide supra). 4-Aminostilbene crystallised from ethanol as colourless needles m.p. 151-152° (lit.[125] 151°).

4-Benzalaminostilbene.

This was prepared by condensing 4-aminostilbene with freshly distilled benzaldehyde.[132] The 4-benzalaminostilbene crystallised as yellow needles from benzene, m.p. 193-194° (lit. 193-194°).

6.5 Irradiations in 22N Sulphuric Acid.

1-Phenylazonaphthalene.

A solution of 1-phenylazonaphthalene (2 g) in 22N sulphuric acid (110 ml) was irradiated with the mercury-quartz lamp, at room temperature, until the ultraviolet absorption spectrum showed the reaction to be complete (8 days). The acidity was then adjusted to c. 2N with sodium hydroxide, and the mixture was extracted with ether. The ethereal extract was washed, dried and evaporated to give a yellow-brown solid (0.85 g, 42%). Recrystallisation from ethanol (charcoal) gave naphtho[1,2-c]cinnoline as yellow needles, m.p. 195-196° (lit.[66] 190°).

(Found: C, 83.35; H, 4.3; N, 11.95. $C_{16}H_{10}N_2$ requires C, 83.45; H, 4.4; N, 12.2%.)

The acidic layer was made weakly alkaline with sodium hydroxide, and then extracted with ether. Evaporation of the washed and dried ethereal extract gave a grey-black solid (0.9 g), which could not be separated into its components. The infrared spectrum (Nujol) showed a peak at 3300 cm^{-1} (NH); and a diazotised solution of the compound gave a red dye when coupled with 2-naphthol. Thin-layer chromatography

showed four fluorescent spots. The faint yellow spot of largest R_F was identified as (unextracted) naphtho[1,2-*c*]cinnoline. The remaining three blue fluorescent spots were compared with the three obtained following thin-layer chromatography of the acid catalysed rearrangement products from *N*-1-naphthyl-*N'*-phenylhydrazine. Only one spot in both chromatograms showed identical R_F values.

Azonaphthalenes.

In preliminary experiments, 10^{-5} *M* solutions of 1,1'-azonaphthalene, 1,2'-azonaphthalene and of 2,2'-azonaphthalene in 10% ethanol in 22*N* sulphuric acid were exposed to sunlight. These solutions were very slowly decolourised, but examination of the ultraviolet absorption spectra showed no peaks attributable to cyclised products. A solution of 1,1'-azonaphthalene (0.5 g) in 10% ethanol/sulphuric acid was irradiated with a mercury-quartz lamp for 7 weeks. At the end of this time, the spectrum still showed the presence of unchanged azonaphthalene, and no peaks attributable to cyclised products were observed. Finally, dilute solutions of the azonaphthalenes were irradiated for prolonged periods at temperatures below -30°, but no cyclised products could be detected.

2-Phenylazonaphthalene.

Similar experiments with 2-phenylazonaphthalene provided no evidence for the formation of cyclised product.

3-Phenylazobenzene.

3-Phenylazobenzene (1 g) was mixed with 22N sulphuric acid, containing 10% (v:v) ethanol (110 ml in all), and irradiated with a mercury-quartz lamp for 23 days. The solubility of 3-phenylazobenzene was unusually low, despite the presence of ethanol in the solvent, and some undissolved material still remained when the irradiation was terminated. The reaction mixture was diluted by pouring it slowly into a beaker containing ice cold water (c. 150 ml). This beaker was kept in an ice-bath and, during the dilution, stirring was continued. The diluted solution was then made slightly basic by the addition of a cold aqueous solution of sodium hydroxide. During the dilution and basification, the temperature was maintained at less than 35°. The precipitated material was extracted with ether, and the washed and dried ethereal solution was evaporated to dryness. The residual solid was then redissolved in benzene and chromatographed on alumina. Two main bands appeared, and these were separated as follows.

The first (red) band was readily eluted with benzene. Evaporation of the eluate yielded a red solid (0.5 g) which, after recrystallisation from light petroleum, proved to be unchanged 3-phenylazobenzene, m.p. and mixed m.p. 51-52°.

Continued elution with benzene resulted in the gradual removal of the second (yellow) band, which was much broader than the first band. In this case, the eluate was collected in a succession of small fractions, and these were separately evaporated to dryness.

The first fractions of the solid material (60 mg) were com-

bined and recrystallised from light petroleum. 1-Phenylbenzo[c]-cinnoline was thereby obtained as yellow plates, m.p. 165-166° - (Found: C, 84.5; H, 4.6; N, 10.95. $C_{18}H_{12}N_2$ requires C, 84.35; H, 4.7; N, 10.9%).

The next fractions of the solid material (60 mg) were likewise combined and recrystallised from light petroleum. Yellow plates were again obtained but these had m.p. 140-155° and therefore appeared to consist of a mixture of the compounds from the preceding, and following, fractions.

The remaining solid material (150 mg) from the later fractions was recrystallised from light petroleum. 3-Phenylbenzo[c]cinnoline was thereby obtained as yellow plates, m.p. 153-154° - (Found: C, 84.8; H, 4.7; N, 10.85. $C_{18}H_{12}N_2$ requires C, 84.35; H, 4.7; N, 10.9%).

The intermediate material (m.p. 140-155°) showed two bands in its ultraviolet absorption spectrum at 253 and 275 mμ respectively. This confirmed (c.f. Fig. 8) that the material was a mixture of 1- and 3- phenylbenzo[c]cinnolines, in roughly equivalent proportions. The total yield of 3-phenylbenzo[c]cinnoline from 3-phenylazobenzene was therefore approximately twice that of 1-phenylbenzo[c]cinnoline.

4-Phenylazobenzene.

