THE PHOTOCHEMICAL CYCLODEHYDROGENATION

OF

AZOBENZENES

by

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CONTENTS

SUMMARY

Azobenzene and a series of substituted derivatives have been photochemically cyclodehydrogenated in strong sulphuric acid to give benzo[c]cinnolines. The reaction involves a disproportionation as products from the acid-catalyzed rearrangement of the corresponding hydrazo compound were also obtained. Azobenzene and its 4-substituted and 4,4'-disubstituted derivatives gave benzo[c]cinnoline, 2-substituted benzo[c]cinnolines, and 2,9-disubstituted benzo[c]cinnolines respectively. 3-Substituted and 3,3'-disubstituted azobenzenes gave 1- and 3-substituted and 1,10-, 1,8-, and 3,8-disubstituted benzo[c]cinnolines respectively. Irradiation of azobenzene-3-carboxylic acid gave 1-hydroxybenzo[c]cinnoline-10-carboxylic acid lactone as well as benzo[c]cinnoline-3-carboxylic acid. Azobenzenes with an ortho substituent photocyclized with some elimination of the substituent. 2-Substituted azobenzenes gave 4-substituted benzo[c]cinnolines and some unsubstituted benzo[c]cinnoline, and 2,2'-disubstituted azobenzenes gave 4,7-disubstituted and 4-substituted benzo[c]cinnolines. 2,4,6-Trimethylazobenzene gave 2,4-dimethyl- and a little 1,2,4-trimethylbenzo[c]cinnoline; the formation of the latter compound presumably involved migration of a methyl group. Irradiation of many of the azo compounds gave combined yields

of benzo[c]cinnolines near 50%; attempts to increase the yield
were unsuccessful.

Unusual rearrangement products were obtained from the
irradiation of 4-methyl- and 2,4,6-trimethylazobenzene. These
were 4-(4'-aminophenyl)-4-methylcyclohexa-2,5-dienone and
4-(4'-aminophenyl)-2,4,6-trimethylcyclohexa-2,5-dienone
respectively, and were presumably formed by abnormal re-
arrangement of the corresponding hydrazo compounds, followed
by hydrolysis. Both dienones underwent dienone-phenol
rearrangement in a mixture of acetic anhydride and sulphuric
acid.

Spectroscopic rate studies showed that the cis-azo
compound was the species which photocyclized. The quantum
yield for the photocyclization of azobenzene was determined
as a function of the sulphuric acid concentration (14-24$\underline{N}$),
the wavelength of irradiation (436 and 405 mμ), and the
temperature (15 and 25°). The quantum yield was 0.016 in
14$\underline{N}$ acid and decreased with increased acid concentration.
Temperature and wavelength of irradiation had only a slight
effect. Quantum yields for the cyclization of 4-chloro-
and 4-methylazobenzene at 25° and 436 mμ were lower than for
azobenzene and these also were found to decrease with an
increase in the acid concentration. For the accurate
determination of quantum yields, a special method was
developed to determine the photoequilibrium composition

of the _cis-trans_ mixture.

The cyclization of a short-lived, ionic, photoexcited state of the _cis_-azo compound is proposed to explain the effect of acid concentration and of substituents. The fate of eliminated substituents is also discussed.

iv.

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
of the thesis.

(Robert J. Drewer)

ACKNOWLEDGMENTS

vi.

CHAPTER I

INTRODUCTION

Photochemical cyclodehydrogenation reactions have been known for many years,[1] and in particular the photochemical cyclization of stilbene (I) to phenanthrene (II) has received considerable attention by many research groups very recently. It was in 1960 that a similar reaction, namely the photochemical cyclization of azobenzene (III) to benzo[g]cinnoline (IV), was first reported. Lewis[2,3] performed the reaction in strong sulphuric acid, and in the same year Hugelshofer, Kalvoda, and

(I)

(II)

(III)

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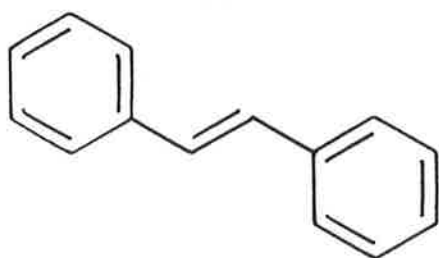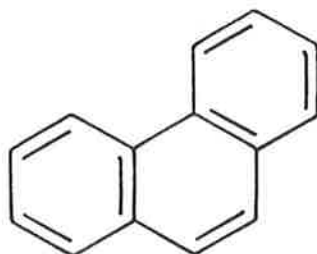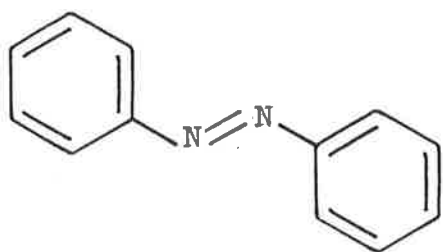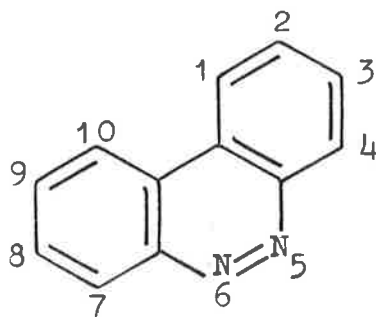
Schaffner[4] photocyclized azobenzene in acetic acid, in the presence of ferric chloride. However, about thirty years before this, azobenzene and some of its derivatives had been cyclized to benzo[c]cinnolines in a melt with aluminium chloride.[5] Furthermore, when stilbene is passed through a red hot tube, some phenanthrene is formed, together with toluene.[6] In fact it has been said that most photochemical reactions will proceed thermally to some degree.[7] The important questions which therefore arise are concerned with the essential differences between photochemical reactions and thermal reactions, and with the synthetic value of photochemistry when the same reactions may occur thermally.

In answer to the first question it may be pointed out that a thermal reaction gains its activation energy by molecular collision, giving rise to increases in the vibrational energy levels of the reacting molecules. A photochemical reaction however, gains its activation energy from the light, which gives rise to an increase in the electronic energy levels, as well as vibrational energy levels of the reacting molecules. Thus there is often a considerable wastage of energy in photochemical reactions, which is important because light usually is a more expensive form of energy than heat, unless of course sunlight may conveniently be used.

In answer to the question on the synthetic value
of photochemistry, it must be pointed out that there are
many chain reactions which can be initiated photochemically.
Hence a large yield of product may be obtained from a
relatively small expenditure of light energy.   Even if
this is not so, the wastage of energy in a photochemical
process is not always very serious, because only an
isolated part of the reacting molecule may be involved
in the activation process.   Thermal activation would
result in the whole molecule being activated more or less
indiscriminately, and this could lead to decomposition at
points which would be relatively unactivated in a photo-
chemical process.   Thus a photochemical reaction may
provide a short, convenient route to a particular product,
which otherwise could be difficult to synthesize.

For a photochemical reaction to occur, several primary
conditions must be fulfilled.   Light of sufficient energy
must be absorbed by the reacting system, either directly
by the reactants, or by a sensitizer which then passes the
energy to the reactants.   The energy of the light quanta
absorbed (given by $E = h\nu$, where h is Planck's constant,
and ν is the frequency of the light) must be sufficient to
bring about the molecular changes involved.   Even if
these conditions are fulfilled, a photochemical reaction
need not occur, as intersystem crossing from an excited

singlet to a triplet state may be required. This process
may not occur to any significant extent. Also the elec-
tronically excited molecules may lose their energy by
internal conversion or fluorescence so rapidly that they
have insufficient time to undergo a chemical reaction.

Several photochemical processes often occur simul-
taneously, or consecutively, in the one system. This is
true for the reaction of azobenzene as described by Lewis,[3]
where photochemical cis-trans equilibration occurred as well
as photocyclization. Photochemical cis-trans equilibra-
tion is a very common phenomenon among systems of the type
R-A=B-R', where R and R' may be alkyl or aryl groups, and
A=B can be CX=CY, CH=N, or N=N. X and Y can be a com-
bination of H, aryl, CN, or halogens, etc. An analogous
process occurs with conjugated polyenes of the type
$R-(CH=CH)_n-R'$.

If we restrict ourselves to the compounds with R and
R' as aryl groups, there are many examples where photo-
chemical cyclodehydrogenation (presumably of the
cis-isomers) also occurs. For example, it is well known
that stilbene and many of its derivatives may be photo-
cyclized to phenanthrenes.[4,3-12] Also 1,4-diphenylbuta-
1,3-diene (V) and 1,6-diphenylhexa-1,3,5-triene (VII) have
been photocyclized to 1-phenylnaphthalene (VI) and chrysene
(VIII) respectively.[13] Recently Perkampus and Senger[14]

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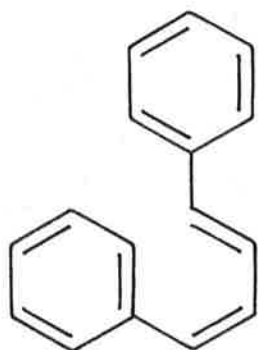
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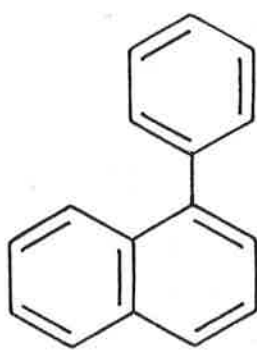
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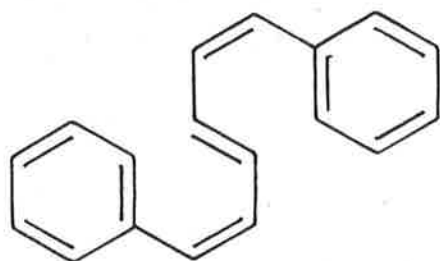
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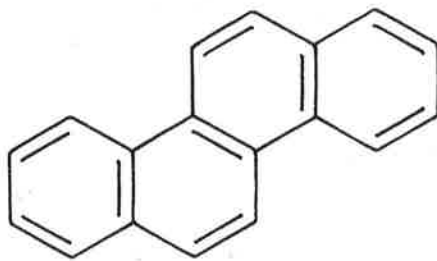
(VIII)

reported photochemical studies on _trans_-1,2-dipyridylethyl-
enes, which presumably gave phenanthrolines, although
only spectroscopic evidence was put forward.   Recently,
most investigators have claimed[11,15-17] that the presence
of an oxidizing agent such as oxygen or iodine is essential
for the photochemical cyclodehydrogenation of diarylethyl-
enes.   Other workers have said[4,13] that oxidizing agents
assist the cyclodehydrogenation, but are not essential.
When oxygen has been used as the oxidizing agent, hydrogen
peroxide has been detected.[16]   Free hydrogen was formed

when stilbene was photocyclized to phenanthrene in the
vapour phase.[17]   The various mechanisms proposed for the
photochemical cyclization of stilbene and related com-
pounds are discussed in Chapter IV.

So far there has been no report of a successful
photochemical cyclization of compounds of the type
Ar-CH=N-Ar' to give phenanthridines, although there have
been some attempts.[4,18]   It is of interest to note that
the cis forms of these anils appear to be very unstable
at room temperature, requiring low temperatures for satis-
factory study.[19]

Both aliphatic[20] and aromatic[21] azo compounds are
known to undergo photochemical cis-trans isomerization.
However, at this point the similarity in their photo-
chemistry ends.   With aliphatic azo compounds, C-N
fission occurs to give free nitrogen,[20] but no C-N
fission occurs with aromatic azo compounds.   In common
organic solvents no photochemical reaction other than
cis-trans isomerization normally occurs; but photo-
chemical cyclodehydrogenation of azobenzene will occur in
strong sulphuric acid,[2] or in acetic acid with ferric
chloride added.[4]

Lewis showed[3] that under the strongly acidic con-
ditions he used, both cis-azobenzene (IX) and trans-

7.

(IX)

(X)

(XI)

(XII)

(XIII)

(XIV)
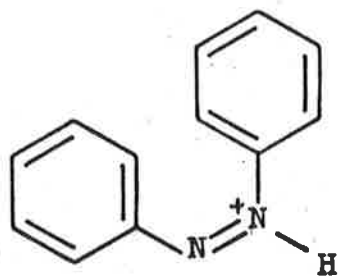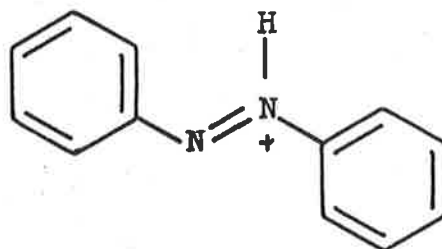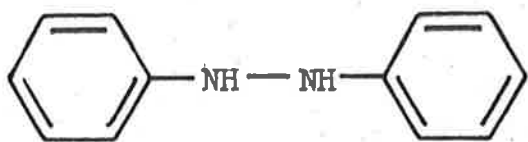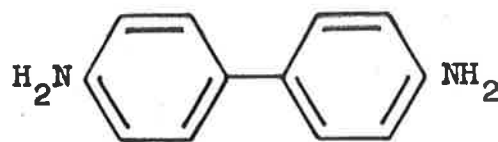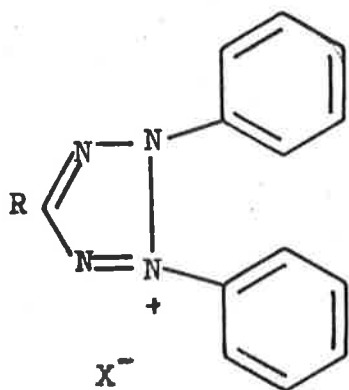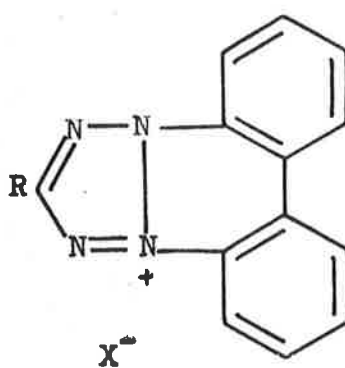
azobenzene (X) were virtually completely monoprotonated.
Spectroscopic studies showed that an equilibrium mixture
containing approximately 55% cis- and 45% trans-azobenzene
was produced on irradiation, whether one started with pure
cis- or pure trans-azobenzene.   Continued irradiation
resulted in the consumption of the azobenzene to give
benzo[c]cinnoline at a rate approximately 100 times less
than the rate of cis-trans equilibration.

In later experiments,[22] benzidine sulphate was
isolated from the reaction mixture when more concentrated
solutions of azobenzene in 22N 10% v/v ethanolic sulphuric
acid were irradiated.   It was concluded that the hydrogen
eliminated in the cyclization process must have reacted
with the remaining azobenzene to form hydrazobenzene (XI),
which then rearranged in the acid solution to give benz-
idine (XII).   Nesmeyanov has found azobenzene in strongly
acidic solutions to be a very powerful abstractor of hydride
ions.[23]   This therefore rationalizes the proposed inter-
mediate formation of hydrazobenzene.

In a photocyclization rather similar to that of
azobenzene, 2,3-diphenyltetrazolium salts (XIII) have been
photocyclized in ethanol to give 2,3-diphenylenetetrazolium
salts (XIV) which, on hydrogenation, gave benzo[c]cinnolines.[24]
This reaction is further discussed in Chapter II.

The investigations on the photochemistry of azobenzenes
which are described in this thesis have had two main aspects.
Firstly, the photochemical formation of benzo[g]cinnoline
from azobenzene has led to a study of the synthetic value
of the reaction.   This aspect is discussed in Chapter II.
Secondly, an investigation on the mechanism of the re-
action was especially timely, because of the vigorous
interest in the mechanism of the photochemical cyclization
of stilbene.   To this end, kinetic studies on the reaction
have been made and these are described in Chapter III.   A
discussion on the mechanism of the cyclization of azobenzenes
is given in Chapter IV.

CHAPTER II

<u>PREPARATIVE PHOTOCHEMISTRY OF AZOBENZENE</u>

<u>AND SOME DERIVATIVES</u>

2.1 Outline

It has been shown that it is possible to prepare a
series of substituted phenanthrenes, or benzo[c]cinnolines,
by photochemical cyclodehydrogenation of the appropriate
stilbenes, or 2,3-diaryltetrazolium salts.   Therefore, it
was considered important to test the generality of the
cyclization of substituted azobenzenes, and also to inves-
tigate the intermediate formation of hydrazo compounds.

In the initial work of Lewis,[2,3] the photochemical
cyclization of azobenzene was carried out in ethanolic
sulphuric acid.   In the investigations described in this
thesis, similar conditions have been used, but it was con-
sidered desirable to omit the ethanol to remove the
possibility of side reactions with ethanol.

The progress of the cyclization reactions was easily
followed from the ultraviolet spectra of the irradiated
solutions.   In 22$\underline{N}$ sulphuric acid, azobenzene showed an
intense broad band at 420 mμ, which eventually disappeared
on irradiation of the solution.   The final spectrum showed
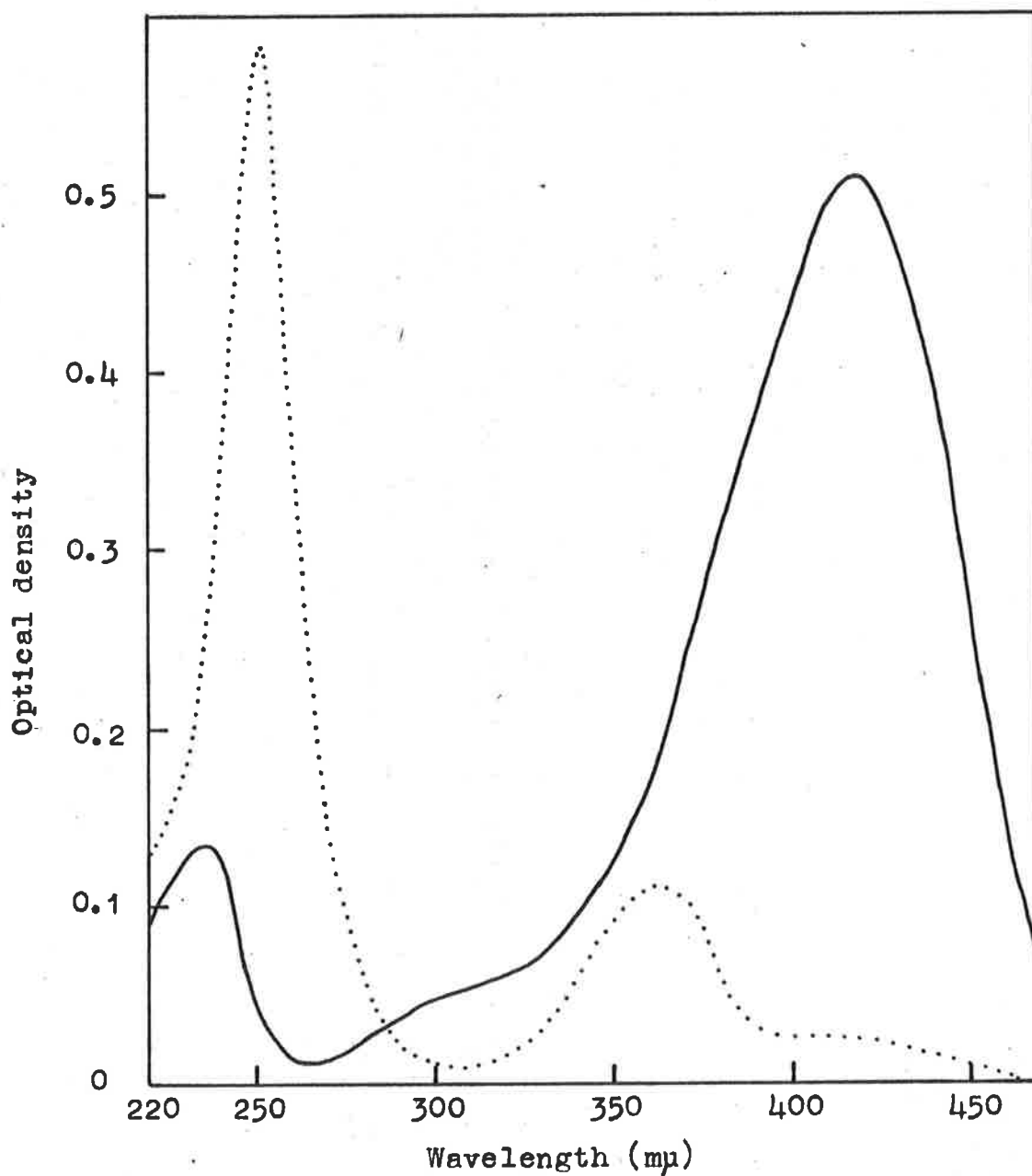
Fig. 1.— The electronic absorption spectra of
2.0 x 10⁻⁵<u>M</u> azobenzene in 22<u>N</u> sulphuric acid before
(————) and after (••••••) exposure to sunlight.

peaks at 252 and 365 mμ, which are characteristic of
benzo[c]cinnoline in acid solution.   The spectra of
azobenzene in 22N sulphuric acid before and after irrad-
iation are shown in Fig. 1.   Marked bleaching of the
strong yellow colour of the azobenzene solution also
indicated the occurrence of cyclization.   The use of
very dilute solutions made this test very sensitive.

In a general survey of various substituted azo-
benzenes, it was found that the presence of hydroxy,
alkoxy, amino, or dimethylamino substituents prevented
any significant reaction.   Simple methyl-, halogeno-,
or carboxy-azobenzenes, however, were rapidly bleached in
the acid solution, on exposure to sunlight.   Their elec-
tronic absorption spectra also underwent the characteristic
change, similar to that of azobenzene.

The photochemistry of the three symmetrical
dimethylazobenzenes, and a series of monosubstituted
azobenzenes was investigated.   The monosubstituents were
methyl, chloro, iodo, and carboxy.   From each azo compound
one or more benzo[c]cinnolines were obtained, as well as
products from the acid-catalyzed rearrangement of the
corresponding hydrazo compound.   In two instances unusual
rearrangement products were isolated.   During the invest-
igations it was found that ortho-substituents (including

methyl) were eliminated to some extent, and therefore the
photochemistry of 2,4,6-trimethylazobenzene was also ex-
amined.   These studies on the preparative photochemistry of
azobenzenes have led to the publication of two papers.[25,26]

2.2 Photochemical Reactions of Azobenzenes

Generally the irradiations were carried out at room
temperature 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 the small amount of heat from the lamp which
managed to reach the solution was found to produce suf-
ficient mixing due to convection currents.   In almost
every case the azo compound was irradiated to completion,
as judged from the ultraviolet spectrum of a sample from
the reaction mixture.