A solution of 4-phenylazobenzene (1 g) in a 10% solution of ethanol in 2N sulphuric acid (100 ml) was irradiated with a mercury-

quartz lamp until the ultraviolet absorption spectrum showed the reaction to be virtually complete (18 days). The acidity of the mixture was then adjusted to c. 2N with sodium hydroxide and the reaction mixture was extracted with ether. The ethereal extract was washed, dried, and evaporated to give a brown solid (0.6 g). Chromatography on alumina, using benzene for elution, gave starting material (0.11 g), and a yellow solid (0.43 g, 43%). Recrystallisation from ethanol gave 2-phenylbenzo[c]cinnoline as yellow needles, m.p. 161-162° -

(Found: C, 84.3; H, 4.8; N, 10.5. $C_{18}H_{12}N_2$ requires C, 84.3; H, 4.7; N, 10.9%).

The aqueous acidic layer was made weakly alkaline with sodium hydroxide and extracted with ether. Evaporation of the dried ethereal extract gave a black tar (0.35 g). The infrared spectrum ($CHCl_3$) indicated the presence of NH, but this product was not investigated further.

4-Phenylazoazobenzene.

Preliminary experiments, using small concentrations of 4-phenylazoazobenzene in 22N sulphuric acid, showed that rapid decolourisation occurred (faster with a tungsten lamp than a mercury-quartz lamp), but that no absorption bands near 252 and 370 mμ (characteristic of benzo[c]cinnolines in acid solution) appeared in the spectrum. In other experiments on a preparative scale (2 g 4-phenylazoazobenzene in 300 ml sulphuric acid under tungsten lamp irradiation), the colour of the solution changed from red to green and a considerable quantity of

tar was formed. The solution was made weakly alkaline with sodium hydroxide, then extracted with ether and benzene. These extracts were washed, dried, and evaporated, and the combined residues were dissolved in benzene and passed through a column of alumina.

Evaporation of the first fractions gave 4-aminoazobenzene. This crystallised from light petroleum in orange needles m.p. 125-126°, not depressed by admixture with an authentic specimen. The infrared and ultraviolet absorption spectra were also identical with those of an authentic specimen.

Evaporation of the second fraction and recrystallisation of the residue from benzene/hexane gave 4-amino-3-(4'-aminophenyl)azobenzene as red prisms, m.p. 155-156° -

(Found: C, 75.1; H, 5.5; N, 19.4. $C_{18}H_{16}N_4$ requires C, 75.0; H, 5.6; N, 19.4%). The ultraviolet absorption spectrum (in 2N sulphuric acid) was very similar to that of 4-aminoazobenzene in the same solvent (c.f. Fig. 3). The infrared spectrum (Nujol) showed peaks at 3200, 3300, and 3500 cm^{-1} (NH), and a diazotised solution gave a red dye when added to 2-naphthol. A salicylidene derivative was prepared by heating together 4-amino-3-(4'-aminophenyl)azobenzene, freshly distilled salicylaldehyde and a trace of p-toluenesulphonic acid, in refluxing ethanol. The bis-salicylidene anil so obtained recrystallised from light petroleum in orange needles, m.p. 218-219° -

(Found: C, 77.2; H, 5.1; N, 11.1. $C_{32}H_{24}N_4O_2$ requires C, 77.4; H, 4.9; N, 11.3%).

In another experiment, it was found that 4-phenylazoazobenzene is decomposed by 22N sulphuric acid, at room temperature, even in the dark. The same decomposition products were observed. Finally, a solution of 4-phenylazoazobenzene and ferric chloride in acetic acid was irradiated; but no absorption peaks attributable to a benzo[c]cinnoline derivative were produced.

4,4'-Bis(phenylazo)biphenyl.

A solution of 4,4'-bis(phenylazo)biphenyl (3 g) in 22N sulphuric acid (300 ml) was irradiated with a tungsten lamp until the ultraviolet absorption spectrum showed that the reaction was virtually complete (3 weeks). Some tar formation was evident. The solution was neutralised with sodium hydroxide (cooling), and then exhaustively extracted with ether and benzene. Evaporation of the solvent gave a red-brown solid (2 g) which was chromatographed on alumina. Four fractions were collected as follows:

Fraction 1, eluant hexane/benzene (1:1);

fraction 2, eluant benzene;

fraction 3, eluant ether/benzene (1:3);

fraction 4, eluant ether/benzene (1:3).

Material was also strongly adsorbed at the top of the column; but elution with ether/methanol gave only an intractable tar.

Fraction 1. - Evaporation gave a red solid (0.22 g). Recrystallisation from benzene gave 4,4'-bis(phenylazo)biphenyl as yellow-red plates, m.p. and mixed m.p. 231-232°.

Fraction 2. - Evaporation gave a red solid (0.3 g), m.p. 60-85°. Thin-layer chromatography showed two spots, and this fraction was therefore rechromatographed on silica gel. Elution with benzene and evaporation of the solvent gave a red solid. Recrystallisation from light petroleum yielded 4-(4'-aminophenyl)azobenzene as red plates, m.p. 151-152°, not depressed by admixture with an authentic sample. Benzylidene and anisylidene anils were also prepared and found to be identical (mixed m.p.) with authentic specimens.

Elution with ether/benzene (1:5) and evaporation of the solvent gave a red solid. Recrystallisation from light petroleum yielded 4-[4'-amino-3'-(4''-aminophenyl)phenyl]azobenzene as red plates, m.p. 55-57°. Reaction with salicylaldehyde gave the bis-salicylidene derivative, which crystallised from light petroleum as orange needles, m.p. 200-201° -

(Found: C, 79.7; H, 5.0; N, 9.7. $C_{38}H_{28}N_4O_2$ requires C, 79.7; H, 4.9; N, 9.8%).

Fraction 3. - Evaporation gave a red solid (0.62 g). Recrystallisation from ethanol gave 2-(4'-aminophenyl)benzo[c]cinnoline as red needles, m.p. 209-210° -

(Found: C, 79.6; H, 4.9; N, 15.7; mol. wt. (Rast), 275. $C_{18}H_{13}N_3$ requires C, 79.5; H, 5.0; N, 15.5%) mol. wt., 271). The ultraviolet absorption spectrum (in 22N sulphuric acid) showed maxima at 255 and 395 mμ (c.f. Fig. 4). The infrared spectrum (Nujol) showed peaks at 3200 and 3300 cm^{-1} (NH). The method of deamination of this compound

was based on the procedure outlined by Nietzki and Zehntner[133] for the deamination of 1-phenylazo-4-aminonaphthalene.

A suspension of this product (150 mg) in ethanol (10 ml) and concentrated sulphuric acid (0.5 ml) was cooled in ice and diazotised with a cold, saturated, aqueous solution of sodium nitrite. The resulting solution was allowed to stand in ice-water for 30 min, heated on the water-bath for 15 min, and then poured into cold water. Ether extraction and evaporation of the ether gave a solid (130 mg), which was chromatographed in benzene on alumina. The first pink band yielded only a very small amount of material and this was discarded. The second, yellow fluorescent fraction was evaporated to give a yellow solid (50 mg, 35%). Recrystallisation from ethanol gave 2-phenylbenzo[c]cinnoline as yellow needles, m.p. 161-162°, not depressed by admixture with a specimen prepared by the photochemical cyclodehydrogenation of 4-phenylazobenzene (vide supra). The infrared and ultraviolet absorption spectra and the R_F value (thin-layer chromatography) were identical with those of the authentic specimen.

Fraction 4. - Evaporation gave a yellow-brown solid (0.61 g). Recrystallisation from benzene gave 2-[4'-amino-3'-(4''-aminophenyl)-phenyl]benzo[c]cinnoline as light brown needles which softened at c. 170° and finally melted at 230-231° -

(Found: C, 81.8; H, 5.6; N, 13.05. $C_{24}H_{18}N_4,C_6H_6$ requires C, 81.8; H, 5.5; N, 12.7%). The infrared spectrum (Nujol) showed a broad band at 3300 cm^{-1} (NH). The ultraviolet absorption spectrum (in 22N

sulphuric acid) was similar to that of 2-(4'-aminophenyl)benzo[c]-cinnoline (c.f. Fig. 4). Reaction with salicylaldehyde gave the bis-salicylidene anil as yellow needles, m.p. 242-243°, from ethanol/chloroform -

(Found: C, 79.7; H, 4.7; N, 9.6; O, 6.4. $C_{38}H_{26}N_4O_2$ requires C, 80.0; H, 4.6; N, 9.8; O, 5.6%).

4-Styrylazobenzene.

In preliminary experiments, 10^{-5} M solutions of 4-styryl-azobenzene in 22N sulphuric acid were found to be slowly decolourised by sunlight and tungsten lamp irradiation; and somewhat more rapidly using the mercury-quartz lamp. However, the ultraviolet absorption spectrum of the irradiated solution showed only a small peak at 255 mμ.

In another experiment, a solution of 4-styrylazobenzene (100 mg) in 10% ethanol in 22N sulphuric acid (100 ml) was irradiated with the mercury-quartz lamp for 3 weeks. The resulting brown solution was neutralised with sodium hydroxide solution and extracted with ether. Evaporation of the dried ethereal extract gave an orange solid (50 mg) which was chromatographed on alumina. Elution with benzene gave 4-styrylazobenzene (10 mg) which crystallised from acetic acid as red-brown plates m.p. and mixed m.p. 196-197°. Elution of the next yellow fluorescent band with ether/benzene (1:5) gave a yellow oil (7 mg). The ultraviolet absorption spectrum (in 22N sulphuric acid) showed a strong absorption band at 255 mμ and one of lower intensity at 370 mμ. The oil could not be induced to crystallise. Elution of the remaining

strongly adsorbed material, with ether, gave an intractable tar.

1-Phenylazoazulene.

Approximately 10^{-5} M solutions of 1-phenylazoazulene in 22N sulphuric acid were irradiated with sunlight and with a mercury-quartz lamp. In neither case was there any change in the ultraviolet absorption spectrum after 8 hours irradiation.

6.6 Irradiations in 98% Analar Sulphuric Acid.

4-Phenylazobenzene.

A solution of 4-phenylazoazobenzene (2 g) in 98% Analar sulphuric acid (110 ml) was irradiated with a mercury-quartz lamp until its ultraviolet absorption spectrum showed that the reaction was virtually complete (7 days). The solution was then diluted by pouring into ice-cold water (c. 300 ml), and made slightly alkaline with sodium hydroxide solution. As was the case with irradiations carried out in 22N acid, during dilution and basification, the temperature was maintained below 35°. The resulting suspension was exhaustively extracted with benzene. Some black solid material remained unextracted and this was filtered off, washed, dried, powdered and extracted with boiling benzene. A small amount (110 mg) of black insoluble solid still remained, and this was discarded.

The benzene extracts were combined washed, dried, and evaporated to dryness. The residual brown solid (1.8 g) was then redissolved in tetrahydrofuran and adsorbed on a column of alumina.

Six fractions were collected and treated as follows:-

Fraction 1. - Elution with benzene and evaporation of the solvent gave a red solid (120 mg). Recrystallisation from ethanol yielded unchanged 4-phenylazoazobenzene as red-brown plates, m.p. and mixed m.p. 167-168°.

Fraction 2. - Elution with ether/benzene (1:5) followed by evaporation of the solvent gave an orange solid (100 mg), which was shown to be 4-aminoazobenzene. The compound was recrystallised from light petroleum, and found to have m.p. and mixed m.p. 125-126°.