The photochemical reactions of substituted azobenzenes
can be conveniently grouped according to the position of the
substituents.   Thus azobenzene and its 4-substituted and
4,4'-disubstituted derivatives gave one benzo[c]cinnoline,
3-substituted and 3,3'-disubstituted azobenzenes gave the
expected mixtures of benzo[c]cinnolines, and 2-substituted
and 2,2'-disubstituted azobenzenes all showed some elimina-
tion of the o-substituent.

(a)   <u>Azobenzene and its 4-substituted and 4,4'-disubstituted derivatives</u>

Benzidine sulphate had been isolated from the irradiation of azobenzene in ethanolic sulphuric acid;[22] this reaction was repeated using 22$\underline{N}$ sulphuric acid to determine the yields of the products.   During the irradiation, benzidine sulphate crystallized from the solution.   On completion of the reaction, benzo[$\underline{c}$]cinnoline was obtained in 48% yield, and benzidine in 35% yield (after recrystallization).   Paper chromatography[27] of the crude rearrangement products suggested the presence of a small quantity of 2,4'-diaminobiphenyl (XV), with a smaller amount of $\underline{o}$-benzidine (XVI).   Both these compounds
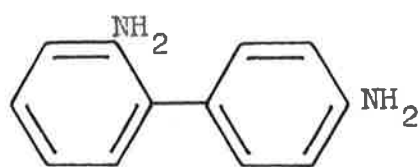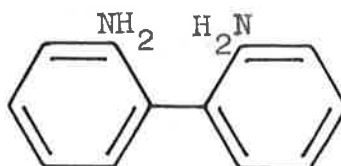
(XV)   (XVI)

are known to be formed in small quantities by acid catalysed rearrangement of hydrazobenzene,[28] and it has been shown that the yield of benzidine decreases as the acid concentration is increased.[29]   This may be one reason for the yield of benzidine being considerably less than 50%.

With p-substituted azobenzenes, the yield of sub-
stituted benzo[c]cinnoline occasionally exceeded 50%.
This is to be expected as rearrangement of p-substituted
hydrazobenzenes often occurs with some disproportionation
to give the azo compound and fission bases (substituted
anilines).[30]   The fission bases were usually observed
in the products from these p-substituted azobenzenes,
and were removed from the other rearrangement products
by steam distillation.

4,4'-Dimethylazobenzene (XVII) gave 2,9-dimethyl-
benzo[c]cinnoline (XVIII) in 57% yield; and
2-amino-4',5-dimethyldiphenylamine (XIX), which is the
expected rearrangement product from 4,4'-dimethyl-
hydrazobenzene, was also obtained.[31]

On irradiation, 4-methylazobenzene (XX, R=CH$_3$) gave
the expected 2-methylbenzo[c]cinnoline (XXI, R=CH$_3$) in 50%
yield.   The rearrangement product, however, was found to
be 4-(4'-aminophenyl)-4-methylcyclohexa-2,5-dienone (XXII).
This is an unusual product and it presumably arose by
p,p-rearrangement of 4-methylhydrazobenzene to give the
imine (XXIII), which then hydrolysed to give the dienone
(XXII).   According to Jacobson,[32] the normal rearrange-
ment product from 4-methylhydrazobenzene is the o-semidine,
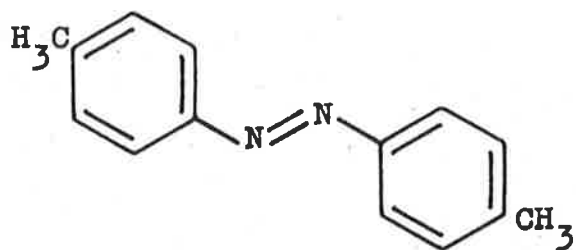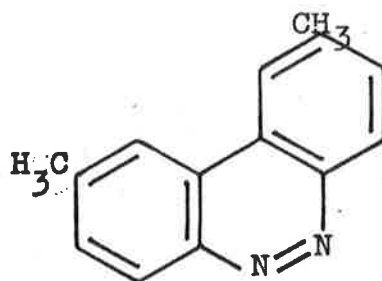
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(XVIII)
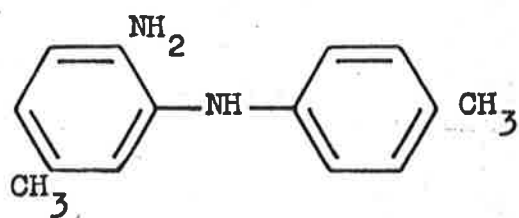
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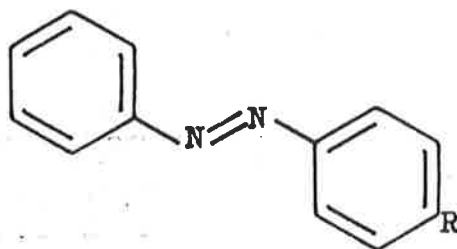
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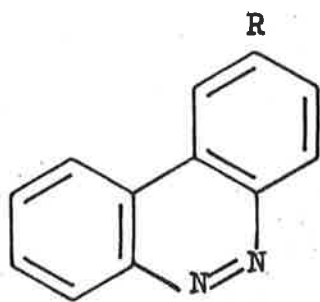
(XXI)
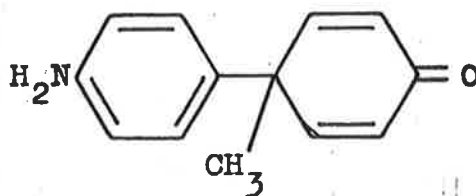
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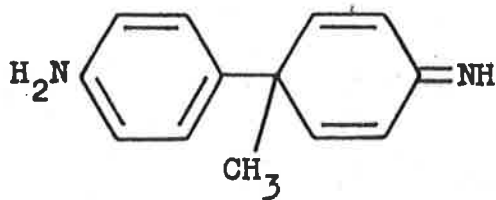
(XXIII)
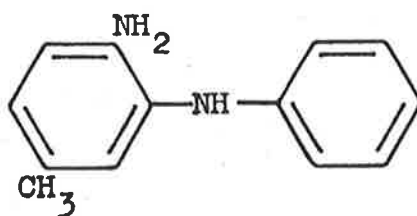
(XXIV)

2-amino-5-methyldiphenylamine (XXIV) (isolated as a
derivative). This o-semidine has now been obtained by
adding solid 4-methylhydrazobenzene to 22N sulphuric acid,
and working up the product by Jacobson's method.[32]
Apparently Jacobson isolated the dienone (XXII) on one
occasion,[32] but he could not repeat the work and was
unable to identify the product. His compound was
obtained as slightly yellowish crystals, m.p. 167° (cf.
this work, m.p. 167-168°), and gave an analysis for carbon
and nitrogen which would fit the dienone (XXII) approx-
imately. The formation of the dienone by irradiation
of 4-methylhydrazobenzene was repeated satisfactorily,
and the structure was established by infrared and n.m.r.
spectroscopy. The infrared spectrum showed a strong
band at 1665 cm^{-1} which is consistent with the presence
of an $\alpha,\beta-\alpha',\beta'$-unsaturated carbonyl group.[33] The
n.m.r. spectrum showed a sharp singlet at τ 8.38 (3
protons) arising from the non-aromatic methyl group, and
two quartets of four protons each, arising from the four
dienone protons, and the four aromatic protons of the
p-disubstituted aromatic ring. The structure was con-
firmed by a dienone-phenol rearrangement to a
methylhydroxyaminobiphenyl, presumably (XXV).[cf. 34]
The position of the hydroxyl group could not be

determined unambiguously from the ultraviolet or n.m.r.
spectra, and it was initially proposed[25] that methyl
migration occurred to give 4-amino-4'-hydroxy-2'-
methylbiphenyl (XXVI).   Mechanistically, however, it
seems more probable that, under the conditions of the
rearrangement, the acetylaminophenyl group would migrate,
to give (after hydrolysis) 4-amino-3'-hydroxy-2'-
methylbiphenyl (XXV).   The probable mechanism of the
dienone-phenol rearrangement is shown in

(XXV)   (XXVI)
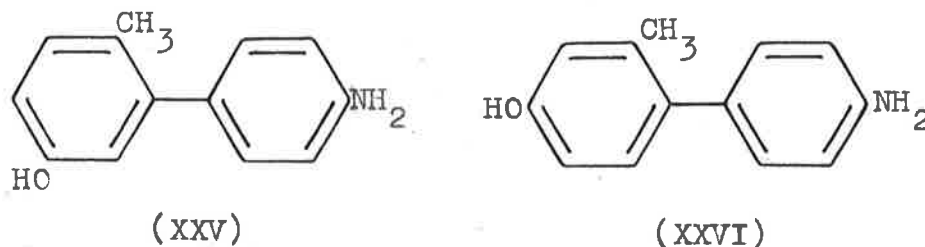
Scheme 1.   It is noteworthy that the dienone is stable
in strong sulphuric acid alone.   The positive charge on
the aminophenyl substituent probably inhibits re-
arrangement.   Thus acetylation of the amino group would
be necessary as the first step.   Some assistance in the
rearrangement would no doubt be provided by the acetyl-
amino group (cf. nitration of acetanilide).

At first sight it is surprising that the dienone
(XXII) did not itself undergo a photochemical reaction as

SCHEME 1 —— Mechanism of dienone-phenol rearrangement
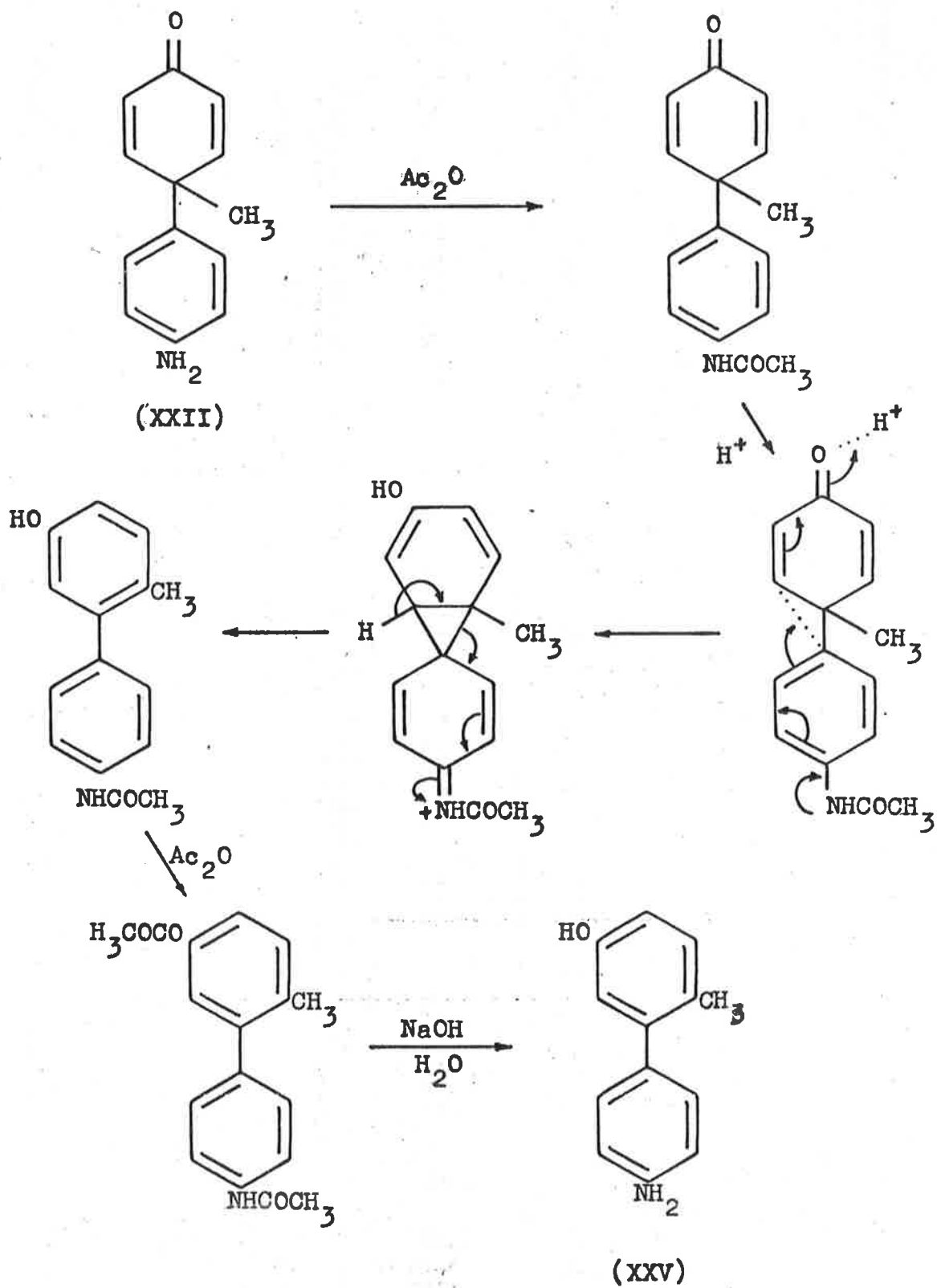
soon as it was formed.[cf.34]   In fact spectroscopic tests
showed that the dienone in 22$\underline{N}$ sulphuric acid was changed
photochemically when irradiated in a thin-walled soda-glass
test tube, a mercury-quartz lamp being used as the source.
The nature of the change was not investigated.   The
spectrum of the dienone in 22$\underline{N}$ sulphuric acid showed a
shoulder of about 320 mμ, and it could be argued that the
normally strong 313 mμ emission lines of the mercury lamp
could have caused some reaction.   However, the emission
spectrum of the mercury lamp through the water-cooled
jacket of the photochemical reactor showed that very
little of the 313 mμ lines was transmitted, when com-
pared with the transmitted emission at 365-366, 405, and
436 mμ.   There was only weak transmitted emission at
334 mμ, none at all below the 313 mμ lines, and a
negligible amount of continuous radiation transmitted
below 330 mμ.   The 2-methylbenzo[$\underline{g}$]cinnoline would also
have acted as a strong internal filter for radiation from
about 330 to 390 mμ, and wavelengths higher than this were
well outside the absorption range of the dienone.   Hence
comparatively little actinic radiation would have been
absorbed by the dienone, compared with the actinic light
absorbed by the reacting azo compound.   Nevertheless, the
yield of recrystallised dienone was small, and some may have

undergone a photochemical reaction during the long period
of irradiation. Suitable filters would prevent this,
unless the reaction was photosensitized by the azo com-
pound or by the 2-methylbenzo[g]cinnoline formed.

It is far from clear why the rearrangement of
4-methylhydrazobenzene (XXVII) should have taken an
unusual course during the photochemical reaction. As
mentioned earlier, the expected o-semidine (XXIV)[32] was
obtained when 4-methylhydrazobenzene was added to 22N
sulphuric acid, so that the high acid concentration is
not the answer in itself, although it may be a factor.
Assuming diprotonation of the π-complex (XXVIII), the
probable mechanism of the abnormal rearrangement of
4-methylhydrazobenzene is shown in Scheme 2. It
would seem that the only complication is some steric
hindrance between the methyl group and the hydrogen
atom in the 4'-position of the other ring. Once the
σ-complex (XXIX) has been reached, the loss of a proton
irreversibly would lead to the dienone (XXII) by way of
the protonated imine (XXX). Nevertheless it seems
that extra energy must be found to favour this par-
ticular σ-complex (XXIX). This energy may result in
speeding up the process of forming the σ-complex, allow-
ing insufficient time for rotational isomerism of the
π-complex (XXVIII) to occur. Normally, rotation of the

SCHEME 2. — Mechanism of abnormal rearrangement of 4-methylhydrazobenzene.
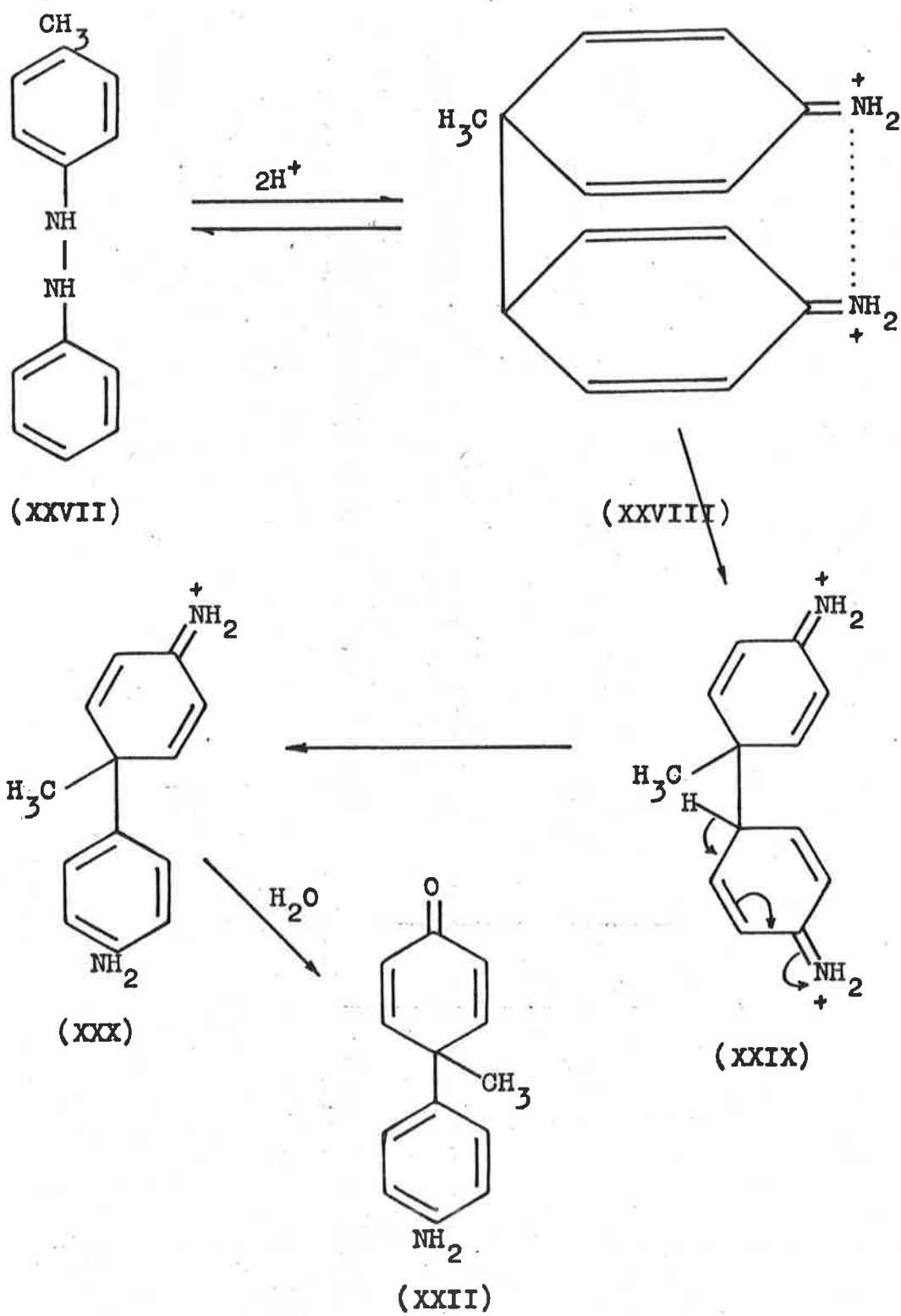
π-complexes from hydrazo compounds would probably occur
faster than collapse to the products.[35]

There are several possible sources for the extra
energy. Firstly, in the photochemical reaction the azo
compound is already protonated before it is reduced,
whereas in most reductive rearrangements of azo compounds,
the acid strength is insufficient to cause much protona-
tion. This could give the resulting hydrazo compound a
higher energy than normal, and as rearrangement would be
almost instantaneous under the strongly acidic conditions,
this energy would probably be retained long enough to
influence the course of the rearrangement. Secondly,
the rearrangement might be photosensitized by the azo
compound or by the 2-methylbenzo[c]cinnoline (XXI, R=CH$_3$).
It may be that, in the reduction of the 4-methylazobenzene,
extra energy is donated by the newly formed dihydro-
benzo[c]cinnoline (see Chapter IV); but this hypothesis
would not explain Jacobson's unusual product.[32] The
hydrazo compound itself would not absorb any radiation
before or during the rearrangement, unless the π-complex
(XXVIII) had an extremely strong absorption in suitable
regions of the spectrum. Even then the lifetime of the
intermediates would be too short for significant photo-
activation.

The third possibility is that photoactivated azo compound undergoes the reduction step. This would imply that the cyclization step is non-photochemical, because the reaction has been found to be first order with respect to the light absorbed (see Chapter III). If direct photoactivation is the answer, it is difficult to see how Jacobson could have accidentally obtained the dienene.[32] The reduction of azo compounds with stannous chloride in hydrochloric acid is quite rapid, and it is inconceivable that sufficient light could have been absorbed by Jacobson's 10 g of 4-methylazobenzene in 150 ml of solution to cause any noticeable affect.

The photochemistry of the other p-substituted azobenzenes was reasonably straightforward. 4-chloro-azobenzene (XX, R=Cl) gave 2-chlorobenzo[g]cinnoline (XXI, R=Cl) in 53% yield. 5-Chloro-2,4'-diaminobiphenyl (XXXI, R=Cl) and a small quantity of benzidine were also obtained. The latter compounds are expected as re-arrangement products from 4-chlorohydrazobenzene.[36]

Similarly, 4-iodoazobenzene (XX, R=I) gave 2-iodobenzo[g]cinnoline (XXI, R=I) (characterized as an N-oxide), 2,4'-diamino-5-iodobiphenyl (XXXI, R=I) (characterized as salicylidene and p-nitrobenzylidene derivatives), and a very small quantity of benzidine.
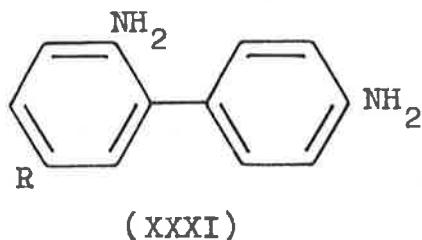
(XXXI)

The diphenyline (XXXI, R=I) is the rearrangement product
expected from 4-iodohydrazobenzene.[37]   The formation of
some benzidine is not very surprising as 4-chloro-
hydrazobenzene rearranges with some elimination of the
chloro substituent[36] (see above).   The yield of the
2-iodobenzo[g]cinnoline (XXI, R=I) was only 34%; this
may have been due to the fact that the 4-iodoazobenzene
solution was irradiated in sunlight (summer), without
cooling.   The mixture became very hot, and some de-
composition of reactant or products may have occurred.
The solar reactor was used because of the very slow
rate of the photochemical reaction.