Fraction 3. - Continued elution with the same solvent mixture, followed by evaporation, gave 4-amino-3-(4'-aminophenyl)azobenzene (50 mg). This was recrystallised from light petroleum and identified by direct comparison with an authentic sample, m.p. and mixed m.p., 155-156°.

Fraction 4. - Elution with ether/benzene (1:1) gave a yellow solution which displayed a yellow fluorescence. A yellow solid (660 mg) was obtained after removal of the solvent. This was shown to be 2-amino-1-(4'-aminophenyl)benzo[c]cinnoline. When recrystallised from aqueous ethanol, it formed yellow needles, m.p. 255-256° -

(Found: C, 75.3; H, 5.1; N, 19.4. $C_{18}H_{14}N_4$ requires C, 75.5; H, 4.9; N, 19.6%). The ultraviolet absorption spectrum, typical of a benzo[c]-cinnoline, is shown in Fig. 5. The infrared spectrum (Nujol) showed strong absorption at 3310 cm^{-1} and weaker absorption at 3190 and 3470 cm^{-1} (NH). The bis-salicylidene derivative was formed by interaction with

salicyaldehyde in ethanol. It was obtained pure, as golden-yellow needles, on recrystallisation from ethanol/chloroform, m.p. 242-243° - (Found: C, 77.55; H, 4.5; N, 11.4. $C_{32}H_{22}N_4O_2$ requires C, 77.7; H, 4.5; N, 11.3%).

2-Amino-1-(4'-aminophenyl)benzo[c]cinnoline (100 mg) and concentrated hydrochloric acid (0.5 ml) were mixed, and slowly heated in an oil-bath to 220°. The mixture was allowed to cool, and then was dissolved in water. The resulting red solution was made alkaline with aqueous sodium hydroxide, and the yellow solid which precipitated (90 mg) was collected. This was shown (m.p., mixed m.p., thin-layer chromatography and infrared spectrum) to be unchanged starting material. No carbazole derivative could be detected.

2-Amino-1-(4'-aminophenyl)benzo[c]cinnoline (100 mg) was refluxed in 5N sulphuric acid (5 ml) for 50 hrs. The resulting red solution was worked up as before. Again, only unchanged starting material was recovered and there was no trace of a carbazole derivative.

2-Amino-1-(4'-aminophenyl)benzo[c]cinnoline (220 mg) was dissolved in a mixture of ethanol (15 ml) and concentrated sulphuric acid (0.75 ml). The red solution was cooled in ice and diazotised with a cold, saturated aqueous solution of sodium nitrite. After the diazotised solution had stood in an ice-bath (30 min), it was warmed on a water-bath (15 min). The reaction mixture, which was then brown, was diluted with water, and the precipitated product was extracted with ether. When the ethereal solution had been washed well with

water, and dried, it was evaporated to dryness. The residual oil (175 mg) was redissolved in benzene and chromatographed on a column of alumina.

The main (yellow) band was the first to be eluted (benzene), and after evaporation of the solvent, a yellow solid (90 mg) remained. This was recrystallised from light petroleum (b.p. 40-60°). 1-Phenylbenzo[c]cinnoline was thereby obtained as yellow plates, m.p. 165-166°. It was shown to be identical (mixed m.p., infrared spectrum and thin-layer chromatography) with the compound formed in the photochemical cyclodehydrogenation of 3-phenylazobenzene.

Fraction 5. - Continued elution with ether/benzene (1:1) and evaporation of the solvent gave a mixture of 2-amino-1-(4'-aminophenyl)benzo[c]cinnoline and the immediately following red compound.

Fraction 6. - Elution with pure ether and evaporation left a red solid (400 mg). This compound was shown to be 2-(4'-aminophenyl)aminobenzo[c]cinnoline. On recrystallisation from aqueous ethanol, it formed red needles which darkened at c. 245° and had m.p. 257 (decomp.) -

(Found: C, 75.5; H, 5.0; N, 19.3. $C_{18}H_{14}N_4$ requires C, 75.5; H, 4.9; N, 19.6%). The ultraviolet absorption spectrum, typical of a benzo-[c]cinnoline, is shown in Fig. 6. The infrared spectrum (Nujol) showed bands at 3220, 3320, 3380, and 3430 cm^{-1}. The nuclear magnetic resonance spectrum (dimethylsulphoxide) showed several complex multiplets, between τc. 1.41 and τc. 2.63, which integrated for seven protons and which were assigned to the benzo[c]cinnoline protons. A

well defined quartet centred at τ c. 3.02, which integrated for four protons, was assigned to the A_2B_2 system of the p-disubstituted phenyl ring. Reaction with salicylaldehyde gave a black solid, m.p. 260-265 (decomp.), which could not be purified.

A solution of 2-(4'-aminophenyl)aminobenzo[c]cinnoline (60 mg) in ethanol (5 ml) was acidified with concentrated sulphuric acid (0.2 ml), cooled in ice, and diazotised with a cold, saturated aqueous solution of sodium nitrite. The reaction mixture was allowed to stand in an ice-bath (30 min), after which it was warmed on a water-bath (15 min), and subsequently diluted with a large volume of water. The material which separated was extracted with ether, and the ethereal solution was washed, dried, and evaporated to dryness. A brown solid remained which was chromatographed on alumina. Elution with ether/benzene (1:3) and evaporation of the solvent yielded an orange-yellow solid (25 mg). This, on being recrystallised from benzene/light petroleum, gave 2-phenylaminobenzo[c]cinnoline as small yellow needles, m.p. 227-228°. The product was identical (mixed m.p., infrared spectrum, and thin-layer chromatography) with that obtained from the reaction of 2-chlorobenzo[c]cinnoline and sodium anilide.

4,4'-Bis(phenylazo)biphenyl.

(i) On a preparative scale. - 4,4'-Bis(phenylazo)biphenyl (3 g) in 98% Analar sulphuric acid (100 ml) was irradiated with a mercury-quartz lamp for 10 days. There was no detectable change in the ultraviolet absorption spectrum at the end of this time.

The reactor was then immersed in a beaker of running water

and irradiated with five 100W tungsten lamps. The entire apparatus was surrounded with aluminium foil to increase the irradiation by reflection. No change was observed in the ultraviolet absorption spectrum after one weeks such irradiation.

(ii) On a micro scale. - A solution of 4,4'-bis(phenylazo)biphenyl (50 mg) in 98% sulphuric acid (130 ml) was irradiated with a mercury-quartz lamp until the ultraviolet absorption spectrum indicated that the reaction was almost complete (4 days). The solution was diluted and basified in the usual way, and then extracted with ether. The ethereal extract was washed, dried, and reduced to a small volume by evaporation. A sample of this solution was subjected to thin-layer chromatography, the chromatogram being developed with ether/benzene (1:1).

A similar ethereal solution of the products obtained from the photochemical reaction of 4,4'-bis(phenylazo)biphenyl in 22N acid, was simultaneously chromatographed on the same plate.

Each chromatogram yielded five spots, the successive R_F values of the spots in the first chromatogram being identical with those in the second. (The two spots of lowest R_F were fluorescent; the other three were visible as coloured spots, more readily distinguishable after brief exposure to iodine vapours.) It was therefore clear that the same products had been formed in the photochemical reaction of 4,4'-bis(phenylazo)biphenyl in 98% sulphuric acid, as in 22N acid.

4,4'-Bis(phenylazo)biphenyl, and the four purified products obtained from its photochemical reaction in 22N sulphuric acid, were

then subjected individually to thin-layer chromatography under the same conditions as above. From the observed R_F values in this experiment it was established that the five spots in each of the foregoing test-chromatograms were due, in order of increasing R_F values, to the compounds 2-(4'-aminophenyl)benzo[c]cinnoline, 2-[4'-amino-3'-(4''-aminophenyl)phenyl]benzo[c]cinnoline, 4-[4'-amino-3'-(4''-aminophenyl)-phenyl]azobenzene, 4-(4'-aminophenyl)azobenzene, and (unchanged) 4,4'-bis(phenylazo)biphenyl.

2-Phenylazobenzo[c]cinnoline.

A solution of 2-phenylazobenzo[c]cinnoline (250 mg) in 98% Analar sulphuric acid (110 ml) was irradiated for 105 hr. After dilution and basification in the usual way, the reaction mixture was extracted with benzene and then with ether. The extracts were washed, dried, and evaporated to dryness; and the remaining brown solid was dissolved in benzene and chromatographed on a column of alumina. The first (yellow) fraction was eluted from the column with benzene. When the solvent was evaporated, a yellow solid (20 mg) remained and this was shown to be a benzodicinnoline, either benzo[1,2-c:4,5-c']dicinnoline or benzo[1,2-c;4,3-c']dicinnoline. Its ultraviolet spectrum (ethanol) more closely resembled that of dibenz[a,h]anthracene than that of dibenzo[c,g]phenanthrene (Fig. 7). It was therefore considered likely that the benzodicinnoline was benzo[1,2-c:4,5-c']dicinnoline. On recrystallisation from carbon tetrachloride, it formed yellow rods, m.p. 287-288° -

(Found: C, 76.4; H, 3.6; N, 19.3. $C_{18}H_{10}N_4$ requires C, 76.6; H, 3.6; N, 19.85%).

The second (yellow) fraction was eluted with ether/benzene (1:3). This yielded 2-amino-1-(4'-aminophenyl)benzo[c]cinnoline (110 mg), which was identified by direct comparison (m.p., mixed m.p., infrared spectrum, and thin-layer chromatography) with the sample prepared by irradiation of 4-phenylazoazobenzene.

The third (red) fraction was eluted with ether/benzene (1:3). A red solid (80 mg) remained after evaporation of the solvent, and this was shown to be 2-(4'-aminophenyl)aminobenzo[c]cinnoline by direct comparison (m.p., mixed m.p., infrared spectrum, and thin-layer chromatography) with the sample obtained from the photochemical reaction of 4-phenylazoazobenzene.

3-Phenylazobenzene.

A solution of 3-phenylazobenzene (0.5 g) in 98% sulphuric acid (100 ml) was irradiated with a mercury-quartz lamp until the ultraviolet spectrum indicated the cyclisation to be complete (60 hr). The solution was then diluted and basified in the usual way, and exhaustively extracted with benzene and then with ether. The extracts were washed and dried but on evaporation left no product.

The irradiation was therefore repeated and the working-up procedure slightly modified. The irradiated solution was poured into ice-water —— which was kept vigorously stirred with a mechanical stirrer —— at such a rate that the temperature remained below 20°.

The basification was carried out in a similar manner. However, on extraction with benzene and with ether, and evaporation of the solvents, no product was obtained. The reaction mixture was then continuously extracted with ether for several days but still no product could be isolated. The irradiation of 3-phenylazobenzene was successfully completed in 22N sulphuric acid (vide supra).

4-Phenylazodiphenylamine.

A 10^{-5} M solution of 4-phenylazodiphenylamine in 98% sulphuric acid was exposed to bright sunlight for 8 hours. At the end of this time, the solution still retained its original blue-purple colour, and no change was observed in the ultraviolet absorption spectrum.

Similar results were obtained when the irradiation was performed with a mercury-quartz lamp.

N-Acetyl-4-phenylazodiphenylamine.