On irradiation, azobenzene-4-carboxylic acid
(XX, R=CO$_2$H) gave benzo[g]cinnoline-2-carboxylic acid
(XXI, R=CO$_2$H); but it was found more convenient to isolate
this as the methyl ester.   Benzidine was also isolated,
and this was expected as the rearrangement of hydrazo-
benzene-4-carboxylic acid is known to occur with a con-
siderable amount of decarboxylation.[38]   The other

possible rearrangement product, namely 2,4'-diamino-
biphenyl-5-carboxylic acid (XXXI, R=CO$_2$H), may have been
present, but it was not isolated.

The products obtained from the photochemical re-
actions of azobenzene and its p-substituted derivatives
are summarized in Table 1. It should be pointed out
that the yields of the rearrangement products of hydrazo
compounds are frequently poor, and furthermore, quanti-
tative isolation of the products is often tedious.

TABLE 1.

Products from the irradiation of azobenzene and its
4-substituted and 4,4'-disubstituted derivatives in
22N sulphuric acid

Azobenzene derivative	Yield of substituted benzo[c]cinnoline. (%)	Rearrangement products		
		Type	yield (%)	Benzidine (%)
Azobenzene	48	benzidine	35	—
4,4'-Dimethyl-	57	o-semidine	5	—
4-Methyl-	50	dienone	40	—
4-chloro-	53	diphenyline	23	8
4-Iodo-	34	diphenyline	14	0.4
4-Carboxy-	44*	—		29

* Isolated as the methyl ester.

(b)   3-Substituted and 3,3'-disubstituted azobenzenes

All the expected isomeric benzo[c]cinnolines were
obtained by irradiation of m- substituted azobenzenes.
3,3'-Dimethylazobenzene gave three isomers, and the mono-
substituted azobenzenes gave two isomers.   It was assumed
that the cyclized products would be obtained in yields
depending on the degree of steric strain in the product.
Substituents in the 1- and 10-positions are well known to
clash sterically, in fact 4,7-diamino-1,10-dimethyl-
benzo[c]cinnoline (XXXII) has been resolved into its
optical isomers.[39]   The ultraviolet spectra of

(XXXII)
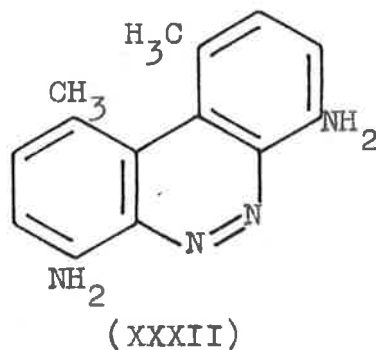
1,10-disubstituted benzo[c]cinnolines also reflect this
strain.[40]   It seemed likely that benzo[c]cinnolines with
a substituent in the 1-position only would also be formed
in lower yield, and this has been confirmed.   Generally,
assignment of the structure of the benzo[c]cinnolines was
made on the basis of the relative yields of the products.
In addition it was noted that for a given substituent,

the order of increasing yield paralleled the order of
increasing melting points of the benzo[g]cinnolines,
without exception.   With two of the azo compounds; some
difficulty was experienced in quantitatively separating
and isolating all the benzo[g]cinnolines, but generally
the total yield of cyclized products approached 50%.   In
addition, the expected substituted benzidine was isolated
following irradiation of each azo compound.   The products
obtained from the irradiation of 3-substituted and
3,3'-disubstituted azobenzenes are summarized in Table 2.

TABLE 2.

Products from irradiation of 3-substituted and 3,3'-disubstituted azobenzenes in 22N sulphuric acid

Azobenzene Derivative	Benzo[g]cinnolines (%)				Substituted Benzidines %
	3,8-dimethyl or 3-R	1,8-dimethyl —	1,10-dimethyl or 1-R	Total yield	
3,3'-Dimethyl-	16	7	3	32	12
3-Methyl-	27		13	47	34
3-Chloro-	35		11	50	29
3-Iodo-	35[+]		14[+]	50[+]	43[+]
3-Carboxy-	14[++]		10[+++]	—	24

[+]   Yield based on azo compound consumed.

[++]   Losses occurred in isolation of this product.

[+++]   1-Hydroxybenzo[g]cinnoline-10-carboxylic acid
         lactone (XLII).

On irradiation, 3,3'-dimethylazobenzene (XXXIII)
gave 3,8-dimethylbenzo[g]cinnoline (XXXIV), 1,8-dimethyl-
benzo[g]cinnoline (XXXV), and 1,10-dimethylbenzo[g]cinnoline
(XXXVI).   The identity of the 3,8- and 1,10- isomers was
established by direct comparison with authentic samples
from Dr. P. F. Holt,[40] and hence the other isomer was
assumed to be 1,8-dimethylbenzo[g]cinnoline.   As expected,
the 3,8-isomer was formed in highest yield and the 1,10-
isomer in the lowest yield.   An intermediate yield of the
1,8-isomer was obtained which shows that 1-substituted
benzo[g]cinnolines are formed in a yield lower than
benzo[g]cinnolines which have no substituents in the 1-
or 10-positions.   It is interesting to note that the
dimethoxyphenanthrene analogous to 1,10-dimethyl-
benzo[g]cinnoline was not isolated from the photo-
cyclization of 3,3'-dimethoxystilbene, although the other
two isomers were isolated.[4]   In addition to the three
benzo[g]cinnolines, 2,2'-dimethylbenzidine (XXXVII) was
isolated as the rearrangement product of 3,3'-dimethyl-
hydrazobenzene.[41]   It was identified by the preparation
of its dibenzylidene, disalicylidene, and diacetyl
derivatives.[41]

3-Methylazobenzene (XXXVIII, R=CH$_3$) gave a mixture
of 3-methylbenzo[g]cinnoline (XXXIX, R=CH$_3$) and 1-methyl-
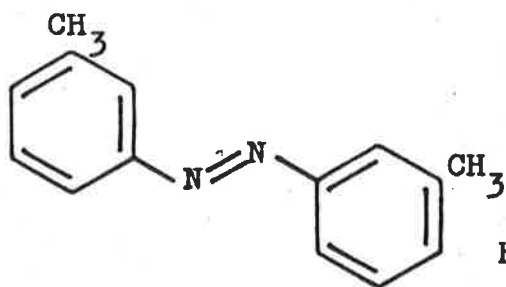
(XXXIII)
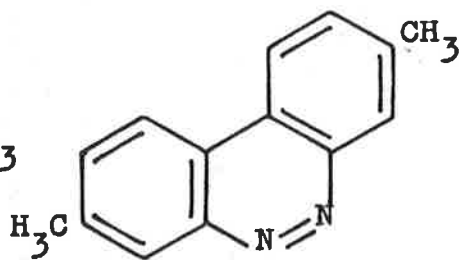
(XXXIV)
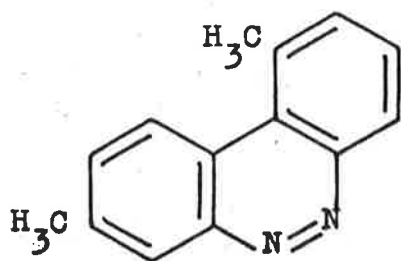
(XXXV)
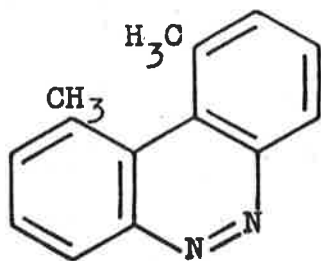
(XXXVI)
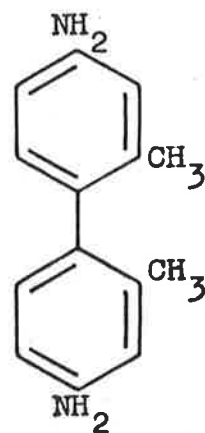
(XXXVII)
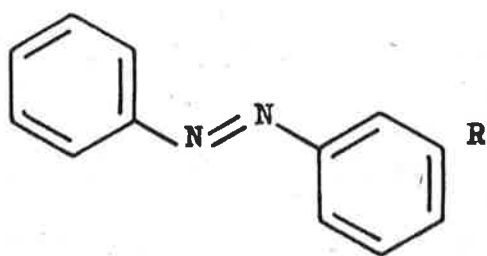
(XXXVIII)
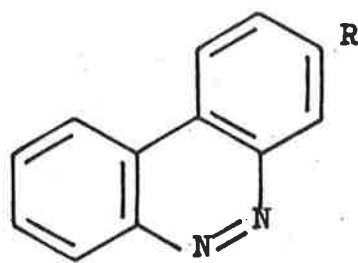
(XXXIX)
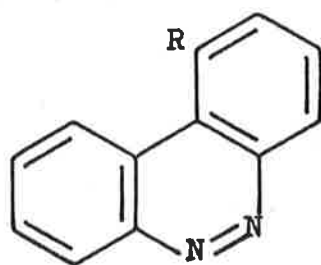
(XL)
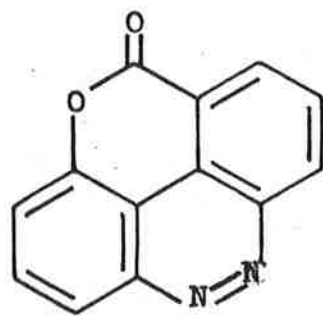
(XLII)
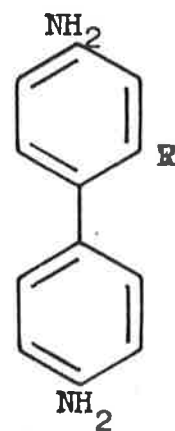
(XLI)

benzo[g]cinnoline (XL, R=CH$_3$). 1-Methylbenzo[g]cinnoline
was formed in the smaller yield and was identified by
direct comparison with an authentic specimen.[40] This
further confirms the finding that 1-substituted
benzo[g]cinnolines are formed in lower yield. 2-Methyl-
benzidine (XLI, R=CH$_3$) was also obtained and it was
characterized as its diacetyl, disalicylidene, and
dibenzylidene derivatives.[42]

Irradiation of 3-chloroazobenzene (XXXVIII, R=Cl)
gave a mixture of 3-chlorobenzo[g]cinnoline (XXXIX, R=Cl)
and 1-chlorobenzo[g]cinnoline (XL, R=Cl). It seems certain
that the major product was the 3-isomer (as shown by
previous examples), and it therefore seems that the com-
pound reported by Jerchel and Fischer[24] as 3-chloro-
benzo[g]cinnoline, m.p. 141-142°, was actually the 1-isomer.
They had prepared it by the photochemical cyclization of a
2,3-diaryltetrazolium salt which should have given both the
1- and 3-isomers, and their supposed 3-isomer was obtained
from ethanol in rather low yield. The 1-isomer obtained
in the present work had m.p. 145-146°; the 3-isomer had
m.p. 189.5-190.5° and was very sparingly soluble, even in
boiling ethanol.

The rearrangement product, 2-chlorobenzidine (XLI, R=Cl)

was obtained and was shown to be identical with an
authentic specimen prepared by reductive rearrangement
of 3-chloroazobenzene.[43]   According to the literature[43]
2-chlorobenzidine (XLI, R=Cl) has m.p. 113°, but the
samples prepared in this work both had m.p. 101.5-102.5°.

Irradiation of 3-iodoazobenzene (XXXVIII, R=I) gave
a mixture of 3-iodobenzo[c]cinnoline (XXXIX, R=I),
1-iodobenzo[c]cinnoline (XL, R=I), and 2-iodobenzidine
(XLI, R=I).   The latter compound was characterized as
its $\underline{N},\underline{N}'$-dibenzylidene derivative.   The starting material
(XXXVIII, R=I) was sparingly soluble in the 22$\underline{N}$ sulphuric
acid, especially after some products had formed, and it
was not possible to carry this reaction to completion.
However, the unused azo compound was easily recovered and
the total yield of benzo[c]cinnolines was 49%, based on
the amount of azo compound consumed.

Azobenzene-3-carboxylic acid (XXXVIII, R=CO$_2$H) on
irradiation gave a mixture of benzo[c]cinnoline-3-
carboxylic acid (XXXIX, R=CO$_2$H) (characterized as the
methyl ester) and 1-hydroxybenzo[c]cinnoline-10-carboxylic
acid lactone (XLII), but no benzo[c]cinnoline-1-carboxylic
acid (XL, R=CO$_2$H) was isolated.   Some losses were en-
countered in the isolation of the benzo[c]cinnoline-
3-carboxylic acid (XXXIX, R=CO$_2$H) and the yield of 14%

does not give a true indication of the actual yield of this compound.   The mechanism of the formation of the lactone is not clear.   Its structure was deduced from its analysis and its infrared spectrum in chloroform which showed no bands in the region 4000-2000 cm^{-1}, apart from a sharp peak around 3000 cm^{-1} (aromatic C-H and chloroform C-H stretching frequencies), but showed strong bands at 1740 (lactone C=O) and 1125 cm^{-1} (lactone -O-C).   Also the compound (yellow needles) was insoluble in cold sodium hydroxide solution, but dissolved on boiling to give a red solution.   The lactone was re-formed on acidification.   The expected re-arrangement product from hydrazobenzene-3-carboxylic acid, namely benzidine-2-carboxylic acid (XLI, R=CO$_2$H), was also isolated from the reaction mixture.[38]

(c)   2-Substituted and 2,2'-disubstituted azobenzenes.

Some elimination of an o-substituent occurred with all the o-substituted azobenzenes investigated.   2,2'-Dimethylazobenzene (XLIII) gave 4,7-dimethylbenzo[c]cinnoline (XLIV), 4-methylbenzo[c]cinnoline (XLV, R=CH$_3$), a very small quantity of another dimethylbenzo[c]cinnoline (XLVI), and some tar.   No unsubstituted benzo[c]cinnoline was detected.   In addition 3,3'-dimethylbenzidine (o-tolidine; XLVII) was obtained.   This is the expected re-arrangement product from 2,2'-dimethylhydrazobenzene.[44]

4,7-Dimethylbenzo[g]cinnoline (XLIV) in 22N sulphuric acid
was found to be stable under irradiation.   Thus 4-methyl-
benzo[g]cinnoline (XLV, R=CH$_3$) could not have arisen from
4,7-dimethylbenzo[g]cinnoline.

4-Methylbenzo[g]cinnoline was obtained from 2,2'-
dimethylazobenzene in the greatest yield, indicating that
cyclization with methyl elimination occurred more extensively
than cyclization without elimination.   The structure of
the monomethylbenzo[g]cinnoline was confirmed by direct
comparison with a sample obtained from the cyclization of
2-methylazobenzene (see later).   The identity of
4,7-dimethylbenzo[g]cinnoline (XLIV) was supported by
thin-layer chromatography on silica-gel using 15% ether
in benzene as solvent.   4,7-Dimethylbenzo[g]cinnoline had
a much higher Rf value than 4-methylbenzo[g]cinnoline or
the dimethylbenzo[g]cinnoline obtained in very small yield.
The high Rf value is attributed to the shielding of the two
nitrogen atoms by the 4- and 7-methyl groups.   Also more
vigorous conditions were required to form 4,7-dimethyl-
benzo[g]cinnoline-5-oxide (XLVIII), compared with
benzo[g]cinnoline-5-oxide (IL).   The hindering effect
of 4-, and 7- substituents to N-oxidation of
benzo[g]cinnolines has been observed by other workers.[45]

The structure of the dimethylbenzo[g]cinnoline (XLVI),
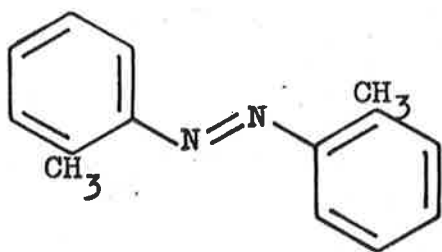
(XLIII)
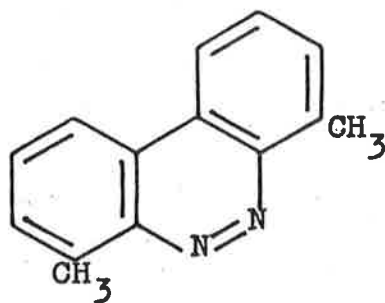
(XLIV)
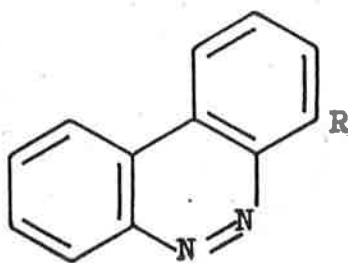
(XLV)
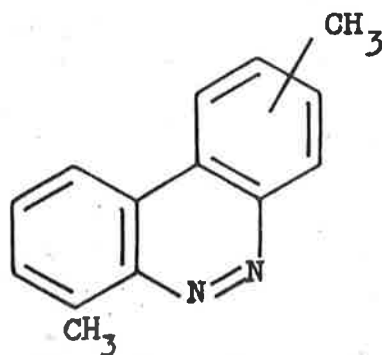
(XLVI)
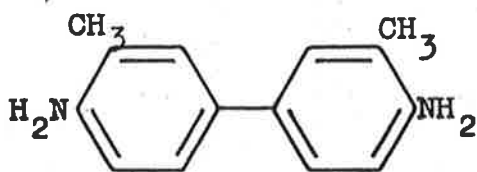
(XLVII)
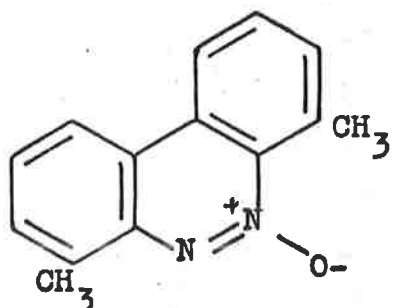
(XLVIII)
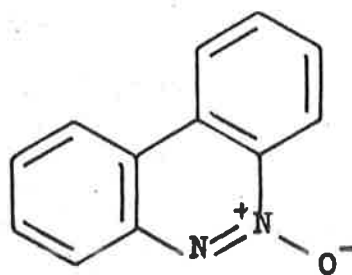
(IL)

obtained in very small yield, could not be established
unambiguously.   Its n.m.r. spectrum showed two sharp
singlets at Υ 6.93 and 6.83 assigned to two non-
equivalent methyl groups, a sharp singlet at Υ 2.33 (two
protons), and two multiplets at about Υ 2.25 and 1.35 (two
protons each).   Probably one methyl group is in the
4-position, but the position of the other methyl group is
not clear.   Also it is difficult to see how the singlet
at Υ 2.33 arises.   It seems to indicate the presence of
two isolated aromatic protons resonating in the same field.
The multiplet at Υ 1.35 is probably due to protons in the
1- and 10- positions or in the 1- and 7- positions, as
protons in these positions would be deshielded to the great-
est extent.   It is probable that the formation of this
dimethylbenzo[c]cinnoline involved the migration of at
least one methyl group.

On irradiation, 2-methylazobenzene (L, R=CH$_3$) gave
4-methylbenzo[c]cinnoline (XLV, R=CH$_3$) with some unsub-
stituted benzo[c]cinnoline, as well as 3-methylbenzidine
(LI, R=CH$_3$) which was the expected rearrangement product
from 2-methylhydrazobenzene.[46]   Some tar was also formed.
The structure of 4-methylbenzo[c]cinnoline was assumed from
the method of formation.
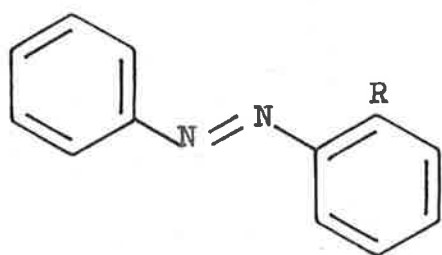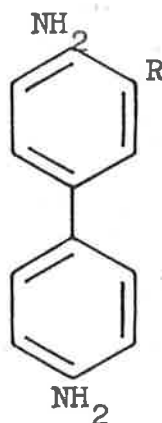
(L)   (LI)

Similarly 2-chloroazobenzene (L, R=Cl) gave 4-chloro-
benzo[ɡ]cinnoline (XLV, R=Cl) with some unsubstituted
benzo[ɡ]cinnoline, as well as 3-chlorobenzidine (LI, R=Cl)
which was the expected rearrangement product from
2-chlorohydrazobenzene.[47]   No chloride ion could be
detected in the reaction mixture.

2-Iodoazobenzene (L, R=I) on irradiation gave
4-iodobenzo[ɡ]cinnoline (XLV, R=I), a little unsubstituted
benzo[ɡ]cinnoline, and 3-iodobenzidine (LI, R=I) as the
rearrangement product.   The reaction was not taken to
completion due to the low solubility of the azo compound
in the acid solution, especially after some products had
been formed.   The combined yield of cyclized product was
43% when based on the azo compound consumed.

On irradiation, azobenzene-2-carboxylic acid (L, R=CO$_2$H)

gave benzo[c]cinnoline-4-carboxylic acid (XLV, R=CO_2H) and
a little unsubstituted benzo[c]cinnoline.   The rearrange-
ment products were benzidine and benzidine-3-carboxylic
acid (LI, R=CO_2H), both of which are expected following
rearrangement of hydrazobenzene-2-carboxylic acid.[38]

The products obtained from the irradiation of
o-substituted azobenzenes are summarized in Table 3.

TABLE 3

Products from irradiation of 2-substituted and
2,2'-disubstituted azobenzenes in 22N sulphuric
acid.

Azobenzene derivative	Benzo[c]cinnolines (%)				Substituted Benzidines (%)
	No elimination of Substituents	Elimination of one Substituent	Others	Total	
2,2'-dimethyl	10	19	0.4[+]	30	21
2-methyl-	23	11	—	35	11
2-chloro-	37	12	—	49	30
2-iodo-	37[++]	6[++]	—	43[++]	38[++]
2-carboxy-	35	6	—	41	31[+++]

[+]   Unidentified dimethylbenzo[c]cinnoline.

[++]   Yields based on azo compound consumed.

[+++]   Some unsubstituted benzidine (6%) was also formed.

It is noteworthy that although carboxy, iodo, and chloro substituents are much better leaving groups than methyl substituents, the extent to which cyclization occurs with elimination of a substituent bears no relationship to this property. Rather it seems that the size of the substituent is important in determining the degree of cyclization with elimination. Apparently there is adequate energy to expel a variety of substituents from the 2-position of azobenzene. Thus the yield of unsubstituted benzo[c]cinnoline probably depends on the proportion of the appropriate conformation of the cis-isomer in the photoexcited state. The distribution of the conformations of the cis-azobenzenes is probably not the same in the photoexcited state as it is in the ground state of the cis-isomers. However, this would depend on the rate of cyclization of the photoexcited cis-azo compound (see Chapter IV).

The fate of the eliminated substituent was not established for any of the o-substituted azobenzenes mentioned above. It was first thought that in the cyclization of 2,2'-dimethylazobenzene (XLIII) to give 4-methylbenzo[c]cinnoline (XLV, R=CH$_3$), some N-methyl-o-hydrazotoluene (LII) could have formed. This is known to rearrange to give N-methyl-o-tolidine[48] (LIII); but

none of the latter compound was isolated.   The formation
of methane is unlikely as no evolution of gas occurred.
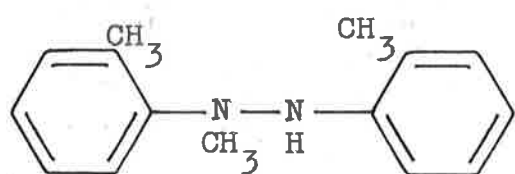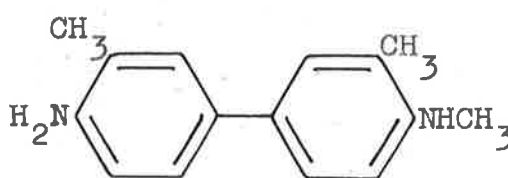
(LII)   (LIII)

In fact 90 ml of methane would be required to account for
all the methyl groups eliminated in the formation of
4-methylbenzo[c]cinnoline from 4 g of 2,2'-dimethyl-
azobenzene.   In one experiment, 2,2'-dimethylazobenzene
was irradiated in vacuo in a sealed system.   No evolution
of gas was observed during the irradiation and the vacuum
was "intact" at the end of the irradiation.

        Chloride ions could not be detected in the products
from 2-chloroazobenzene, and this suggests that the species
eliminated (either Cl$^+$ or Cl·) attacked either the azo
compound or the organic products of the reaction.   Thin-
layer chromatography (on silica-gel) of the crude re-
arrangement products suggested that traces of compounds
other than 3-chlorobenzidine (LI, R=Cl) might have been
present.   The crude rearrangement products were

chromatographed and subjected to countercurrent dis-
tribution, but no additional products were obtained.

Probably the carboxy group was eliminated as
carbon dioxide, although no gas was observed.

(d) 2,4,6-Trimethylazobenzene

The lack of information on the fate of the eliminated
substituents (especially methyl) prompted an investigation
of the photochemistry of 2,4,6-trimethylazobenzene (LIV).
Two compounds of special interest were obtained, namely,
1,2,4-trimethylbenzo[c]cinnoline (LV) (2%) and
4-(4'-aminophenyl)-2,4,6-trimethylcyclohexa-2,5-dienone
(LVI) (17%).   The major product was the expected
2,4-dimethylbenzo[c]cinnoline (20%) (LVII).   A con-
siderable amount of tar (30%) was also obtained.   This
irradiation was performed in 20.5 $\underline{N}$ sulphuric acid as
the reaction proceeded too slowly in 22$\underline{N}$ acid.

The structure of the trimethylbenzo[c]cinnoline was
deduced from its ultraviolet and n.m.r. spectra.   Its
ultraviolet spectrum was characteristic of a
benzo[c]cinnoline, and its n.m.r. spectrum showed three
sharp singlets at τ 7.50, 7.25, and 6.98 of three protons
each.   These were assigned to methyl groups in the
2-, 4-, and 1-positions respectively.   It was expected
from the method of formation that two of the methyl groups
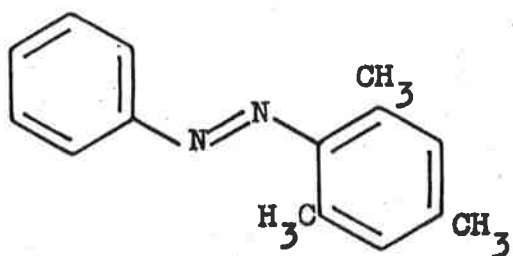
(LIV)
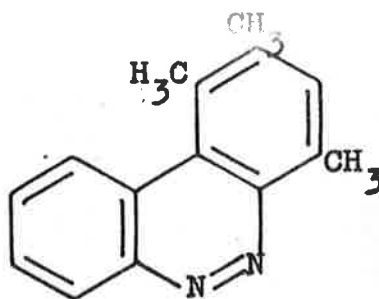
(LV)
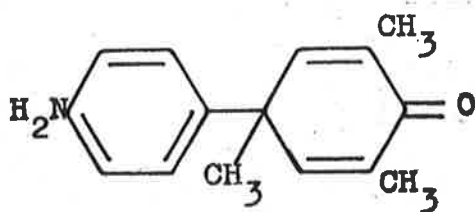
(LVI)
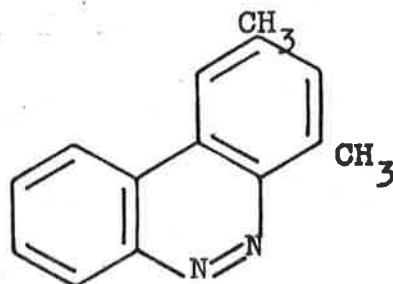
(LVII)
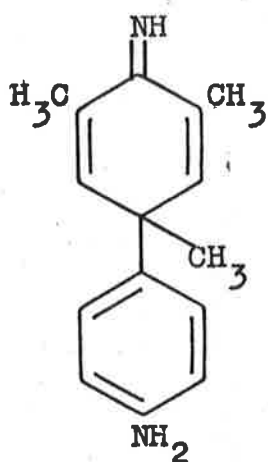
(LVIII)
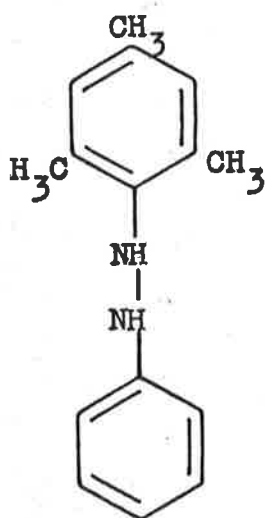
(LIX)

would be in positions 2- and 4-. There was only one
aromatic singlet (at γ 2.58, one proton), which confirmed
that all three methyl groups were attached to the same
benzo ring. This aromatic singlet was assigned to a
proton in the 3-position rather than the 1-position
because of the relatively high field at which it occurred
compared with the other aromatic peaks. Thus, this con-
firmed the presence of the third methyl group in the
1-position. The remaining aromatic peaks consisted of
two multiplets which were assigned to the four aromatic
protons on the other benzo ring.

The structure of the trimethylbenzo[c]cinnoline (LV)
suggests that a 1,2-shift of a methyl group occurred during
cyclization; but this does not account for the methyl groups
actually eliminated during the formation of 2,4-dimethyl-
benzo[c]cinnoline (LVII).

Accordingly the rearrangement products were
chromatographed; but the only product obtained in sig-
nificant yield was the trimethylcyclohexadienone (LVI).
Presumably this was formed from the imine (LVIII) by an
abnormal rearrangement of 2,4,6-trimethylhydrazobenzene
(LIX) analogous to the abnormal rearrangement of 4-methyl-
hydrazobenzene (see p. 15). The structure of the
trimethyldienone was established by infrared and n.m.r.
spectroscopy, and by dienone-phenol rearrangement to

4-amino-3'-hydroxy-2',4',6'-trimethylbiphenyl (LX).
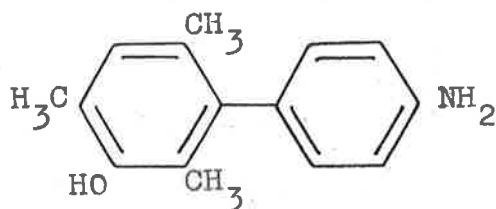
(LX)

The n.m.r. spectrum of the dienone showed a sharp singlet
at τ 8.47 assigned to the 4-methyl group, and a sharp singlet
at τ 8.17 assigned to the 2- and 6-methyl groups.   The
dienone protons (3- and 5-) gave a sharp singlet at τ 3.48,
and the four aromatic protons gave a quartet centred at
about τ 3.3.

The structure of the phenol (LX) was established by
infrared, ultraviolet, and n.m.r. spectroscopy.   Its
n.m.r. spectrum showed that the hydroxyl group must be in
the 3'-position (cf.p.18).   To show this it is important
to note that a hydroxyl group in a benzene ring causes a
shift of +0.37 ppm in the resonance of o-, m-, and
p-aromatic protons,[49] and it is probable that there is an
equal (but smaller) effect on the resonance positions of
o-, m-, and p-aromatic methyl protons.   Hence the sharp
singlet at τ 7.75 (three protons) may be assigned to the

4'-methyl group and the sharp singlet at τ 8.05 (six
protons) must be due to the methyl groups in the 2'- and
6'-positions, twisted into the shielding region of the
aminophenyl ring.   The fact that there were no aromatic
protons below τ 3.13 supports the presence of a 2',6'-
dimethylbiphenyl structure.

If the methyl group had migrated in the dienone-phenol
rearrangement, the product would have been 4-amino-4'-
hydroxy-2,3,5-trimethylbiphenyl (LXI).   Here one would
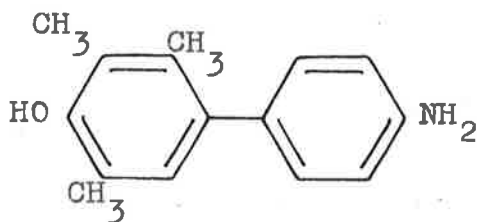
(LXI)

expect a 3,5-dimethyl singlet (six protons) to occur at a
field lower than a 2-methyl singlet (three protons).

Thus the fate of the eliminated methyl groups has not
been elucidated.   The formation of tar, however, appears
to be a feature common to the photochemical cyclization
o-methylazobenzenes, and the yield of tar appears to
increase as the proportion of methyl elimination increases.

Moreover the total yield of cyclised product decreases
with an increasing proportion of methyl elimination (see
Table 4). In fact the tar may hold the answer to the
fate of the eliminated methyl groups; for no tar was
obtained from azo compounds other than 2,2'-dimethyl-
azobenzene, 2-methylazobenzene, and 2,4,6-trimethyl-
azobenzene.

TABLE 4.

Cyclization products from azobenzenes containing o-methyl groups

Azobenzene derivative	Benzo[c]cinnolines (%)			
	No elimination	Elimination	Rearrangement	Total
2-Methyl-	23	11	—	35
2,2'-Dimethyl-	10	19	0.4	30
2,4,6-Trimethyl-	—	20	2	22

(e) Attempts to increase the yield of benzo[c]cinnolines

The formation of the rearrangement products of
hydrazobenzenes in the photochemical cyclization of azo-
benzenes has no synthetic value, except perhaps for the
production of the unusual dienones. To reduce the yield
of the intermediate hydrazobenzenes several dehydrogenating
agents were added to compete with the protonated azobenzene.

Nitrobenzene, p-nitrobenzaldehyde, chloranil,
9,10-phenanthraquinone, 4-dimethylaminoazobenzene, and
4-methoxyazobenzene in turn were irradiated with azobenzene
in 22N sulphuric acid on a spectroscopic scale.   Where
necessary, some ethanol was added as a co-solvent.   There
was, however, no indication of an increased yield of
benzo[g]cinnoline, except for the possibility of a slight
improvement in the yield when using a 50-fold molar excess
of nitrobenzene.   This would be useless for preparative
work.

The addition of benzil and of 1,2-naphthoquinone-4-
sulphonic acid to the reaction mixture was investigated on
a preparative scale.   The latter compound itself appeared
to undergo a photochemical change in the sulphuric acid and
was therefore unsatisfactory.   With benzil as the added
dehydrogenating agent, the reaction was performed in 89%
w/w sulphuric acid, the strength of which was just sufficient
to dissolve the benzil.   When 0.3 g of azobenzene was used
the reaction required three months exposure to sunlight for
completion.   Benzil was recovered unchanged and the yield
of benzo[g]cinnoline was only 41%.   There was no sign of
any phenanthraquinone in the recovered benzil.

There appears to be a considerable problem in competing
with the protonated azobenzene as the dehydrogenating agent.

Azobenzene in sulphuric acid was found to abstract hydride
ions from a number of organic compounds such as n-hexane,
cyclohexane, cyclohexanone, acetone, benzaldehyde, formic
acid, acetic acid, succinic acid, nitrobenzene, benzene,
thiophene, dibutyl ether, and benzyl alcohol.[23]   A more
fruitful investigation could involve the use of dehydro-
genating agents in solvents which would not protonate the
azo compound.   This would more closely resemble the
photochemical cyclization of azobenzene described by
Hugelshofer, Kalvoda, and Schaffner.[4]

(f)   Separation of mixtures of benzo[c]cinnolines.

        In the study of the preparative photochemistry of
o- and m-substituted azobenzenes it was necessary to
devise satisfactory methods for separation of the mixtures
of benzo[c]cinnolines.   Fractional crystallization was
generally found to be unsatisfactory as yields could not
be determined with any precession.   Chromatography on
alumina was useful only for the separation of 4,7-dimethyl-
benzo[c]cinnoline (XLIV) from 4-methylbenzo[c]cinnoline
(XLV, R=CH$_3$) and the unknown dimethylbenzo[c]cinnoline
(XLVI).   With other compounds little or no separation was
achieved and the use of silica-gel as absorbent gave no
advantage.

        It was found that the distribution coefficients of a

number of methyl- and dimethylbenzo[g]cinnolines differed
widely when using the system hexane-dilute hydrochloric
acid, and that the distribution coefficients could be
adjusted to an appropriate range by varying the acid con-
centration. Countercurrent distribution using this type
of system was very satisfactory. Separation of
benzo[g]cinnoline mixtures generally appeared to depend on
the solubility of the components in the light petroleum,
provided that the components had approximately equal
basicities. For example, in the separation of products
from g-substituted azobenzenes the solubility of the com-
ponents in light petroleum paralleled the degree of steric
strain in the molecule, and in fact the components were
separated in this order. The solubility of both 1- and
3-iodobenzo[g]cinnoline in light petroleum was very low,
and benzene-light petroleum was used as the moving layer.
However, this eliminated all separation and the distribution
had to be repeated using hexane and 4N hydrochloric acid.

When there were considerable differences in the
basicity of the components, the less basic component
usually moved faster than the more basic one. For example,
in the separation of 4-halogenobenzo[g]cinnolines from
benzo[g]cinnoline, the latter was a little more soluble in
the organic layer than the 4-halogenobenzo[g]cinnolines.
The 4-halogenobenzo[g]cinnolines apparently were much less

basic, and in the countercurrent distribution they moved
faster than benzo[c]cinnoline. Here the use of benzene
in the moving layer did not upset the separation.

Some investigations with paper and thin-layer
chromatography were also carried out, as it was desirable
to have a method for testing the efficiency of the separa-
tions when using countercurrent distribution. Partially
acetylated paper[50] and thin-layers of partially acetylated
cellulose[51] gave negligible separation of benzo[c]cinnolines
using the systems methanol-ether-water (4:4:1) or ethanol-
toluene-water (17:4:1). Paper chromatography using butanol-
3N hydrochloric acid also gave no separation. With acetic
acid-water-hexane mixtures, streaky chromatograms were
produced. The most satisfactory system was thin-layer
chromatography using silica-gel with benzene-ether in
varying proportions, according to the compounds being used.
Nevertheless, the degree of separation of components in a
mixture was often very small, and the Rf values were
noticeably dependent on the load of material.

2.3 The Preparation of Benzo[c]cinnolines

To assess the photochemical formation of benzo[c]cinnolines
from azobenzenes as a synthetic method, it is necessary to
examine the other methods which have been used to prepare

benzo[c]cinnolines. There are two logical approaches.
First, starting from a biphenyl, an azo linkage has to be
formed across the 2,2'-position. Secondly, starting with
a -N=N- or -N-N- linkage between two aryl groups, cyclo-
dehydrogenation has to be effected at the 2,2'-positions.
The first approach has been used to a far greater extent
than the second.

Tauber[52] first prepared benzo[c]cinnoline by reduction
of 2,2'-dinitrobiphenyl (LXII) with sodium analgam and
methanol. Ever since, the reduction of 2,2'-dinitrobiaryls
has been the most important method for the preparation of
benzo[c]cinnolines and also many polycyclic cinnolines. A
large number of reducing methods have been used. They include
electrolytic reduction,[53,54] chemical reduction with zinc dust
and alkali,[52,55,56] sodium amalgam,[52,56,57] lithium aluminium
hydride,[56,58,59] ferrous oxide,[60] iron,[61] and catalytic
hydrogenation with platinum oxide,[62] or Raney nickel.[63]

In the reduction of 2,2'-dinitrobiphenyl, other products
along the reduction sequence may be formed, such as
benzo[c]cinnoline di-N-oxide (LXIII),[52] benzo[c]cinnoline
N-oxide (IL),[52,64] and 5,6-dihydrobenzo[c]cinnoline (LXIV).[65]
The extent of reduction is probably very sensitive to the
reaction conditions because different results have been
obtained when different groups of workers have used the same
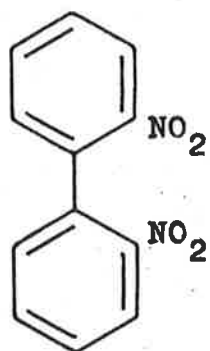
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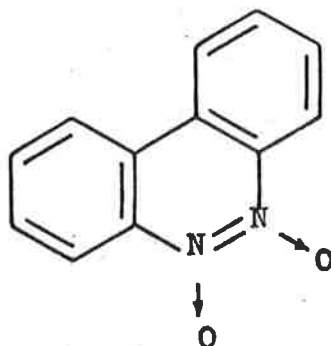
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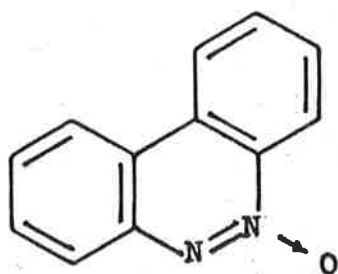
(IL)
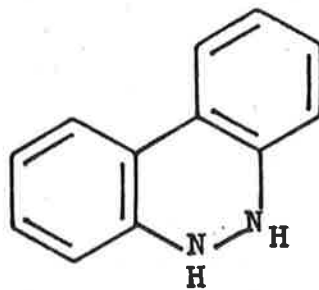
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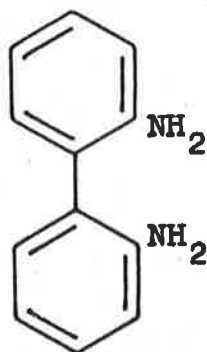
(LXV)

methods.[55,58]   In certain cases, reduction has yielded
2,2'-diaminobiaryls.   This occurred in the reduction of
2,2'-dinitrobiphenyl with Raney nickel[55] or with zinc and
hydrochloric acid;[52] 2,2'-diaminobiphenyl (LXV) was formed.
The most reliable methods appear to be the reduction of a
2,2'-dinitrobiaryl to a benzo[c]cinnoline N-oxide using
sodium sulphide[64] or sodium polysulphide,[56] followed by
reduction to the benzo[c]cinnoline electrolytically[64] or
with lithium aluminium hydride,[58] or direct reduction of
the nitro compound electrolytically,[53,54] or with lithium
aluminium hydride.[56,58,59]   The yields are generally very
good.

The azo linkage has also been formed across the
2,2'-position of biaryls from 2,2'-diaminobiaryls.   The
methods include reduction of the tetrazotized biaryl with
sodium arsenite and copper sulphate,[66,67] or direct
oxidation of the diaminobiaryl with sodium perborate.[68]
Oxidation with hydrogen peroxide in acetic acid has been
shown to give benzo[c]cinnoline N-oxides.[68] The yields in
these oxidations were excellent for the preparation of simple
benzo[c]cinnolines, but only moderate to poor for higher
polycyclic cinnolines.[68]   The oxidation method is advan-
tageous when the reduction of a 2,2'-dinitrobiaryl would
remove labile groups (e.g., some halogens).[69]   The
-N=N-linkage has been formed from 2-amino-2'-nitrobiphenyls.[70]

Very recently Dewar reported a new synthesis of
benzo[g]cinnoline.[71] 10-Methoxy-10,9-borazorophenanthrene
(LXVI) was diazotized to give the diazoarylboronic acid
(LXII) which on standing gave benzo[g]cinnoline in 98%
yield. Polycylic cinnolines were prepared similarly.[71]
Borazarophenanthrenes may be prepared by heating
2-aminobiphenyl (LXVIII) and boron trichloride in benzene
to give 2-biphenylylaminoboron dichloride (LXIX) which then
undergoes a Friedel-Crafts cyclization with aluminium
chloride to give 10-chloro-10,9-borazarophenanthrene (LXX).
The chloro compound is readily hydrolysed to the hydroxy
compound (LXXI) which may be diazotized directly, or first
methylated.

The advantage of the method is that only one functional
group is initially required where the N=N linkage is to be
formed. Difficulty could be experienced, however, in
preparing benzo[g]cinnolines substituted in the 4- or
7-positions as the Friedel-Crafts cyclization to give the
borazaro compound is inhibited by g-substituents.[72] More-
over, substituents in the ortho-position of 2-aminobiphenyl
are known to prevent the Friedel-Crafts cyclization, presumably
because of steric hindrance to coplanarity in the biphenyl.[73]

The main disadvantage of these methods involving biaryls
is that the Ullmann reaction, by which they are usually
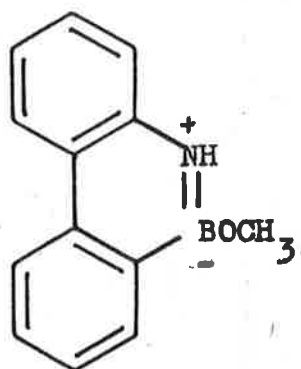
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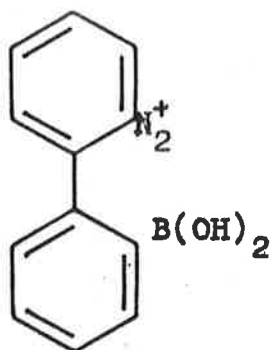
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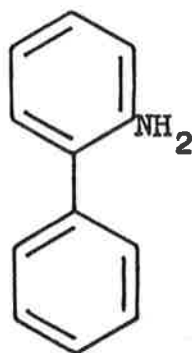
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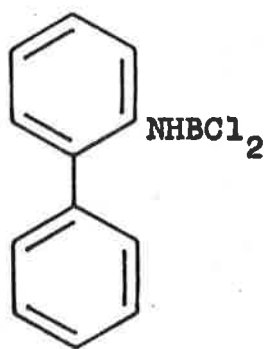
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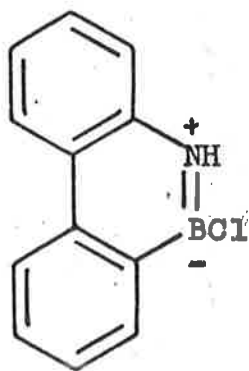
(LXX)
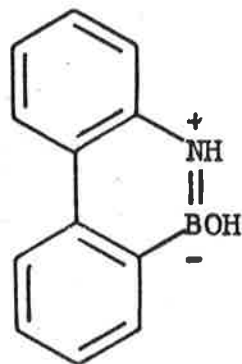
(LXXI)

prepared, often gives a very low yield.[68] Also the
synthesis of some benzo[g]cinnolines requires mixed
Ullmann reactions, giving mixtures of biaryls which are
difficult to separate.