(i) In dilute solution. - The yellow colour of a 10^{-5} M solution of N-acetyl-4-phenylazodiphenylamine in 98% sulphuric acid was discharged by five minutes exposure to bright sunlight. The ultraviolet absorption spectrum showed the disappearance of the original λ_{max} at 430 mμ and the appearance of a new peak at 257 mμ.

(ii) On a preparative scale. - (a) N-Acetyl-4-phenylazodiphenylamine (1 g) was dissolved in 98% sulphuric acid (100 ml) to give a dark yellow-green solution. This was irradiated overnight with a mercury-quartz lamp. By the end of this time, the solution had

adopted the colour of 4-phenylazodiphenylamine in acid; the ultraviolet absorption spectrum was also identical with that of the non-acetylated amine. Irradiation was continued for a further 48 hours but no change in the ultraviolet absorption spectrum occurred. In another experiment, 50 mg of the acetate were irradiated, but hydrolysis was still found to be faster than cyclisation.

(b) N-Acetyl-4-phenylazodiphenylamine (250 mg) in 98% sulphuric acid (100 ml) was irradiated in bright sunlight for 90 min. At the end of this time, the original yellow-green colour of the solution had been replaced by a purple one. The ultraviolet absorption spectrum confirmed that hydrolysis, but no cyclisation, had occurred.

N-Benzoyl-4-phenylazodiphenylamine.

(i) In dilute solution. - The yellow colour of a 10^{-5} M solution of N-benzoyl-4-phenylazodiphenylamine was discharged by one hours exposure to bright sunlight. The ultraviolet absorption spectrum showed the disappearance of the original λ_{max} at 430 mμ and the growth of a new peak at 257 mμ.

(ii) On a preparative scale. - Separate irradiations of N-benzoyl-4-phenylazodiphenylamine (200 mg) in 98% sulphuric acid (100 ml) with a mercury-quartz lamp, and with sunlight, again resulted in hydrolysis and not in cyclisation.

4-Styrylazobenzene.

The photochemical behaviour of 4-styrylazobenzene in 98%

sulphuric acid was similar to that in 22N sulphuric acid. Irradiation of dilute (c. 10^{-5} M) solutions caused changes in the ultraviolet absorption spectrum normally associated with cyclisation. However, when the reaction was repeated on a preparative scale (0.5 g), no products could be isolated.

1-Phenylazoazulene.

No change in the ultraviolet absorption spectrum was observed when c. 10^{-5} M solutions of 1-phenylazoazulene in 98% sulphuric acid were irradiated with either a mercury-quartz lamp, or with sunlight.

4-Aminostilbene.

Irradiation of c. 10^{-5} M solutions of 4-aminostilbene with either a mercury-quartz lamp, or with sunlight, for 8 hr produced no change in the ultraviolet absorption spectrum.

4-Benzalaminostilbene.

The photochemical behaviour of this Schiff base was similar to that of the parent amine. Irradiation of dilute solutions caused no change in the ultraviolet absorption spectrum.

4-Acetylstilbene.

(i) In dilute solution. - A 10^{-5} M solution of 4-acetylstilbene in 98% sulphuric acid is yellow-green in colour and exhibits a strong green fluorescence. Irradiation of such dilute solutions

with a mercury-quartz lamp caused the slow growth of a peak at 260 mμ.

(ii) On a preparative scale. - A solution of 4-acetylstilbene (0.5 g) in 98% sulphuric acid was irradiated for one week with a mercury-quartz lamp. The reaction mixture was worked up in the usual way by dilution and basification. However, extraction of the basic solution with ether, benzene, and chloroform yielded no product. A continuous ether extraction was therefore carried out for 10 days. The ethereal extract had a faint blue fluorescence but on evaporation yielded only an insignificant amount of material.

4-Acetylstilbene anil.

The photochemical behaviour of this anil was similar to that of the parent compound. The very slow growth of a peak at about 240 mμ was observed on irradiation of c. 10^{-5} M solutions. However, no products could be isolated, even after continuous ether extraction, when the irradiation was repeated on a 0.5 g scale.

4,4'-Bis(phenylazo)diphenylmethane.

A solution of 4,4'-bis(phenylazo)diphenylmethane (0.5 g) in 98% sulphuric acid (120 ml) was irradiated with a mercury-quartz lamp until the ultraviolet absorption spectrum indicated that the reaction was complete (7 days). The reaction mixture was diluted and basified in the usual way, and the yellow-grey precipitate (450 mg) which formed was collected. The filtrate was extracted with ether and with benzene but no additional material was obtained on evaporation

of the solvents. The solid was washed, dried, and exhaustively extracted with boiling benzene. Some black residue (50 mg) remained undissolved and, as it was insoluble in all common organic solvents, it was discarded. The red-brown benzene extracts were chromatographed on alumina.

Elution with ether/benzene (1:1) caused the separation of several coloured fractions, but these yielded insignificant amounts of material which was discarded.

Elution with ether, and evaporation of the solvent, yielded a yellow solid (320 mg) which could not be purified by recrystallisation, but which was precipitated from benzene with light petroleum. It did not melt sharply and was obviously impure. The ultraviolet absorption spectrum showed this compound to possess a benzo[c]cinnoline nucleus, and the infrared spectrum showed absorption at 3210, 3350, and 3420 cm^{-1} (NH). Thin-layer chromatography ,developed with ethanol/chloroform, (1:4) showed a major component of R_F 0.69 contaminated with a minor impurity of R_F 0.81. This compound was considered to be an impure sample of 2-[4'-amino-3'-(4"-aminophenyl)benzyl]benzo[c]-cinnoline.

The bis-salicylidene anil was prepared in the usual way, and was recrystallised from chloroform/ethanol to give small yellow needles, m.p. 208-209° -

(Found: C, 78.7; H, 4.8; N, 9.5; O, 5.8. $C_{39}H_{28}N_4O_2$ requires C, 80.1; H, 4.8; N, 9.6; O, 5.5%). This compound migrated as a single spot when examined by thin-layer chromatography and was obviously pure.