The second main method for the preparation of
benzo[g]cinnolines involves the cyclization of compounds of
the type Ar-N=N-Ar, where a new C-C bond is formed between
the 2- and 2'-positions. This has been accomplished by
the thermal or photochemical cyclization of azo compounds,
by the photochemical cyclization of 2,3-diaryltetrazolium
salts, and by the cyclodehydration of cyclohexane-1,2-dione-
1-arylhydrazones, followed by catalytic dehydrogenation.

Several azo compounds have been cyclized in a melt
of aluminium chloride and sodium chloride[5] or by heating an
azo compound with aluminium chloride in dichloromethane
under reflux.[74] A summary of the reaction conditions and
yields of some benzo[g]cinnolines obtained by this method is
shown in Table 5. In addition to sodium chloride, potassium
chloride and sodium fluoride have been used to lower the
melting point of aluminium chloride mixtures.[5,57] Polycyclic
cinnolines have been successfully prepared from azonaphthalenes
and 2-phenylazonaphthalene.[74] The advantage of the cycliza-
tion of azo compounds is that they can be prepared in good
yields from readily accessible starting materials.   Un-

TABLE 5.

Thermal formation of benzo[c]cinnolines from azobenzenes

Azobenzene derivative	Medium	Temperature	Time (hr)	Benzo[g]cinnoline derivative and yield	Reference
Azobenzene	$AlCl_3$, NaCl (under nitrogen)	120^0	20	Benzo[c]cinnoline (60%)	5
Azobenzene	$AlCl_3$, NaCl, KCl, NaF (under oxygen)	60^0	30	Benzo[c]cinnoline (45%)	5
Azobenzene	$AlCl_3$, NaCl, KCl, MnO_2	90^0	6	Benzo[c]cinnoline (40%)	5
Azobenzene	$AlCl_3$, trichlorobenzene	80^0	12	Benzo[c]cinnoline (20%)	5
Azobenzene	$AlCl_3$, pyridine	140^0	48	Benzo[c]cinnoline (10%)	5
3,3'-Dimethyl-	$AlCl_3$, NaCl	100^0	0.5	3,8-Dimethyl- (25%)	5
4-Dimethylamino-	AlCl , NaCl, KCl, NaF	$88-93^0$	3.5	2-Dimethylamino- (30-31%)	57

57.

symmetrical azo compounds are also simple to prepare. The main disadvantage of the method is that p-substituted azobenzenes may give mixtures of benzo[c]cinnolines.

2,3,5-Triphenyltetrazolium chloride (LXXII) in aqueous solution has been shown to undergo a photochemical change to give the formazan (LXXIII).[75] In ethanolic solution, however, the tetrazolium salt photocyclizes to give 2,3-diphenylene-5-phenyltetrazolium chloride (LXXIV). Reduction of this photoproduct with Raney nickel gives benzo[c]cinnoline in almost quantitative yield.[24] Table 6 shows a summary of the benzo[c]cinnolines which have been obtained by this method. The benzo[c]cinnolines so obtained served to prove the structures of the photoproducts. For preparative purposes the yield on hydrogenation and subsequent isolation could possibly be improved. The tetrazolium salts may be prepared by the reaction of an arylhydrazone of an aliphatic or aromatic aldehyde with an aryl diazonium salt to give a formazan. The formazan may be oxidized to the 2,3-diaryltetrazolium salt with nitric acid in ethyl acetate, lead tetraacetate in chloroform, N-bromosuccinimide in ethyl acetate, or amyl nitrite and hydrochloric acid in chloroform.[24,76,77] The synthesis is illustrated in Scheme 3. The yields of tetrazolium salts are usually very good, and a wide range

TABLE 6.

Benzo[c]cinnolines from the photoproducts of 2,3-diaryltetrazolium salts[24]

Tetrazolium salt Anion and scale in parenthesis	Yield (%) of Photoproduct	Irradiation time (hr)	Hydrogenation products Yield (%) in parenthesis
2,3,5-Triphenyl- (chloride, 5 g)	80	24	Benzo[g]cinnoline (Almost quantitative)
2,3-Diphenyl-5-methyl- (chloride, 1.9 g)	42	8	Benzo[g]cinnoline (Almost quantitative)
2,3-Diphenyl- (bromide, 1 g)	69	40	Benzo[c]cinnoline (Almost quantitative)
2-(4-chlorophenyl)-3,5-diphenyl- (nitrate, 1 g)	73	30	2-Chlorobenzo[g]cinnoline (53)
2-(3-chlorophenyl)-3,5-diphenyl (nitrate, 2 g)	85	15	1-Chlorobenzo[g]cinnoline[+] (32)

+ Jerchel and Fischer considered this product to be
   3-chlorobenzo[g]cinnoline but it now seems that it
   is the 1-isomer (see p. 31).

TABLE 6.

(Continued)

Tetrazolium salt Anion and scale in parenthesis	Yield (%) of photo-product	Irradiation time (hr)	Hydrogenation products Yield (%) in parenthesis
2-(3,4-dichlorophenyl)-3,5-diphenyl- (nitrate, 1 g)	40	60	2,3- and 1,2-dichlorobenzo[c]-cinnolines (No yield stated)
2,3-Di-(3-chlorophenyl)-5-phenyl- (nitrate, 1 g)	35	40	3,8- and 1,8-dichlorobenzo[c]-cinnolines. (47)
2-(3-methoxyphenyl)-3,5-diphenyl- (nitrate, 1 g)	40	80	1- and 3-methoxybenzo[c]-cinnolines. (46)
2-(4-carboxyphenyl)-3,5-diphenyl- (bromide, 2 g)	65	24	Benzo[c]cinnoline-2-carboxylic acid. (40)
2-(4-ethoxycarbonylphenyl)-3,5-diphenyl- (bromide, 2 g)	83	8	Methyl benzo[c]cinnoline-2-carboxylate. (94)

(LXXII)   Cl⁻   (LXXIV)   Cl⁻

(LXIII)
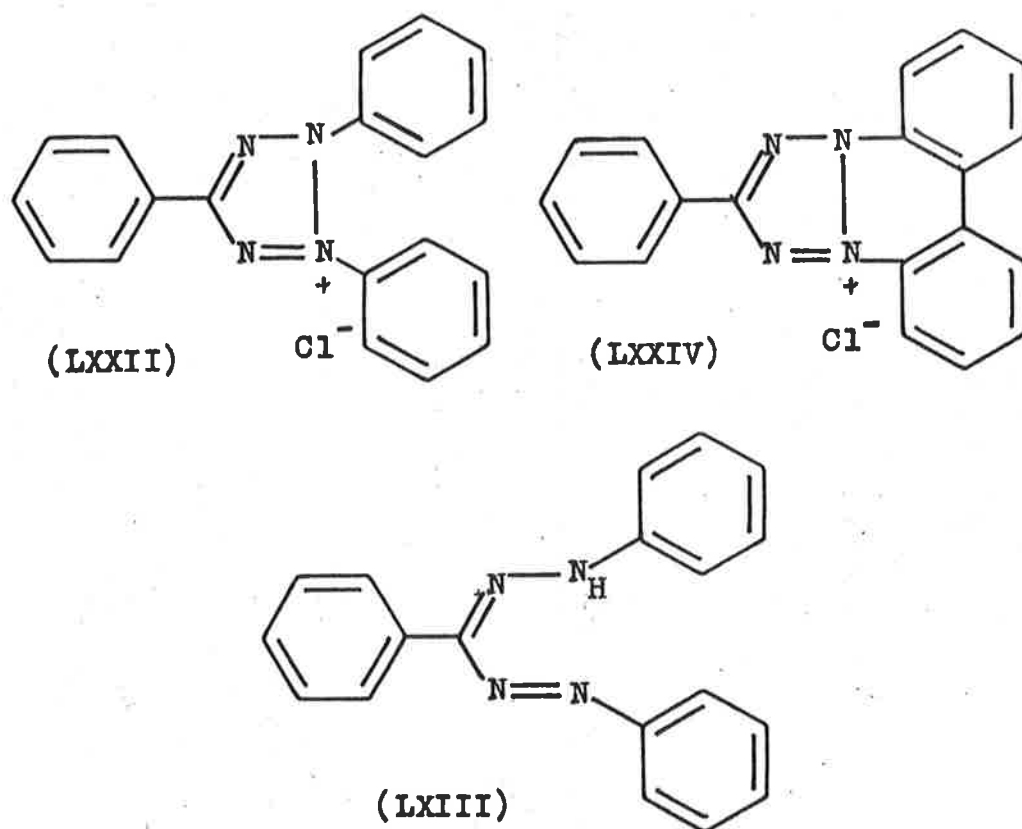
SCHEME 3 —— Formation of 2,3-diaryltetrazolium salts.

Oxidation
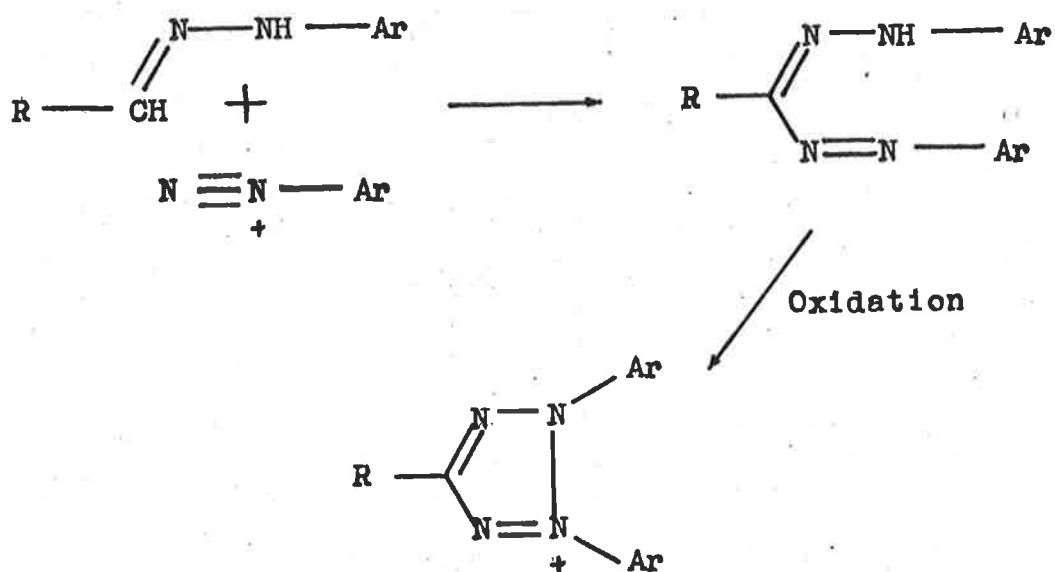
of derivatives can be made.   Certain tetrazolium salts
failed to undergo a photochemical cyclization.[24]   These
had biphenylyl, 1- or 2-naphthyl, p-nitrophenyl, or
p-methoxyphenyl substituents in the 2- or 3-position of
a tetrazolium halide.

1,2,3,4-Tetrahydrobenzo[g]cinnolines may be formed by
the cyclodehydration of cyclohexane-1,2-dione-1-phenylhydra-
zones, using concentrated sulphuric acid (see Scheme 4).[78]

SCHEME 4   ———   Formation of

1,2,3,4-tetrahydrobenzo[g]cinnolines.
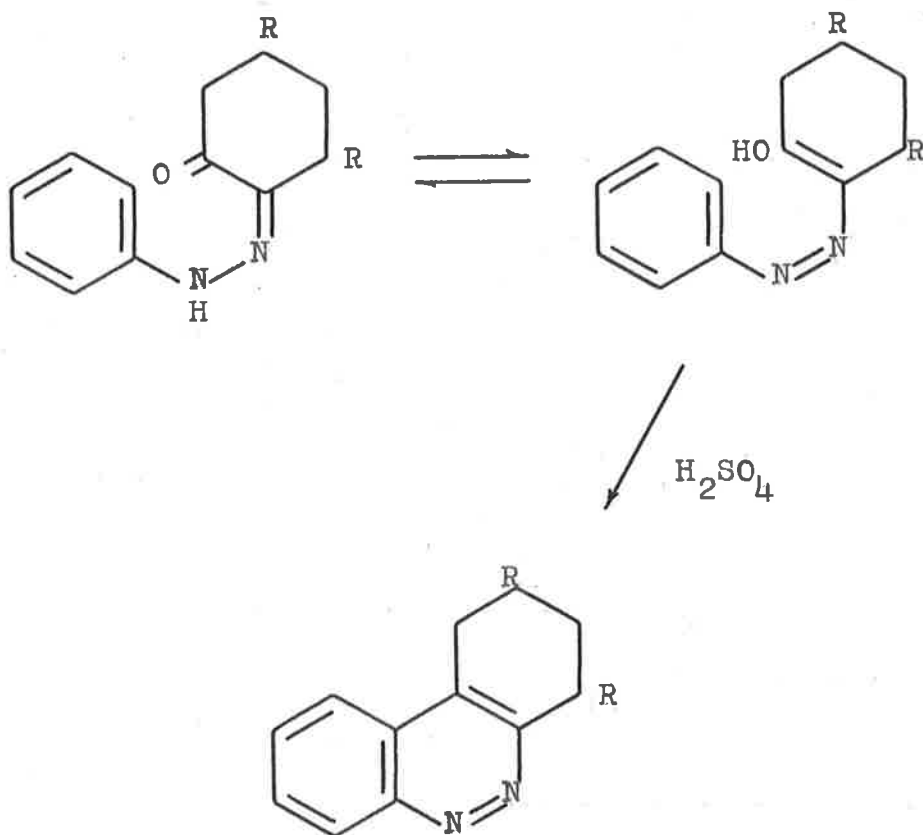
When R=methyl, an 85% yield was obtained, but when R=H only
a 15% yield of tetrahydrobenzo[g]cinnoline was obtained.
Braithwaite and Robinson[79] have used the method to prepare
higher tetrahydro polycyclic cinnolines in moderate yields.
These were dehydrogenated with palladium on carbon in boil-
ing naphthalene to give the fully aromatic compounds in
good yield.   The scope of this method has not been very
well explored.

Once the benzo[c]cinnoline nucleus has been formed,
several substituted derivatives may be obtained by nitra-
tion with subsequent reactions involving the nitro group.
Direct bromination has not been very satisfactory as much
starting material was recovered, and 1-Bromobenzo[c]cinnoline
(XL, R=Br) was obtained in only 27% yield.[45]

Several groups of workers have shown that
benzo[c]cinnoline undergoes nitration with nitric and
sulphuric acids to give 1-nitrobenzo[c]cinnoline (XL, R=NO$_2$)
and some 4-nitrobenzo[c]cinnoline (XLV, R=NO$_2$).   The ratio
of the two isomers was about 4:1 respectively,[80] and no
3-nitrobenzo[c]cinnoline (XXXIX, R=NO$_2$) was found.[81]
Nitration of benzo[c]cinnoline N-oxide with nitric acid
and sulphuric acid gave 1- and 4-nitrobenzo[c]cinnoline
N-oxides,[81] but when fuming nitric acid alone was used
2-nitrobenzo[c]cinnoline N-oxide was formed in good
yield.[81,82]   Further nitration of benzo[c]cinnoline

affected the 1-isomer only, yielding 1,10-dinitro-
benzo[c]cinnoline (LXXV).[83]
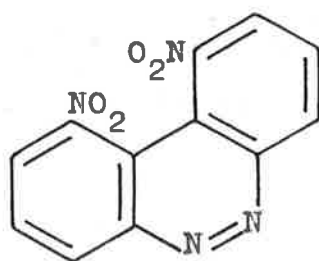
(LXXV)

The nitro and dinitrobenzo[c]cinnolines and their
N-oxides have been reduced to the corresponding
aminobenzo[c]cinnolines, and the amino groups have been
replaced with halogens in many examples.[80,81,83]

In conclusion it may be said that the synthesis of
unsymmetrical benzo[c]cinnolines from compounds of the
type Ar-N-N-Ar has the advantage over the method using
biaryls; but this advantage is lost when cyclization can
occur to give mixtures.   The photochemical cyclization
of azobenzenes at present appears to have no particular
synthetic advantage over the thermal cyclization of
azobenzenes or the photochemical cyclization of
tetrazolium salts.

2.4 Preparation of Azo Compounds

3,3'-Dimethylazobenzene[84] and 4-iodoazobenzene were
kindly supplied by Dr. G. E. Lewis.   The azobenzene-4-
carboxylic acid used was a recrystallized commercial
sample.   The other azo compounds were prepared by
standard methods.   2,2'-Dimethyl- and 4,4'-dimethyl-
azobenzene were prepared by reduction of the appropriate
nitrotoluenes.   The monosubstituted azobenzenes were
obtained by condensation of nitrosobenzene with the
appropriate substituted aniline.   When 2-substituted
anilines were used it was often necessary to warm the
mixture to effect the condensation.   This caused some
of the nitrosobenzene to decompose.   All the azo com-
pounds, however, were chromatographed on alumina, followed
by recrystallization or distillation.   Azobenzene-2-
carboxylic acid and azobenzene-3-carboxylic acid were
prepared _via_ their ethyl esters so that the esters
could be purified by chromatography on alumina before
being hydrolysed to the acids.

CHAPTER III

PHOTOCHEMICAL KINETICS

3.1 Introduction

The usual aim of a kinetic study of a photochemical
reaction is to determine its quantum yield.   This may be
defined as the number of molecules formed (or transformed)
per quantum of light absorbed by the reacting system.
Modification of this definition may be necessary in a com-
plex reaction where the reactant or reactants may give
several products in different molar proportions.   Thus it
should be specified as to which product or reactant the
quantum yield refers.   Allowance for competitive absorption
by non-reactive species may also be necessary.

Quantum yields can provide valuable information on the
mechanism of a photochemical reaction, especially if the
effect of temperature, concentration of reactants, wavelength
of light used, light intensity, and the medium are determined.
It was considered important to measure the quantum yield of
the photochemical cyclization of azobenzene, and some deriva-
tives.   Azobenzene and its 4-chloro- and 4-methyl- derivatives
were investigated because only one cyclized product was
obtained from each compound and the corresponding cis-azo

compounds were known. The rate of reaction was found to be proportional to the rate of light absorption. Most of the quantum yields were determined at 25° using the 436 mμ mercury line. The quantum yield was found to decrease with an increase in the sulphuric acid concentration, and there was no apparent relationship between the quantum yields and the Hammett σ-constants of the substituents. Azobenzene was also irradiated at 15° with 436 mμ light and at 25° with 405 mμ light, but for a given acid concentration, any change in the quantum yield was small.

These investigations did not cover all the variables, so there are gaps in the understanding of the reaction. Nevertheless, some difficulties in the accurate measurement of the quantum yields were overcome and hence further work should be somewhat more straightforward.

Accurate, meaningful quantum yields should be measured with monochromatic light, as the extinction coefficient of the reactant and the quantum yield may vary with wavelength. Mercury lamps are generally used and the desired emission line (or lines) is selected with a prism monochromator or appropriate filters which absorb the unwanted emission. For this work appropriate filter solutions were used in conjunction with a high pressure mercury lamp. To measure the quantum yield, the rate of the photochemical reaction and the rate of

absorption of light quanta by the system must be determined.
Spectrophotometric measurement was used to measure the rate
of the photochemical reaction of the azobenzenes.

The rate of absorption of quanta may be determined with
a calibrated thermopile, or photocell, or by chemical actino-
metry.   A thermopile can be calibrated against the emission
from a true black body, but this is difficult in practice.[85]
A standard lamp, for which the total emission has been
determined, can be used to calibrate a thermopile-galvano-
meter system.   The response of a photocell is dependent on
the wavelength of the light, and hence it cannot be calibrated
with a standard lamp.   However, if a suitable monochromatic
source is used, a photocell may be calibrated against a prop-
erly calibrated thermopile for the particular wavelength used.

When either a thermopile or a photocell is used to
measure the absolute value of the incident radiation, measure-
ments must be made systematically over the entire cross-
sectional area of the light beam entering the reaction vessel.
The intensity must be integrated over this area and also with
respect to time, as fluctuations in the lamp occur almost
invariably.   If all due care is used, an accurate value of
the incident radiation in quanta per unit time can be obtained.

An actinometer consists of a chemical system which under-
goes a photochemical reaction of known quantum yield for a

given wavelength. Originally the quantum yield would have
been determined by exhaustive comparisons with a calibrated
thermopile at various wavelengths. The percentage absorption
of the actinometer system should be measured at the wavelength
being used, as the obvious correction must be applied to
allow for the light transmitted by the actinometer. If the
percentage absorption changes during exposure of the actinometer
to light, the absorption would have to be integrated over the
exposure time. For slight changes in the absorption, the
arithmetic mean of the initial and final values would be
sufficiently accurate, provided that the products in the actino-
meter reaction do not absorb significantly at the wavelength
of irradiation.

The use of an actinometer to determine the incident
light intensity has many advantages over the thermopile or
photocell. Integration over time and area of the light beam
occurs naturally if the entire beam is absorbed by the
actinometer and if the time of exposure is long, relative to
fluctuations in the light source. Furthermore, if the
actinometer cell and reaction cell are placed in an identical
environment with respect to the light source, the reflection
losses at the cell faces may be neglected. If, however, the
actinometer cell is placed behind the reaction cell, as is
often done,[35] then a correction for reflected light must be
made if accurate results are to be obtained.

The actinometer system most commonly used for many years has been uranyl oxalate.[86] This system has many desirable features, e.g. small variation of quantum yield with wavelength, small temperature dependence, a rate of reaction proportional to the first power of the light intensity, and no troublesome side reactions. It involves the reaction

$$H_2C_2O_4 \xrightarrow[\text{light}]{UO_2^{++}} H_2O + CO_2 + CO$$
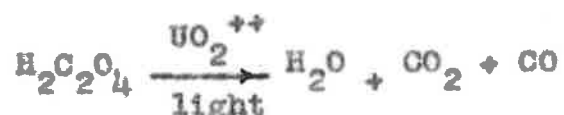
and at $25°$ the quantum yield for the disappearance of oxalate ranges from 0.60 at 254 mμ to 0.58 at 436 mμ with a minimum of 0.49 at 366 mμ. It is an exceptionally useful system for measuring large quantities of light. Normally the uranyl oxalate is titrated with potassium permanganate before and after irradiation; the difference between the two titrations allows the light intensity to be calculated. The sensitivity may be improved greatly by the addition of excess ceric sulphate, which oxidizes the residual oxalate. The unused ceric ion can be estimated spectrophotometrically.[87] Recently, gas chromatography has been used to measure the carbon monoxide formed, and this has increased the sensitivity of the system by a factor of about 3000.[88]

For the study of the photochemistry of azobenzenes, the uranyl oxalate system as normally used,[86] and also with the ceric sulphate modification,[87] was considered insufficiently

sensitive. The method using carbon monoxide analysis[88] was considered too sensitive. Furthermore, the absorption of uranyl oxalate in a 1 cm cell is inconveniently low at 436 mµ, at which wavelength most of this work was to be carried out.

Potassium trisoxalatoferrate(III) (potassium ferrioxalate), however, appeared well suited as an actinometer system,[89] and was found to be very satisfactory. The reaction proceeds according to equation (3.1). The system is virtually

$$2[Fe(C_2O_4)_3]^{3-} \longrightarrow 2Fe(C_2O_4) + 3[C_2O_4]^{2-} + 2CO_2 \quad (3.1)$$
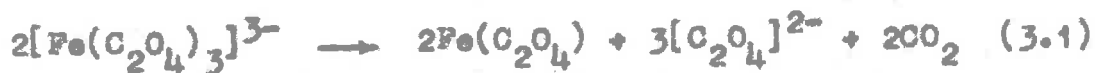
insensitive to oxygen, and is claimed to have a linear response to the light absorbed, up to 72% decomposition.[90] The ferrous ion formed is estimated spectrophotometrically using 1,10-phenanthroline.

The ferrioxalate system is more sensitive than the ceric sulphate modification of the uranyl oxalate system for several reasons. Its quantum yield is about twice that of the uranyl oxalate system; below 450 mµ it absorbs more strongly than uranyl oxalate, which is important when cell paths of only 1 cm are being used; and the extinction coefficient of ferrous phenanthroline at its $\lambda_{max.}$ is about twice that of the ceric ion at its $\lambda_{max.}$.

The rate of the photochemical cyclization of azobenzenes could be obtained either from the rate of disappearance of the azo compound, or from the rate of formation of the products.

It was much more convenient to measure the disappearance of
the azo compound as these measurements were made at the same
wavelength as the irradiating light.   From the preparative
studies described in Chapter II it may be assumed that the
rate of disappearance of azo compound is linearly related to
the rate of formation of cyclized product, although the con-
version factor would have to be determined.   A suitable
differential equation was required to relate the observed rate
of decrease of the absorption to the proportion of incident
light absorbed by the reacting species.

As a first approximation, absorption of light by the
reaction products was neglected.   At 436 mμ, this is a
reasonably good approximation.   Equation (3.2) is the required
differential equation and its derivation is described in
Appendix I.   D is the measured optical density at the wave-

$$\frac{dD}{dt} = K(1-10^{-D}) \tag{3.2}$$

length of irradiation, t is the time, and K is the rate constant
having units of time^{-1}.   Integration of equation (3.2) gives
equation (3.3), where D_o is the initial value of D.

$$\log_{10}(10^{D_o}-1) - \log_{10}(10^{D}-1) = Kt \tag{3.3}$$

Azobenzene in 22N sulphuric acid was irradiated with a
constant source of 436 mμ light and D was measured at this
wavelength as a function of time.   A graph of $-\log(10^{D}-1)$

against time gave a straight line after the cis-trans
equilibrium had been reached, but toward the end of the run,
there was a deviation from linearity.   Accordingly, allowance
was made for the absorption due to benzo[c]cinnoline formed
in the reaction.   The derivation of the improved differential
equation (3.4) is described in Appendix II; b is the fraction

$$-\frac{dD}{dt} = \frac{bk}{z}(1-\frac{D_\infty}{D})(1-10^{-D}) \tag{3.4}$$

of light absorbed by the reacting species relative to the
light absorbed by all the azo compound, k is the rate constant
for the actual cyclization process in units time^{-1}, z is the
yield fraction of the cyclized product, and D_∞ is the value of
the optical density after all the azo compound has been con-
sumed.   Since this work was carried out, Kling, Nikolaiski,
and Schläfer[91] have published a similar derivation which
agrees with the one described in Appendix II.

Equation (3.4) does not integrate to give an elementary
solution, and it was found convenient to integrate it numer-
ically, using an I.B.M. 1620 computer.   Tables of

$$-\int_3^D \frac{dy}{(1-\frac{D_\infty}{y})(1-10^{-y})}$$

for values of D_∞ ranging from $D_\infty = 0$ to 0.30 at 0.01 intervals
were computed.   The integration range of 3 to D was chosen
arbitrarily as, in this work, an initial optical density of
3 would not be exceeded.   For each value of D_∞ the intervals

of D were 0.2 from 3.0 to 2.0, 0.1 from 2.0 to 1.0, and 0.04
from 1.0 to D_∞ + 0.04. A graph of the appropriate integral
against time was found to give a straight line (slope = bk/z)
after cis-trans equilibrium had been reached, and showed no
significant deviation from linearity towards the end of the
run. This helped to confirm the validity of equation (3.4).

At cis-trans equilibrium, b is assumed to be constant
and may be determined experimentally. As the constant z may
be measured, the value of k $(time^{-1})$ may be determined from
the slope of the linear portion of the graph. The rate
constant of the cyclization reaction, k', (moles. $time^{-1}$) is
given by

$$k' = \frac{k.v}{\varepsilon^e 1} = \frac{Slope.z.v}{\varepsilon^e.b.l} \tag{3.5}$$

where ε^e is the decadic molar extinction coefficient of the
equilibrium cis-trans mixture, l is the length of the optical
path in the reaction cell (cm), and v is the volume of the
solution in the reaction cell (l.). The quantum yield of
the cyclization process (ø), is given by

$$ø = k'/Q \tag{3.6}$$

where Q is the amount of light entering the reaction solution
with units einsteins. $time^{-1}$. An einstein is Avogadro's
number of quanta (i.e. 6.023×10^{23}).

3.2 Experimental

(a) Apparatus

The accuracy of all volumetric glassware was checked
with water at 20°, and the maximum error allowed was ± 0.2%.

The irradiations for the determination of quantum yields
were performed in an apparatus illustrated in Fig. 2 (approx-
imately half scale). The light source (1), a Philips HPK
125W high pressure mercury lamp, was enclosed in a housing (2)
which allowed some ventilation. The light passed through a
series of masks (3) to remove reflected light, and then passed
the shutter (4) into a 1 cm glass cell (5) which contained
water to remove most of the heat. The 0.5 cm filter cell (6)
contained the appropriate solution to select the desired
mercury line. Both filter cells (5) and (6) were masked to
prevent reflection from their side walls. The filtered light
was passed through two identical slots (7), each with an
effective area of approximately 1.6 sq. cm. The slots were
symmetrically placed in the light beam to divide the latter
into two equal portions, and had a width of 0.6 cm so that the
two light beams were not reflected by the side walls of the
matched 1 cm quartz cells (8). The cells each had a con-
stricted neck, designed for a ground glass stopper. In a
given experiment, one cell was used for the actinometer and
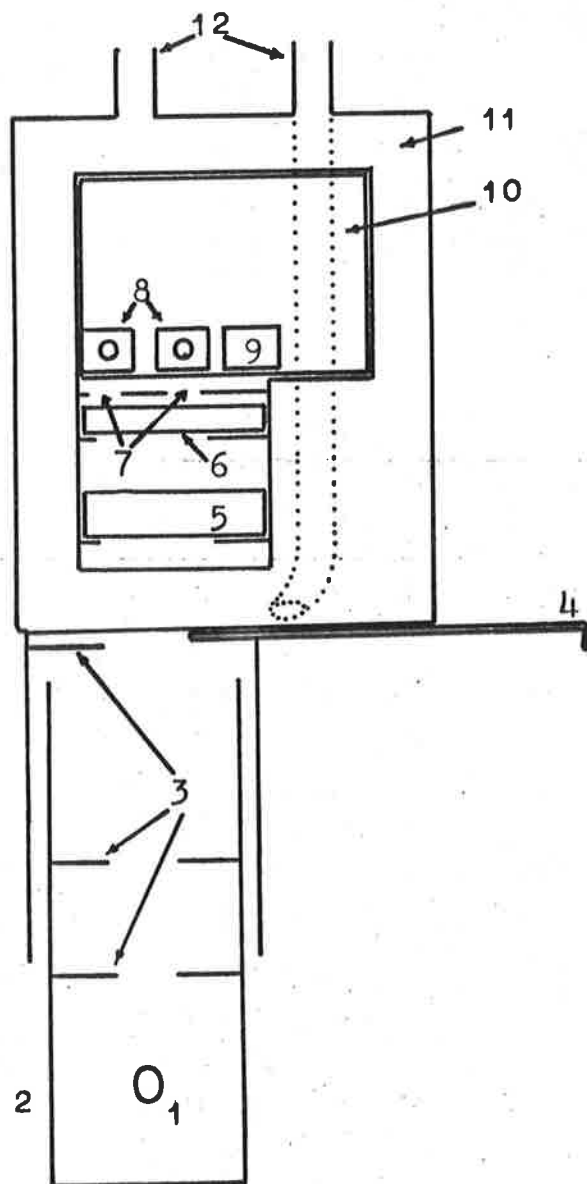
Fig. 2. — Plan of apparatus for rate measurements.

the other for the azo compound.   The contents of each cell
was stirred by a Teflon stirrer, powered by a small electric
motor.   The stirrers were arranged so that they did not
project into the path of the light beam.   The matched cells
(8), as well as a solvent cell (9), were contained in the
cell carriage (10) from a Hilger Uvispek Spectrophotometer.
Both the cell carriage and the filter cells (5) and (6) were
surrounded by a metal water jacket (11) through which
thermostatted water ($\pm$ 0.1°) was circulated _via_ the two pipes
(12).   It is probable that the temperature variation of the
solutions in the quartz cells was greater than $\pm$ 0.1°.   The
lid of the cell compartment contained the two stirrers and
could be removed easily to allow periodic removal of the cell
carriage (10) for measurements in the Uvispek spectrophotometer.

The 436 mμ mercury line was isolated with an ethanolic
solution of crystal violet (0.02%) and nitromesitylene (3%),
which transmitted 70% of the incident light at 436 mμ in the
0.5 cm cell (6).   In the initial experiments, p-nitrotoluene
(10%) was used in place of the nitromesitylene (3%), but it
was found that the high concentration of p-nitrotoluene caused
leakage in the epoxy resin used in the construction of the
filter cell.   Isolation of the 405 mμ line was effected using
a solution of 4-dimethylaminoazobenzene (0.02%) and
8-methylquinoline (0.5%) in 3.5$\underline{N}$ sulphuric acid, and had a
transmittance of 30% at 405 mμ.   Both the filter systems were

found to be stable to irradiation for many hours in the
apparatus described. Emission spectra of the mercury lamp
were taken through the two filter systems in turn, using an
Optica CF_4 Recording Spectrophotometer. The transmitted
emission from mercury lines other than those at 436 or 405
mμ respectively was negligible.

All manipulations of photosensitive materials were per-
formed in a dark-room illuminated by two Kodak OB safelights
(25W each), and by diffuse light from a sodium vapour lamp.
Exposure of all solutions to these lights was kept to a
minimum, especially solutions containing cis-azo compounds,
as their absorption tailed off rather slowly toward longer
wavelengths. During normal manipulations, however, there
were no significant photochemical changes induced by the
safelights or the sodium lamp.

(b) Calibration of actinometer

A calibration graph of optical density of ferrous phen-
anthroline at 510 mμ against molar concentration of ferrous ion
was constructed using ferrous ammonium sulphate of known con-
centration. The method of Hatchard and Parker[89] was modified
slightly to adapt to the conditions used in the rate measure-
ments. A series of ferrous ammonium sulphate solutions were
prepared in 0.1N sulphuric acid with concentrations 0, 0.5, 1.0,
1.5 ..... 4.0 x 10^{-4}N with respect to ferrous ion. From each

freshly prepared solution in turn, a 2 ml aliquot was pipetted
into a 10 ml volumetric flask and treated with an aqueous 0.1%
solution of 1,10-phenanthroline monohydrate (1.0 ml) and sodium
acetate buffer[89] (2.5 ml). The volume was made up to 10 ml
with distilled water, the solution was well mixed, and allowed
to stand for 1-1½ hr. The optical density was measured at
510 mμ in the Uvispek spectrophotometer, and corrected for the
blank reading, given by the solution which contained no added
ferrous ion. After the initial rapid increase, the optical
densities remained constant over several hours. The graph of
nett optical density against moles of ferrous ion per ml was a
straight line; the slope (least squares) gave an extinction co-
efficient of 10900 for ferrous phenanthroline (lit.[92] 11050).
The concentration of ferrous ion ($C_{Fe}{}^{++}$ moles/ml) in the 2 ml
aliquot was related to the optical density of the ferrous
phenanthroline at 510 mμ (D^{510}) by equation (3.7).

$$C_{Fe}{}^{++} = 4.59 \times 10^{-7} \times D^{510} \qquad (3.7)$$

Potassium trisoxalatoferrate(III) was prepared,[90] and a
0.00601 $\underline{M}$ solution in 0.1$\underline{N}$ sulphuric acid was used for actino-
metry. Approximately 2.8 ml was required to fill one of the
quartz cells; the actual volume was determined from the weight
of the solution and its density (1.001 g/ml at 25°). After
the irradiation of actinometer solution in the apparatus des-
cribed above, a 2 ml aliquot was pipetted into a 10 ml vol-
umetric flask which contained 0.1% aqueous 1,10-phenanthroline

(1 ml) and acetate buffer[89](1 ml), and the volume was made up
to 10 ml with water. The solution was well mixed and allowed
to stand for at least $\frac{1}{2}$ hr., after which D^{510} was measured.
A 2 ml aliquot of non-irradiated ferrioxalate solution was
treated similarly, to determine the blank value for D^{510}.
After an initial rapid increase in D^{510}, the solutions prepared
both from irradiated and non-irradiated ferrioxalate showed a
very slow but significant increase in D^{510} which continued for
at least a week. Hence a second reading was always made
several hours after the first reading, and extrapolated to
zero time. The extrapolated blank reading was subtracted from
the extrapolated reading for irradiated ferrioxalate. The
resultant nett value of D^{510} was used to calculate the number
of quanta per minute (Q^a) in einsteins which entered the
actinometer cell (equation 3.8); v is the volume of the

$$Q^a = \frac{D^{510} \times 4.59 \times 10^{-7} \times v}{\emptyset^a \times (1-T) \times t} \qquad (3.8)$$

actinometer solution (ml), $\emptyset^a$ is the quantum yield of the
actinometer system,[89] (1-T) is the fraction of incident light
absorbed by the actinometer solution at the wavelength of
irradiation, and t is the duration of irradiation (min).

An alternative procedure for the use of the ferrioxalate
actinometer was tried at 436 mμ, but was found to be unsatis-
factory. It involved the measurement of the decrease in the
optical density of the 0.00601 N ferrioxalate solution at 436 mμ

at intervals during irradiation. The final value of the
optical density (D_∞) was measured after the solution had
been exposed to sunlight for some time, and the appropriate
tabulated function

$$- \int_3^D \frac{dy}{(1-\frac{D\infty}{y})(1-10^{-y})}$$

was plotted against time of irradiation.   A straight line was
obtained only for the initial portion of the run; thereafter
the slope of the function decreased, probably due to a side
reaction which may occur after a significant quantity of
ferrous ion has been formed.[cf. 89,93]   Thus, this method of
analysis was proven unsatisfactory, but the experiment
demonstrated that it was desirable to decompose only a small
part of the ferrioxalate solution when the 1,10-phenanthroline
was used to estimate the ferrous ion formed.

(c) Rate measurements

A stock solution of trans-azo compound was prepared in
25N sulphuric acid (for azobenzene and 4-chloroazobenzene) or
20N sulphuric acid (for 4-methylazobenzene), and diluted with
the appropriate quantities of sulphuric acid and water to give
a series of solutions, the normality of which ranged from 12 to
24 at 2N intervals.   The concentration of azo compound was
arranged to give an optical density of between 0.6 and 1.0 at
436 or 405 mμ.   Approximately 2.8 ml of solution was used in

each run and the actual volume was determined from the weight
of the solution and the density of the acid at the particular
normality.

The optical density of the solution of azo compound was
measured at the irradiation wavelength, as a function of the
irradiation time. During the first part of each run, the azo
compound was irradiated for short time intervals. As the rapid
cis-trans equilibration proceeded, the rate of change of the
optical density decreased, and thus the exposure time was
gradually increased, until it was of a magnitude suitable for
the irradiation of the actinometer in the adjacent compartment.
The aim was to decompose sufficient ferrioxalate so that the
ferrous phenanthroline gave D^{510} near 0.5, which could be
measured with a high degree of accuracy in the Uvispek
spectrophotometer. After irradiation of the actinometer and
the subsequent manipulation to form the ferrous phenanthroline
(see above), the irradiation of the azo compound was continued;
measurements of the optical density were made at suitable
intervals.

When the optical density had dropped to near 0.20, a
second determination was made with the actinometer in the
adjacent cell compartment. The number of quanta per minute
which entered the actinometer cell was calculated for both
determinations and averaged. The two values usually differed
by not more than a few per cent, due mainly to a slow decline

in the emission of the mercury lamp. After the second
actinometer determination, the run was terminated and the
solution of partly decomposed azo compound was irradiated to
completion in sunlight or diffuse daylight to determine D_∞.
The same value of D_∞ was obtained when the solution was exposed
to direct sunlight, diffuse daylight, direct light from the
mercury lamp, or light from a 200W tungsten lamp.

In a second run, the above procedure was repeated,
except that the positions of the cell containing azo compound
and the actinometer cell were interchanged. This allowed a
correction to be made for the slight difference between the
number of quanta per minute which entered each cell (see
Section 3.3).

The solutions of _trans_-azo compounds were stable in the
dark for many weeks, except at lower acid concentrations (12,
14 and 16$\underline{N}$) where a significant decrease in the optical density
was observed after one or two days. Thus for rate measure-
ments, freshly prepared solutions were used. 4-Chloro-
azobenzene was the most susceptible and 4-methylazobenzene
the least susceptible to this slow reaction, which may have
been hydrolysis of the azo compounds. Spectral measurements
definitely showed that benzo[_c_]cinnolines were not formed in
the process.

(d) Yield measurements

In the photochemical reaction of azobenzenes, some azo

compound was consumed by reduction to the hydrazo compound.
Thus to determine the quantum yield of the actual photo-
cyclization process, the yield fraction (z) of cyclised pro-
duct was measured spectroscopically. Measurements were
made at the long wavelength band of the appropriate
benzo[c]cinnoline (i.e. near 370 mμ) as the other reaction
products did not absorb in this region. The $\varepsilon_{max.}$ of the
appropriate benzo[c]cinnoline was determined in this region
in sulphuric acid with normalities of 14 to 24 at 2N inter-
vals, and also in 12N acid with 2-methylbenzo[c]cinnoline.

Solutions of trans-azo compounds were prepared in sul-
phuric acid of the same strengths as listed above (including
12N for 4-methylazobenzene), and were irradiated to completion
in pyrex volumetric flasks with sunlight or diffuse daylight.
The concentration of azo compound was such that the final
optical density in the region of 370 mμ was near 0.5. The
hypothetical $\varepsilon_{max.}$ values were calculated from this optical
density and the initial molar concentration of azo compound;
the yield fraction (z) was given by

$$z = \frac{\varepsilon_{max.} \text{ from irradiated azo compound}}{\varepsilon_{max.} \text{ for the benzo[c]cinnoline produced}} \quad . \quad (3.9)$$

The wavelengths of the two $\varepsilon_{max.}$ values were always found to
correspond to the nearest mμ. Optical densities were also
measured at 405 and 436 mμ and the value of z so obtained
agreed approximately with the value from measurements at
the $\lambda_{max.}$.

(e) <u>Measurement of the position of</u> cis-trans <u>equilibrium</u>

From equation (3.5) it is clear that the product $\varepsilon^e b$ must be determined, where ε^e is the extinction coefficient of the cis-trans equilibrium mixture and b is the fraction of the light absorbed by azo compound which is in turn absorbed by the reactive species (presumably the cis-isomer). It can be shown (see Appendix III) that if the cis-isomer is the cyclizing species, then

$$\varepsilon^e b(cis) = \frac{\varepsilon^c(\varepsilon^t - \varepsilon^e)}{\varepsilon^t - \varepsilon^c} \qquad (3.10)$$

where ε^c and ε^t are the molar decadic extinction coefficients of cis- and trans-azo compounds respectively. Thus the determination of ε^e, ε^c, and ε^t was required. The accurate determination of ε^e posed a considerable problem, the solution of which is described in Appendix III.

ε^t was determined in sulphuric acid solutions where the normality ranged from 14 to 24 at 2$\underline{N}$ intervals. 12$\underline{N}$ acid was also used for trans-4-methylazobenzene. The concentration of azo compound was arranged so that the optical density at 436 and 405 mμ was near 0.5 (ca. 1.7 to 2.0 x $10^{-5}\underline{M}$).

It was found that direct dissolution of solid cis-azo compound in sulphuric acid caused appreciable isomerization. Therefore ε^c was determined by the following procedure. Freshly recrystallized cis-azo compound (see Chapter V) was used to prepare a stock solution in 95% ethanol (ca. 6 x $10^{-3}\underline{M}$)

which was immediately placed in an ice-salt bath to reduce
thermal cis-trans isomerization. An aliquot of 0.1 ml was
added to each of several solutions of sulphuric acid (10 ml)
at room temperature, so that on mixing, the normality ranged
from 14 to 24 at 2N intervals with respect to sulphuric acid.
With cis-4-methylazobenzene, 12N acid was also used. The time
of mixing was noted, and optical densities were measured at
436 and 405 mμ at room temperature.