A sample of this anil was refluxed in dilute sulphuric acid for one hour. The solution was cooled, extracted with ether to remove the liberated salicylaldehyde, and then made slightly basic with sodium hydroxide. The yellow solid which precipitated was collected and dried. Recrystallisation from benzene gave 2-[4'-amino-3'-(4''-aminophenyl)-benzyl]benzo[c]cinnoline as fine yellow needles, m.p. 98-99°.

(Found: C, 81.5; H, 5.5; N, 12.3. $C_{25}H_{20}N_4,C_6H_6$ requires C, 81.9; H, 5.8; N, 12.3%.) Thin-layer chromatography confirmed that this was a pure compound. The nuclear magnetic resonance spectrum (deuterochloroform) showed a sharp singlet at τ5.84 (2 protons) assigned to the methylene group; and a broad peak at τ6.45 (4 protons) assigned to the two amino groups. The benzene of crystallisation appeared as a sharp singlet at τ2.65 (6 protons).

4,4'-Bis(phenylazo)bibenzyl.

A solution of 4,4'-bis(phenylazo)bibenzyl (1 g) in 98% sulphuric acid (130 ml) was irradiated with a mercury-quartz lamp until the ultraviolet absorption spectrum showed the reaction to be virtually complete (2 weeks). The solution was then diluted and made basic in the usual way, and the precipitated brown solid (400 mg) was collected, washed and dried. It was extracted several times with boiling benzene and the black insoluble solid which remained (30 mg) was discarded. The aqueous filtrate was extracted with benzene and with ether and the extracts were washed and dried. The combined extracts were evaporated

to leave a brown oil (550 mg) which was redissolved in tetrahydrofuran and adsorbed on a column of alumina.

Elution with benzene and evaporation of the solvent yielded unchanged 4,4'-bis(phenylazo)bibenzyl (35 mg). This, after recrystallisation from light petroleum had m.p. and mixed m.p. 187-188°.

Elution with ether/benzene (1 : 4) and evaporation of the solvent yielded 1-(2'-benzo[c]cinnolinyl)-2-[4"-amino-3"-(4'"-aminophenyl)phenyl]ethane as a brown oil (50 mg). Reaction with salicylaldehyde gave the bis-salicylidene anil as yellow needles, m.p. 193-194° from ethanol -

(Found: C, 80.1; H, 5.4; O, 4.9. $C_{40}H_{30}N_4O_2$ requires C, 80.2; H, 5.05; O, 5.35%).

A strongly adsorbed red band remained at the top of the column. This was eluted with methanol/ether (1:5); and evaporation of the solvent left a red-brown solid (250 mg). This could not be purified but its ultraviolet absorption spectrum showed the presence of a benzo[c]cinnoline nucleus and its infrared spectrum ($CHCl_3$) showed strong absorption at 3500 cm^{-1} and weaker absorption at 3300 cm^{-1} (NH). The compound would not form a salicylidene derivative. It was assumed to be the c-semidine 1-(2'-benzo[c]cinnolinyl)-2-(4"-amino-3"-phenylamino)phenylethane.

Azobenzene.

(i) On a preparative scale. - (a) Azobenzene (1 g) in 98% sulphuric acid (100 ml) was irradiated with a mercury-quartz lamp until

the ultraviolet absorption spectrum showed the reaction to be complete (112 hr). During the irradiation, sulphur dioxide was evolved (potassium chromate paper). The green reaction mixture was poured slowly, and with cooling, into cold water (c. 250 ml), but no precipitate of benzidine sulphate was observed. The solution was basified and extracted with ether in the usual way. Evaporation of the dried ethereal extract left a black solid (910 mg) which was redissolved in benzene and chromatographed on alumina.

Evaporation of the first (orange) fraction yielded a red solid (50 mg). Recrystallisation from aqueous ethanol gave azobenzene as red prisms, m.p. and mixed m.p. 68°.

Evaporation of the next yellow, fluorescent fraction left a yellow solid (600 mg, 63%). Recrystallisation from light petroleum yielded benzo[c]cinnoline (520 mg, 55.4%) as yellow needles, m.p. 155-156° (lit.[134] 156°).

The polarity of the eluant was gradually increased and elution with pure ether gave a reddish solution with a blue fluorescence. Evaporation of the solvent left a brown oil (175 mg), the infrared spectrum ($CHCl_3$) of which showed strong absorption at 3450 cm^{-1} with a shoulder at 3300 cm^{-1} (NH).

Elution with methanol yielded a dark solution with a blue fluorescence. Evaporation of the solvent left a black oil, the infrared spectrum ($CHCl_3$) of which showed absorption at 3300 cm^{-1} (NH).

(b) Azobenzene (1 g) in 98% sulphuric acid (100 ml) was irradiated as before. When the cyclisation was complete, the solution

was made slightly basic and the precipitated solids were removed by filtration. These residues were washed with water and the filtrate and washings were steam distilled. The distillate (500 ml) was saturated with salt and extracted with ether. The ethereal extract was dried and evaporated to leave a brown oil (30 mg). This was dissolved in dilute sulphuric acid, and to the solution was added bromine water. The brown solid (20 mg) which formed was removed by filtration. This was spotted on a thin-layer chromatography plate alongside an authentic sample of 2,4,6-tribromoaniline. The plate was developed with benzene. On exposure of the plate to iodine vapour, tribromoaniline appeared as a brown spot of R_F 0.67. A very faint spot of the same R_F appeared from the unknown compound. However, the majority of this material was divided between the starting line, and a very slow-moving (R_F = 0.03) blue fluorescent spot.