Because of thermal isomerization of the cis-isomers,
the optical densities of the solutions gradually increased
and a second reading was taken at each wavelength to allow the
true optical density of pure cis-isomer to be obtained by
extrapolation back to the time of mixing. It was found that
negligible isomerization occurred in the cold, stock ethanolic
solution, during the determinations.

The use of a 0.1 ml pipette and also of the very cold
ethanolic solution caused irregular variations in the concen-
tration of the cis-azo compound. The accurate concentrations
were determined at the end of the experiment by irradiation of
the solutions of cis-azo compound to completion. The optical
densities at the $\lambda_{max.}$ near 370 mμ were measured, and the
original concentrations were calculated by comparison with the
results obtained in the yield measurements. It was assumed
that the presence of 1% ethanol would not affect the results.

In all experiments the calculated concentration agreed within
a few per cent of that obtained on the assumption that the
0.1 ml pipette regularly delivered an accurate volume.   The
value of ε^c was then calculated.

3.3 Results and Discussion

From the rate measurements on the azo compounds the
function

$$-\int_{3}^{D} \frac{dv}{(1-\frac{D_\infty}{v})(1-10^{-v})}$$

(hereafter abbreviated to $-\int_{3}^{D} (D_\infty)$) was plotted against
time, for the appropriate value of D_∞ (to the nearest 0.01).
A typical result is shown in Fig. 3, obtained from irradia-
tion at 436 mμ of 3.99×10^{-5}M trans-azobenzene (2.84 ml) in
14N sulphuric acid at 25°; D_∞^{436} was 0.031.

The initial steep portion of the graph represents the
rapid trans-cis photoisomerization, which caused a fall in the
optical density at 436 mμ (D^{436}).   The linear portion
represents the rate of disappearance of azobenzene due to
cyclisation and reduction, after cis-trans equilibrium has
been established, and shows the reaction to be first order
with respect to light absorbed.   An approximate value for ε^c
could be obtained by extrapolation of the linear portion of
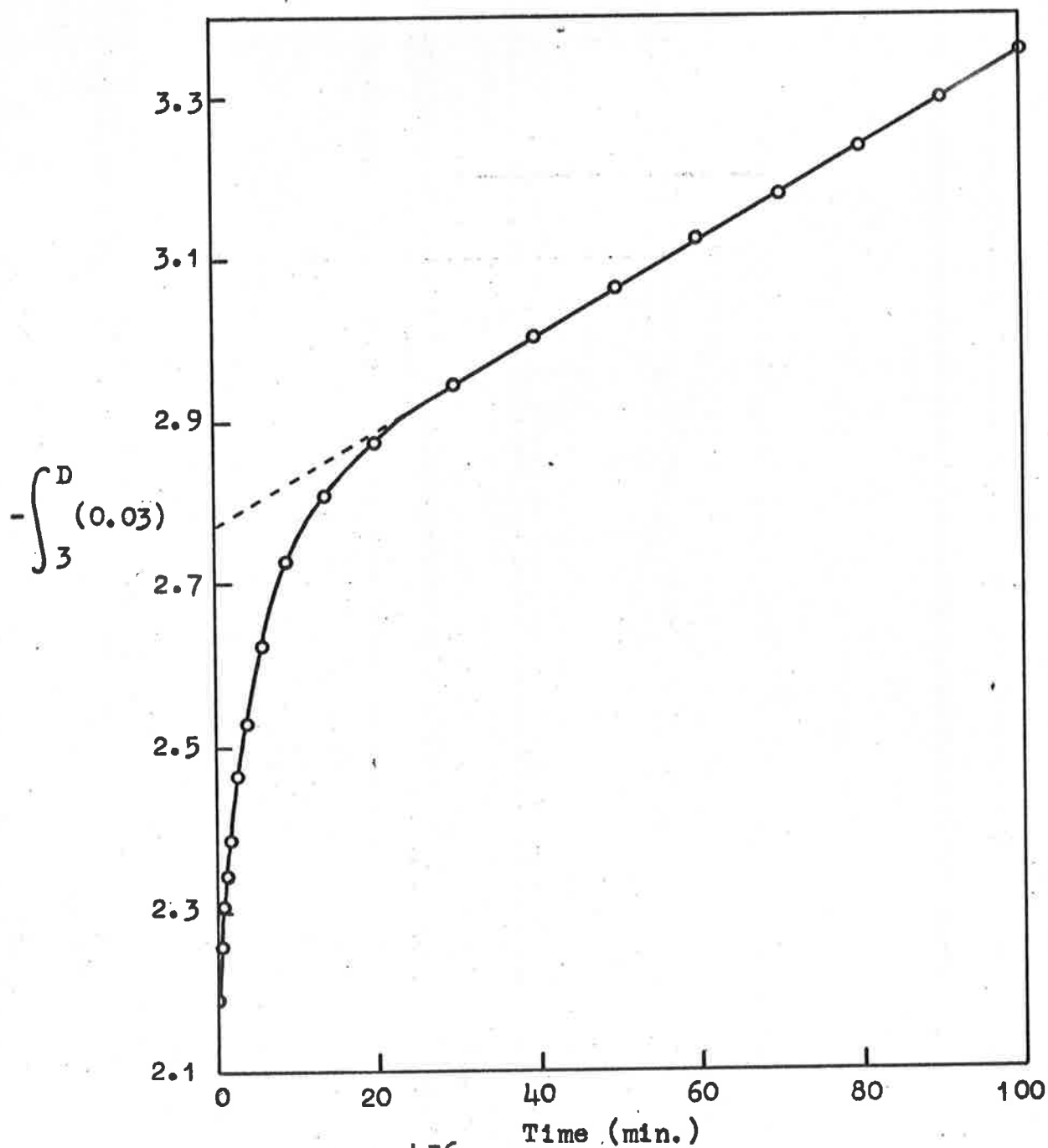
Fig. 3 — Graph of $-\int_{3}^{D436} \dfrac{dy}{(1-\frac{0.03}{y})(1-10^{-y})}$ against time for

irradiation of $3.99 \times 10^{-5}\underline{M}$ azobenzene in $14\underline{N}$ sulphuric acid

at 25° with 436 mμ light.

the graph to zero time (see Appendix III). The slope of the line is equal to bk/z (equation 3.4). To determine b it was necessary to establish whether or not only cis-azobenzene could photocyclize directly. It had been shown for stilbene that only the cis-isomer could photocyclize.[94] Several rate runs had suggested that azobenzene underwent the cyclization process most rapidly in 16N sulphuric acid, and hence this solvent was chosen for an experiment to determine whether or not trans-azobenzene could photocyclize directly, on absorption of light at 436 mμ.

A solution of 3.83×10^{-5}M trans-azobenzene in 16N sulphuric acid was irradiated at 436 mμ as described in the experimental section, but in addition to measurements of D^{436}, readings of the optical density at 252 mμ (D^{252}) were also made, in order to follow the formation of benzo[c]cinnoline. It was necessary to use the hydrogen lamp of the spectro-photometer for the measurement of D^{436}, as the hydrogen and tungsten lamps could not be operated simultaneously. A slit width larger than normal was therefore required for D^{436} measurements.

A graph of $-\int_{3}^{D^{436}} (0.03)$ against time had a slope at cis-trans equilibrium of 4.87×10^{-3} min^{-1}. The graph of $-\int_{3}^{D^{436}} (0.00)$ had an initial slope of 93×10^{-3} min^{-1}.

$\frac{dD^{252}}{dt}$ was determined graphically and $\frac{dD^{252}}{dt}/A^{436}$ was found to be 20.7×10^{-3} min^{-1} at the beginning of the run, and about 10.5×10^{-3} min^{-1} during cis-trans equilibrium. A^{436} was the fraction of light absorbed at 436 mμ. At 436 mμ, $\varepsilon^{t}(436)$ = 23800, $\varepsilon^{c}(436)$ = 6770, $\varepsilon^{e}(436)$ for the cis-trans equilibrium mixture =12000 (approx.), $\varepsilon_{\infty}(436)$ for the final irradiation products = 800, b(trans) = 0.60 during cis-trans equilibrium, and therefore b(cis) = 0.40. At 252 mμ, $\varepsilon^{t}(252)$ = 1250, $\varepsilon^{c}(252)$ = 4900, $\varepsilon^{e}(252)$ = 3800, and $\varepsilon_{\infty}(252)$ = 34300. Determination of Q was not necessary as the problem was discussed from the point of view of relative rates, and it was only necessary to have constant illumination throughout the experiment. Actinometer measurements showed the illumination to be constant to within 2%.

If the unlikely assumption is made that only trans-azobenzene could photocyclize directly, then the rate of disappearance of azobenzene (R_{1}) during cis-trans equilibrium would be given by

$$R_{1} = \frac{4.87 \times 10^{-3}}{\varepsilon^{e}(436) \times b(trans)} \qquad (3.11)$$

$$= 6.8 \times 10^{-7} \text{ moles. litres}^{-1}. min^{-1}.$$

At the beginning of the run, the rate of decrease of D^{436} $(R_{2};$ corrected for complete absorption) due to cyclization and reduction would be given by

$$R_{2} = R_{1}[\varepsilon^{t}(436) - \varepsilon_{\infty}(436)] = 16 \times 10^{-3} \text{ } min^{-1}. \qquad (3.12)$$

The residual rate of decrease in D^{436} (R_3), due to trans-cis photoisomerization would be given by

$$R_3 = 93 \times 10^{-3} - R_2 = 77 \times 10^{-3} \text{ min}^{-1}. \qquad (3.13)$$

Thus the rate of increase in D^{252}, due to trans-cis photoisomerization (R_4) would be given by

$$R_4 = R_3 \frac{\varepsilon^{c}(252) - \varepsilon^{t}(252)}{\varepsilon^{t}(436) - \varepsilon^{c}(436)} = 16.5 \times 10^{-3} \text{ min}^{-1}. \qquad (3.14)$$

The residual rate of increase of D^{252} (R_5) would be given by

$$R_5 = 20.7 \times 10^{-3} - R_4 = 4.2 \times 10^{-3} \text{ min}^{-1}. \qquad (3.15)$$

This residue (R_5) should be due to photoreaction of trans-azobenzene to form benzo[c]cinnoline and benzidine, and the rate of formation of products (R_6) would be given by

$$R_6 = \frac{4.2 \times 10^{-3}}{\varepsilon_{\infty}(252) - \varepsilon^{t}(252)} \qquad (3.16)$$

$$= 1.3 \times 10^{-7} \text{ moles. litres}^{-1}. \text{ min}^{-1}.$$

This quantity (R_6) is much less than the expected value (R_1), or R_7, obtained from the rate of increase of D^{252} during

$$R_7 = \frac{10.5 \times 10^{-3}}{\varepsilon_{\infty}(252) - \varepsilon^{c}(252)} \qquad (3.17)$$

$$= 5.8 \times 10^{-7} \text{ moles. litres}^{-1}. \text{ min}^{-1}.$$

cis-trans equilibrium (equation 3.17). The difference be-tween R_1 and R_7 is probably due to inaccuracy in the graphical measurement of $\frac{dD^{252}}{dt}$ at cis-trans equilibrium. The great

disparity between R_1 (or R_7) and R_6 shows that the original assumption, that only _trans_-azobenzene can photocyclize directly, is incorrect.

If an alternative assumption is made that only _cis_-azobenzene may photocyclize, then the initial rates of change of D^{436} (93×10^{-3} min^{-1}) and of D^{252} (R_8) would be due to _trans-cis_ photoisomerization alone, and they should be related by equation (3.18).

$$R_8 = \frac{93 \times 10^{-3} \times [\mathcal{E}^c(252) - \mathcal{E}^t(252)]}{\mathcal{E}^t(436) - \mathcal{E}^c(436)} \qquad (3.18)$$

$$= 19.9 \times 10^{-3} \text{ min}^{-1}.$$

The residual rate of increase in D^{252} (R_9) would be given by

$$R_9 = 20.7 \times 10^{-3} - R_8 = 0.8 \times 10^{-3} \text{ min}^{-1}. \qquad (3.19)$$

In view of the experimental errors, especially in the determination of $\mathcal{E}^c(252)$, R_9 must be considered negligible. This confirms that the initial rate of formation of benzo[c]cinnoline and benzidine from _trans_-azobenzene is zero. The possibility of direct cyclization of a very small fraction of the excited _trans_-azobenzene cannot be excluded in view of experimental accuracy. In the rest of the discussion, however, this possibility is neglected for the three azo compounds examined.

In each rate measurement on the azo compounds, the two actinometer determinations were averaged to give the average number of quanta per minute ($\overline{Q^a}$) which entered the actinometer

cell. To determine Q for the light entering the solution
of azo compound, $\overline{Q^a}$ must be multiplied or divided by a
constant a, where a is defined as the ratio of the amount of
light entering the right hand side (RHS) cell to the light
entering the left hand side (LHS) cell (Fig. 2), per unit
time. The relationship between Q and $\overline{Q^a}$ is shown in equations
(3.20) and (3.21). Rate determinations were made in pairs,

$$Q_{RHS} = a\overline{Q^a_{LHS}} \qquad (3.20)$$

$$Q_{LHS} = \frac{1}{a}\overline{Q^a_{RHS}} \qquad (3.21)$$

with interchange of the positions of the actinometer cell and
the cell of azo compound. If R_{RHS} and R_{LHS} are the rates of
reaction of the azo compound in the respective light beams,
then a is given by

$$a = \left[\frac{R_{RHS} \cdot \overline{Q^a_{RHS}}}{\overline{Q^a_{LHS}} \cdot R_{LHS}} \right]^{\frac{1}{2}} \qquad (3.22)$$

Generally a ranged between 1.03 and 1.05, the variations being
due to disturbance of the filter cell block when the filter
solution was renewed. It was not necessary to assume that
the output from the lamp was the same for each run of a pair.

The constants ε^t, ε^c, and z, for azobenzene,
4-chloroazobenzene, and 4-methylazobenzene are given in Table
7. The constants for azobenzene were assumed to be valid both

TABLE 7

Extinction coefficients of trans-(ε^t) and cis-(ε^c) azo compounds in sulphuric acid, and the yield fraction (z^*) of the corresponding benzo[c]cinnolines

Sulphuric acid ($\underline{N}$)	Wavelength mμ	Azobenzene			4-Chloroazobenzene			4-Methylazobenzene		
		ε^t	ε^c	z^*	ε^t	ε^c	z^*	ε^t	ε^c	z^*
12	436	-	-	-	-	-	-	29940	8140	0.492
14	436	22700	6550	0.501	30020	8060	0.538	31290	8270	0.496
16	436	23800	6770	0.504	32070	8280	0.545	31820	8330	0.503
18	436	24500	6820	0.510	32540	8380	0.559	31940	8460	0.509
20	436	25200	6840	0.541	33060	8480	0.573	32180	8520	0.519
22	436	25900	7010	0.563	33440	8570	0.582	32290	8590	0.531
24	436	26500	6920	0.596	33820	8670	0.589	32590	9020	0.566
16	405	25700	6820	0.504	-	-	-	-	-	-

* z was determined with polychromatic light (e.g. sunlight).

94.

at 15° and 25°. It is interesting to note the marked increase
in z, toward higher acid concentrations. This would probably
be due to an increase in the extent of disproportionation
of the hydrazo compound, although the reason for this is not
clear.

Rate measurements on azobenzene were made in 14-24$\underline{N}$
sulphuric acid. The quantum yields (Φ) for photocyclization
of $\underline{cis}$-azobenzene with 436 mμ light at 25°, together with the
associated data, are given in Table 8. At each acid con-
centration, the first line of data was obtained with the azo
compound in the right hand cell, and the second line of data
with azo compound in the left hand cell (see Fig. 2). For
the determinations in 14, 16, and 18$\underline{N}$ acid, the values of the
extinction coefficient of the $\underline{cis}$-$\underline{trans}$ equilibrium mixture
(ε^e) were determined by the computer method (see Appendix III),
whereas in 20, 22, and 24$\underline{N}$ acid the values of ε^e were deter-
mined (less precisely) by extrapolation to zero time of the
linear portion of the graph $-\int_3^D (D_\infty)$ against time. The term
C_o is the initial molar concentration of the azo compound.
Φ was determined for each set of data with the use of equations
(3.5) and (3.10). Somewhat less accurate determinations of
Φ were also made in 14, 16, and 18$\underline{N}$ sulphuric acid with
2.03×10^{-5} $\underline{M}$ azobenzene, using the simple extrapolation
procedure to determine ε^e. These results were up to 5%
higher than the corresponding ones shown in Table 8.

TABLE 8

Quantum yields and related data for the photochemical cyclization of azobenzene in sulphuric acid at $25°$ with 436 mμ light

Sulphuric acid (N)	C_o M x 10^5	v 1. x 10^3	ε^e	$\varepsilon^e_{b(cis)}$	Slope min^{-1} x 10^3	Rate (k') moles.min^{-1} x 10^9	Q E.min^{-1} x 10^7	Φ
14	3.99	2.85	11220	4660	6.01	1.84	1.189	0.0155
	3.99	2.84	11270	4640	5.87	1.80	1.160	0.0155
16	3.99	2.82	11550	4870	6.16	1.80	1.199	0.0150
	3.99	2.83	11700	4810	5.81	1.72	1.129	0.0153
18	3.99	2.81	11900	4860	5.80	1.71	1.201	0.0142
	3.99	2.83	11720	4930	5.47	1.60	1.132	0.0142
20	2.03	2.88	12810	4620	5.62	1.90	1.266	0.0150
	2.03	2.87	12810	4620	5.36	1.80	1.206	0.0150
22	2.03	2.89	13200	4710	4.92	1.70	1.268	0.0134
	2.03	2.89	13200	4710	4.76	1.64	1.227	0.0134
24	2.03	2.91	13450	4610	4.00	1.50	1.307	0.0115
	2.03	2.88	13450	4610	3.69	1.37	1.205	0.0114

Similarly, Table 9 shows the quantum yields and related data for the photocyclization of azobenzene at 15° with 436 mμ light and at 25° with 405 mμ light. Tables 10 and 11 show the quantum yields and associated data for the photo- cyclization at 25° with 436 mμ light of 4-chloroazobenzene and 4-methylazobenzene respectively.

The quantum yields for the cyclization of azobenzene, 4-chloroazobenzene, and 4-methylazobenzene are shown as a function of the normality of the sulphuric acid in Fig. 4. An increase in acid concentration caused a decrease in the quantum yield. In the region of room temperature, the quantum yield for azobenzene at a given acid strength was relatively insensitive to temperature changes. The reasonably close agreement between the quantum yields at 405 and 436 mμ for azobenzene indicates at the most only a small wavelength dependence, within this region of the absorption band. This behaviour is typical of many photochemical reactions, and to detect any significant temperature or wavelength effects, the range of these variables would have to be considerably extended. This ideal could be restricted in the case of temperature variation, as at higher temperatures, the rate of thermal cis-trans isomerization would greatly increase, and at lower temperatures, the freezing point of the sulphuric acid solutions would be reached.

TABLE 9

Effect of temperature and wavelength of irradiation on the quantum yield for the photocyclization of azobenzene in sulphuric acid

Sulphuric acid $\underline{N}$	C_0 $\underline{M} \times 10^5$	v $l. \times 10^3$	$\varepsilon^\ominus$	$\varepsilon^\ominus b(\underline{cis})$	Slope min^{-1} $\times 10^3$	Rate (k') moles.min^{-1} $\times 10^9$	Q E.min^{-1} $\times 10^7$	Φ
Temperature, 15°; wavelength of irradiation, 436 mμ.								
16	3.87	2.80	12180	4620	5.07	1.55	0.951	0.0163
	3.87	2.82	12240	4600	4.63	1.43	0.869	0.0165
	3.87	2.79	12000	4820	4.82	1.40	0.977	0.0143
18	3.87	2.82	12180	4750	4.40	1.33	0.892	0.0149
Temperature, 25°; wavelength of irradiation, 405 mμ.								
16	3.83	2.81	12050	4930	1.302	0.374	0.2289	0.0163
	3.83	2.83	12050	4930	1.258	0.364	0.2212	0.0165

TABLE 10

Quantum yields and related data for the photochemical cyclization of 4-chloroazobenzene in sulphuric acid at 25° with 436 mμ light

Sulphuric acid $\underline{N}$	C_o $\underline{M}$ x 10^5	v 1. x 10^3	ε^θ	ε^θ_b(cis)	Slope min^{-1} x 10^3	Rate (k') moles.min^{-1} x 10^{10}	Q E.min^{-1} x 10^7	ϕ
14	2.01	2.78	14410	5730	2.56	6.68	1.128	0.0059
	2.01	2.82	14410	5730	2.49	6.60	1.097	0.0060
16	2.05	2.79	15620	5730	2.39	6.35	1.135	0.0056
	2.05	2.81	15670	5710	2.22	5.96	1.054	0.0057
18	2.06	2.78	15870	5780	2.19	5.89	1.115	0.0053
	2.06	2.81	16020	5730	2.11	5.78	1.074	0.0054
20	2.05	2.80	16330	5770	2.17	6.03	1.217	0.0050
	2.05	2.83	16140	5840	1.94	5.39	1.087	0.0050