(ii) On a spectroscopic scale. - The amount of benzo[c]cinnoline produced by the irradiation of a 0.01 M solution of azobenzene in 98% sulphuric acid was estimated by comparing the 370 mμ peak height with that of a known concentration of benzo[c]cinnoline in 98% sulphuric acid. The yield of benzo[c]cinnoline calculated in this way was 59.4%.

Aniline.

Freshly distilled aniline (1 ml) was dissolved in 98% sulphuric acid (100 ml) and irradiated with a mercury-quartz lamp for 112 hours. During this irradiation, sulphur dioxide was evolved

(potassium chromate paper). The reaction mixture was worked up in the usual way of dilution, basification, and extraction with ether. The ethereal extract, which had a blue fluorescence, was washed, dried and evaporated to leave a brown oil. This was chromatographed on alumina.

Elution with benzene and evaporation of the solvent yielded unchanged aniline, identified as its acetyl derivative.

Elution with ether gave a reddish solution with a blue fluorescence. Evaporation of the solvent left a brown oil, the infrared spectrum ($CHCl_3$) of which showed absorption at 3450 cm^{-1} (NH). The spectrum closely resembled that of the similarly isolated oil following the irradiation of azobenzene.

Elution with methanol gave a dark solution with a blue fluorescence. Evaporation of the solvent left a black tar, the infrared spectrum ($CHCl_3$) of which exhibited absorption at 3500 cm^{-1} (NH). Again, this spectrum closely resembled that of the similarly isolated product following the irradiation of azobenzene.

6.7 Other Non-Photochemical Reactions.

Acid-catalysed rearrangement of 2-(2'-phenylhydrazino)benzo[c]cinnoline.

2-Phenylazobenzo[c]cinnoline (250 mg) was dissolved in boiling acetone (30 ml). The solution was cooled quickly in ice to ensure that only very small crystals of the compound were deposited. To this mixture, zinc dust and a concentrated aqueous solution of

ammonium chloride were added, in small portions, until the red colour had been discharged. The yellow reaction mixture was maintained at 0° in an ice-bath for 15 min, and then the zinc residues were removed by filtration. The residues were washed with acetone until no more yellow material could be extracted, and the combined filtrates were evaporated *in vacuo* to a small volume. Benzene was then used to extract the precipitated hydrazo compound. After the extract had been washed with dilute aqueous ammonia, it was dried and evaporated to a small volume. Addition of light petroleum to the benzene solution caused 2-(2'-phenylhydrazino)benzo[c]cinnoline to be precipitated as a yellow solid. This was further purified by dissolution in benzene and reprecipitation with light petroleum. The compound was obviously very susceptible to atmospheric oxidation, as an orange tinge soon appeared in the solid. The bulk of the material was therefore used as soon as possible for the acid catalysed rearrangement. An elementary analysis was not carried out, but spectral examinations were made with small samples. The infrared spectrum (Nujol) showed a peak at 3300 cm^{-1} (NH) and the ultraviolet absorption spectrum (ethanol) showed bands at 255 and 330 mμ (characteristic of benzo[c]cinnoline derivatives).

The 2-(2'-phenylhydrazino)benzo[c]cinnoline, so obtained, was dissolved in 98% sulphuric acid (10 ml), and the solution was allowed to stand at room temperature in a stoppered flask for 6 hr. The solution was then diluted (ice) and made slightly alkaline (NaOH), following which it was extracted with benzene. After the benzene

solution had been washed and dried, it was concentrated and passed through a column of alumina.

The first (orange) fraction was eluted from the column with benzene. The solvent was evaporated, and a red solid (20 mg) remained. This was shown to be 2-phenylazobenzo[c]cinnoline, by comparison (m.p. and mixed m.p., 218-219°) with the starting material.

Following this, two small red bands were eluted but these contained only 1-2 mg material each, which was not examined further.

The next (yellow) fraction was eluted with ether/benzene (1:1), and this yielded 2-amino-1-(4'-aminophenyl)benzo[c]cinnoline (20 mg) which was identified by direct comparison (m.p., mixed m.p., infrared spectrum, and thin-layer chromatography) with the sample obtained from the photochemical reaction of 4-phenylazoazobenzene.

The final (red) fraction was eluted with ether/benzene (1:1). After evaporation of the solvent, 2-(4'-aminophenyl)aminobenzo[c]-cinnoline (20 mg) remained. This was shown to be identical with the compound obtained from the irradiation of 4-phenylazoazobenzene by direct comparison (m.p., mixed m.p., infrared spectrum and thin-layer chromatography).

Rearrangement of hydrazobenzene in 98% sulphuric acid.

A sample of hydrazobenzene was prepared by the reduction of a solution of azobenzene in acetone with zinc dust and ammonium chloride. The colourless product was isolated and purified as described for 2-(2'-phenylhydrazino)benzo[c]cinnoline.

Hydrazobenzene (1 g) was dissolved in 98% sulphuric acid (100 ml) and the resulting green solution was allowed to stand at room temperature in a stoppered flask for 3 hr. The solution was then poured into ice-cold water (c. 300 ml) and the benzidine sulphate which precipitated was removed by filtration. The free base was liberated with aqueous sodium hydroxide and was recrystallised from aqueous ethanol. Benzidine was obtained as buff coloured plates, m.p. 125-126° (lit. 127°).

The filtrate, after removal of benzidine sulphate, was basified and extracted with ether. The ethereal extract was washed, dried, and evaporated to leave a brown oil (300 mg). This was chromatographed in benzene, on alumina, but no trace of azobenzene could be found.

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PHOTOCHEMICAL REACTIONS OF AZO COMPOUNDS

IV. FURTHER PHOTOCHEMICAL CYCLODEHYDROGENATIONS

By G. M. Badger, N. C. Jamieson, and G. E. Lewis

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