TABLE 11

Quantum yields and related data for the photochemical cyclization of 4-methylazobenzene

in sulphuric acid at 25° with 436 mµ light

Sulphuric acid $\underline{N}$	C_0 $\underline{M} \times 10^5$	v l. $\times 10^3$	ε^e	$\varepsilon^e b(\underline{cis})$	Slope min^{-1} $\times 10^3$	Rate (k') moles.min^{-1} $\times 10^{10}$	Q E.min^{-1} $\times 10^7$	ϕ
12	2.76	2.80	14010	5950	2.45	5.67	1.131	0.0050
	2.76	2.82	14220	5870	2.45	5.79	1.132	0.0051
14	2.76	2.80	15060	5830	2.31	5.50	1.136	0.0048
	2.76	2.82	15350	5730	2.08	5.08	1.023	0.0050
16	2.76	2.80	15750	5700	2.10	5.19	1.091	0.0048
	2.76	2.83	15600	5750	1.95	4.83	1.011	0.0048
18	2.76	2.79	15860	5790	1.87	4.58	1.059	0.0043
	2.76	2.83	15930	5770	1.69	4.22	0.957	0.0044
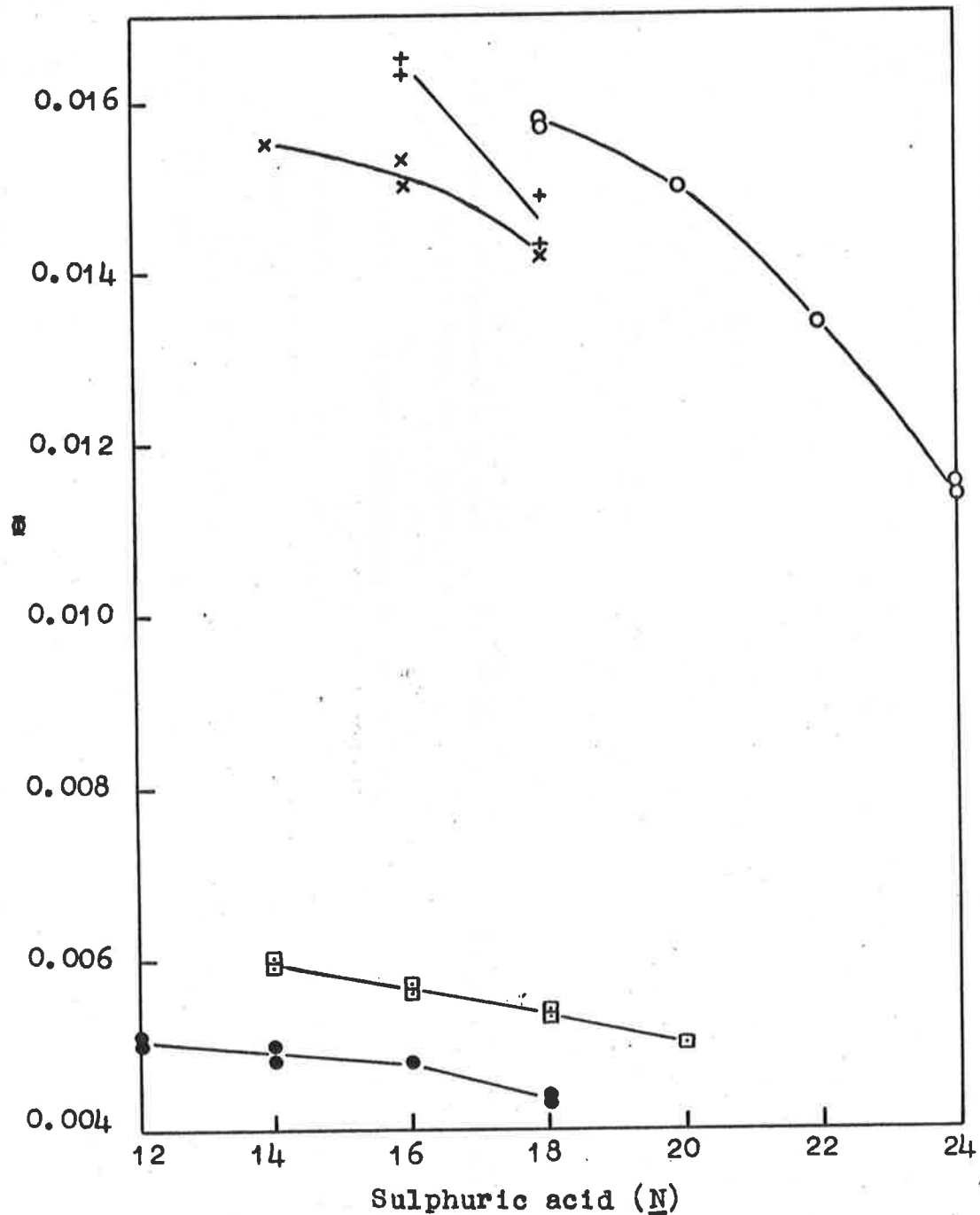
Fig. 4.— Quantum yields for the cyclization of azobenzenes at 25° and 436 mμ: 2 x 10⁻⁵M azobenzene, o——o; 4 x 10⁻⁵M azobenzene, x——x; 2 x 10⁻⁵M 4-chloroazobenzene, □——□; 2.8 x 10⁻⁵M 4-methylazobenzene, ●——●: at 15° and 436 mμ, 4 x 10⁻⁵M azobenzene, +——+.

No obvious dependence of the quantum yield on the nature of the p-substituent is apparent from Fig. 4. The quantum yields are discussed in relation to the mechanism of the reaction in Chapter IV.

The quantum yields for trans-cis photoisomerization (ϕ^t) were calculated from the initial rates of disappearance of the trans-azo compounds which were determined from the

TABLE 12

Quantum yields for trans-cis and cis-trans photoisomerization

of azobenzenes

Sulphuric acid $\underline{N}$	Temp. $^\circ C$	λ mμ	Azobenzene		4-Chloro-azobenzene		4-Methyl-azobenzene	
			ϕ^t	ϕ^c	ϕ^t	ϕ^c	ϕ^t	ϕ^c
12	25	436	-	-	-	-	0.18	0.26
14	25	436	0.16	0.23	0.17	0.26	0.15	0.25
16	25	436	0.19	0.26	0.15	0.26	0.15	0.25
16	15	436	0.18	0.30	-	-	-	-
16	25	405	0.17	0.25	-	-	-	-
18	25	436	0.18	0.26	0.15	0.27	0.13	0.23
18	15	436	0.18	0.27	-	-	-	-
20	25	436	-	-	0.15	0.26	-	-

graphs of $-\int_3^D (0.00)$ against time. These were effectively the same as graphs of $-\log_{10}(10^D-1)$ against time. The initial slopes were measured and the rates (k') were calculated from equation (3.5), where k is the initial slope, l = 1, and

$\mathcal{E}^e$ is replaced by $\mathcal{E}^t-\mathcal{E}^c$ at the wavelength of irradiation.
Quantum yields (Φ^t) were then calculated from equation (3.6).
There was some inaccuracy in the measurement of the initial
slopes so that the resultant quantum yields were not as
accurate as those for the cyclisation reaction.

The quantum yields for cis-trans photoisomerization (Φ^c)
were determined from the equilibrium condition

$$b(\text{cis}).\Phi^c = b(\text{trans}).\Phi^t \qquad (3.23)$$

where $b(\text{trans}) = 1-b(\text{cis})$. The values of Φ^t and Φ^c for
azobenzene and its 4-chloro- and 4-methyl- derivatives are
summarized in Table 12. Each line of data was obtained from
the average of two determinations. Because of the probable
errors, it is not possible to determine the dependence of
Φ^t and Φ^c on acid concentration, temperature, or wavelength
of irradiation with any certainty.

CHAPTER IV

MECHANISM OF THE CYCLIZATION

4.1 Introduction

Before the mechanism of the photocyclization of
azobenzenes is discussed it is desirable to examine the
present knowledge on the mechanism of the photocyclization
of stilbenes.   This should include an examination of the
cis-trans photoisomerization of stilbenes, which has been
actively studied by many workers in recent years, and has
provided some information on the photoexcited states of
stilbene.

The photocyclization of stilbene is generally thought
to occur by internal coupling of the diradical (LXXVIII).
In the mechanism proposed by Schaffner and co-workers,[4] a
common intermediate excited state, which had the cis-
configuration (LXXVI), was proposed for the cis-trans
photoisomerization of stilbene.   This intermediate would
have other resonance forms, one of which would be (LXXVIII).
It was proposed[4] that cyclization occurred to give the
dihydrophenanthrene (LXXIX) which was dehydrogenated to
phenanthrene (II).   Stegemeyer,[94] however, showed that the
initial rate of formation of phenanthrene from trans-
stilbene (I) was zero, whereas from cis-stilbene (LXXVII)
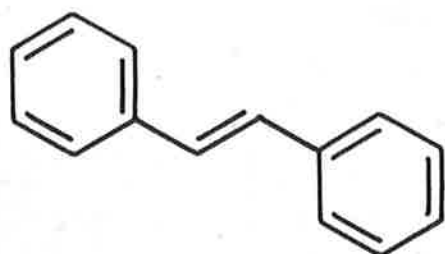
(I)
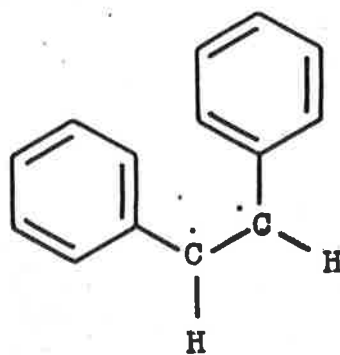
(LXXVI)
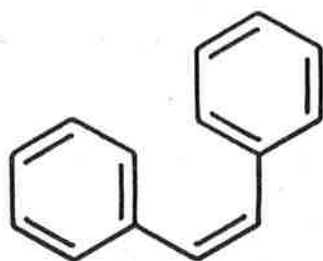
(LXXVII)
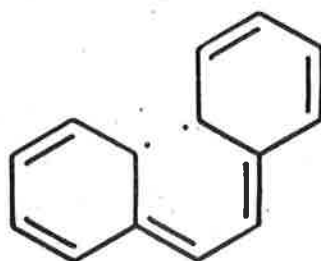
(LXXVIII)
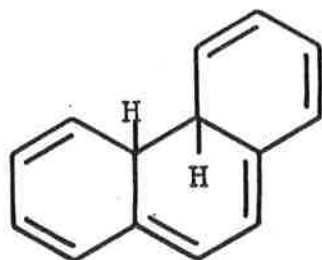
(LXXIX)
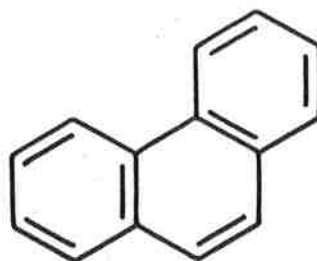
(II)

it was finite. He proposed that the first excited singlet
state of cis-stilbene could be represented by the diradical
(LXXVIII) which cyclised to give the dihydrophenanthrene
(LXXIX), and then underwent dehydrogenation to give
phenanthrene, or that the cyclization of the diradical
proceeded with concerted elimination of hydrogen to give
phenanthrene directly. The singlet state was required
for the formation of the new C–C bond, and because oxygen
enhances the rate of reaction, it is unlikely that triplet
states are involved in the cyclization, as these are quenched
by oxygen.

Moore et al.[16] obtained spectroscopic evidence for the
existence of the dihydrophenanthrene (LXXIX). A yellow
substance with $\lambda_{max.}$ 447 mμ was produced on irradiation of
cis- or trans-stilbene with wavelengths less than 310 mμ.
This substance reacted with oxygen, to give phenanthrene
and hydrogen peroxide, and it disappeared slowly in the
absence of light and oxygen to give mainly cis-stilbene.
The yield of this substance was greater at lower temperatures.
A trans-configuration has been favoured for the two tertiary
hydrogens in the dihydrophenanthrene (LXXIX)[15] produced by
irradiation in solution, but Srinivasan and Powers[17]
favour a cis-configuration for irradiation of stilbene in
the vapour phase. There is, however, no real evidence in
either case.

Further evidence for the existence of the dihydro-
phenanthrene (LXXIX) was obtained from the irradiation of
some α,β-disubstituted stilbenes (LXXX) in the absence of
oxygen. The corresponding 9,10-dihydrophenanthrenes
(LXXXI) were isolated,[11] and n.m.r. studies suggested a
cis-configuration for the hydrogens at the 9- and 10-
positions. The fully aromatic phenanthrenes were readily
obtained on recrystallization or fusion of the dihydro-
phenanthrene.

It seems that an oxidizing agent is required to con-
vert the dihydrophenanthrene (LXXIX) to phenanthrene, and
reports to the contrary[4,13] have been ascribed to the
presence of traces of oxidant being inadvertently present.[15]
There is evidence that stilbene itself does not act as the
dehydrogenating agent. Stegemeyer[94] failed to detect any
bibenzyl in the products. Srinivasan and Powers[17]
reported the possible formation of bibenzyl from the
irradiation of cis-stilbene in thoroughly degassed
cyclohexane solution. Bicyclohexyl was also found and
therefore the bibenzyl need not have arisen from a reaction
between dihydrophenanthrene (LXXIX) and stilbene. No
phenanthrene was detected, but the accuracy in the estima-
tion of phenanthrene was very poor.

Kinetic studies[12] on the photocyclization of
triphenylethylenes (LXXXII) to give 9-phenylphenanthrenes
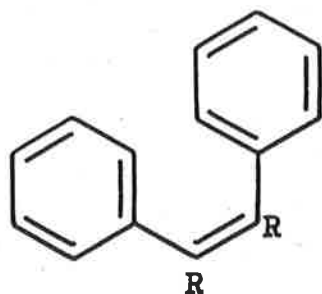
(LXXX)
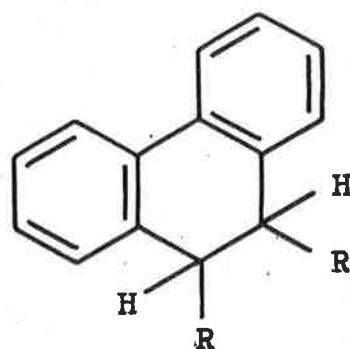
(LXXXI)
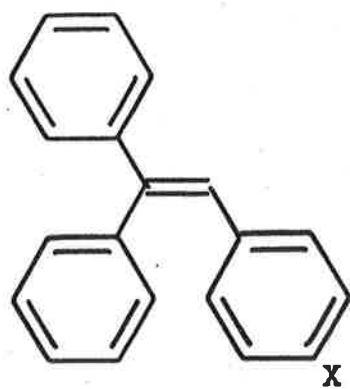
(LXXXII)
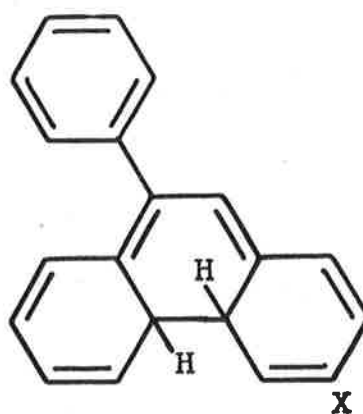
(LXXXIII)
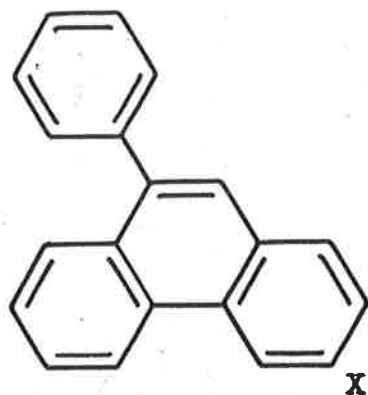
(LXXXIV)

(LXXXIV) showed that the quantum yield for the formation
of the proposed dihydro intermediate (LXXXIII) was linearly
dependent on the Hammett m-σ-constant of the substituent X.
It was concluded that an energy barrier, dependent on X,
existed between the first excited singlet state and the
dihydro intermediate (LXXXIII).   The more electron with-
drawing substituents reduced the quantum yield and this was
interpreted to mean that electron withdrawal from the
π-system was required to form the new C-C bond.   Pre-
liminary experiments showed a very small temperature
dependence, and the most electron withdrawing substituent
(chloro) produced the largest temperature dependence, which
agreed with the interpretation of the substituent effect.

Quantum yields for the photocyclization of stilbene in
solution are low (e.g. 0.02[17]).   This is not surprising as
the first excited singlet state (which presumably cyclizes)
is thought to have a very short life[95] (10^{-13} to 10^{-14} sec[94]).
The evidence for this short life is the lack of fluorescence,
lack of fine structure in the absorption spectrum (except
at 20°K[96]), and the inability of cis-stilbene to photodimerize.
The quantum yield for cis-trans photoisomerization is much
higher than for cyclization (e.g.[97] ca. 0.3), and as triplet
states are probably responsible for photoisomerization (see
below), cis-singlet-triplet conversion probably competes
heavily with the cyclization.

It is clear that cis- and trans-stilbene cannot have a
common first excited singlet state, because the cis-isomer
has its longest wavelength absorption band at shorter wave-
lengths than the trans-isomer.   However, there has been
some argument[95-98] on whether or not the cis-trans
photoisomerization proceeds through a common intermediate,
derived from the cis- and trans-singlets.   It seems fairly
well established that the intermediate or intermediates are
triplet states.   Very good quantitative agreement was
obtained between sensitized and unsensitized photoisomeriza-
tion of stilbene and some derivatives.[98,99] Dyck and McClure,[96]
however, have calculated for stilbene that there are
probably four triplet states of lower energy than the first
excited singlet state, any one of which may be involved in
the cis-trans photoisomerization.

The mechanism of cis-trans photoisomerization of
azobenzene is also not fully understood.   It has been
said[100] that a common intermediate is not involved because
the sum of the quantum yields for trans-cis and cis-trans
photoisomerization is less than unity.   Fischer[101] found
that the energy barrier to trans-cis was greater than for
cis-trans photoisomerization, but the problem of whether
or not a common transition state exists has not been
unambiguously resolved.

As with cis-stilbene, no fine structure is usually

observed in the electronic absorption spectra of cis-azo
compounds. The long-wavelength absorption band in both
cis- and trans- azobenzene is ascribed to a π^*n transition
and the strong band at shorter wavelengths to a $\pi^*\pi$
transition.[102] Both bands are active in the promotion of
cis-trans photoisomerizations.[100] No detailed discussion
on the nature of the intermediates has been given and it
has not been demonstrated as to whether triplet states are
involved. The absence of luminescence with most azo com-
pounds makes the problem a little more difficult than with
stilbene, but photosensitized isomerization of azo compounds
with suitable sensitizers could determine whether or not
triplet states are involved. The iodine photosensitized
isomerization of cis-stilbene reported by Yamashita
et al.[103] does not appear to resolve the problem.

4.2 Discussion

The quantum yields for the photocyclization of
azobenzenes were found to be of the order of 0.01. It
should first be established whether or not it is possible
that the small quantity of free base in the acid solutions
could absorb light and photocyclise. The function of
the protonated azo compound would then be to act as
dehydrogenating agent.[23] The relationship[104]

$$H_o = pK_a - \log_{10} \frac{[BH^+]}{[B]} \qquad (4.1)$$

where H_o is the Hammett acidity function, and $[BH^+]$ and $[B]$ are the molar concentrations of protonated and unprotonated azobenzene respectively, was used to determine the ratio of free base to conjugate acid. The pK_a of cis-azobenzene[3] was taken to be -1.6 and the ratio $\varepsilon^{BH^+}/\varepsilon^B$ as 4:1; ε represents the appropriate extinction coefficient at the wavelength of irradiation. In 20N sulphuric acid a quantum yield of 100 would be required to account for the observed rate of cyclization. Furthermore the values of the observed quantum yield bore no relationship to the ratio of free base to conjugate acid. It may therefore be safely assumed that the protonated cis-isomer absorbed the light responsible for the cyclization.

To interpret the quantum yields for the cyclization reaction, it is necessary to examine the present knowledge on the nature of electronic absorption spectra of monoprotonated cis- and trans-azobenzenes. Jaffé considers that the longest wavelength absorption band (at 420 mµ) is due to a $\pi^*\pi$ transition.[102] Even though at the time Jaffé erroneously considered the conjugate acid of azobenzene to have the cis-configuration, this assignment is probably still valid as his arguments for band assignment did not depend on the configuration. The conjugate acid of cis-azobenzene also has a broad, relatively intense, absorption band at about 420 mµ which also probably involves

a $\pi^*\pi$ transition. If this is so, the π^*n transition probably occurs near 300 mμ where a band of low intensity can be observed.[3] Jaffé considers the π^*n transition to occur in this region.[102] Thus, on protonation, the $\pi^*\pi$ band of cis-azobenzene would have undergone a large bathochromic shift which could be related to a large increase in basicity in the photoexcited state.[105]

If, however, the band at 420 mμ in protonated cis-azobenzene is due to an enhanced π^*n transition, there would be a slight hypsochromic shift on protonation of cis-azobenzene, and therefore a slightly lower basicity in this photoexcited state. This second hypothesis is less likely than the first, but is worth some consideration. For example one could explain the decrease in quantum yield with an increase in acidity on the necessity for the protonated cis-isomer to lose the proton before cyclization could occur, probably via a diradical, as in the cyclization of stilbene. The dependence of the quantum yield on the substituent would be complex, as an electron donating substituent (e.g. methyl) would reduce deprotonation but enhance cyclization, and an electron withdrawing substituent (e.g. chloro) would enhance deprotonation but inhibit cyclization. For a given compound, however, it would be expected that deprotonation would be linearly dependent on H_o, but consideration of equation (4.1) showed that the

quantum yield did not decrease nearly fast enough as the acidity was increased.

The other more probable hypothesis mentioned above involves an increase in basicity in the first excited state of protonated cis-stilbene, compared with the ground state. This favours a polar mechanism for the cyclization for the following reasons. A large increase in basicity implies that the positive charge has moved from the azo nitrogen to one or both of the aromatic rings. If such a shift may be represented by normal electronic movements as understood in the ground state, then the positive charge is likely to be concentrated on the ring furthest from the original protonated nitrogen atom. This process is outlined in Scheme 5. Structure (LXXXV) is only one of three similar resonance forms which are assumed to predominate in the photoexcited state, whereas their contribution is presumably small in the ground state. Such an excited state would readily undergo 2,2'-ring closure with considerable assistance from the lone pair of electrons on the sp^3 hybridized nitrogen atom (Scheme 6). It may be noted here that because of the N-N single bond in the proposed excited state, this intermediate could be involved in cis-trans isomerization.

The effect of the acid concentration on the quantum yield for cyclization could be explained by competitive protonation

115.

SCHEME 5

(IX)   hν →   (LXXXV)

SCHEME 6

(LXXXV)   →   (LXXXVI)

SCHEME 7

(LXXXVI)   →   (LXXXVII)

H⁺

(LXIV)   ←   (LXXXVIII)
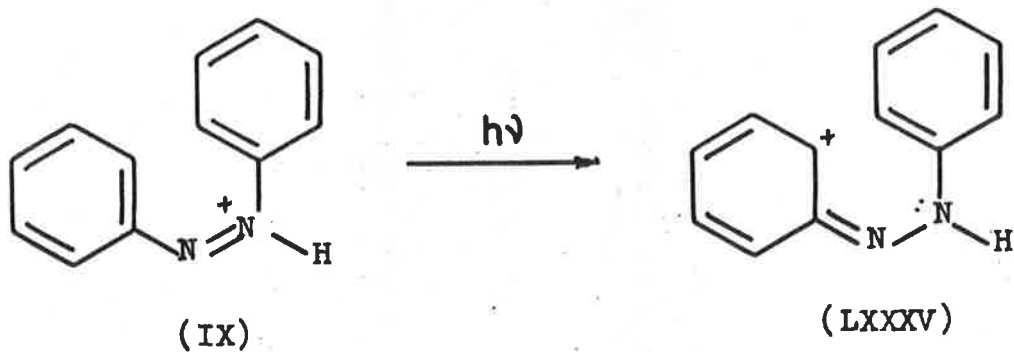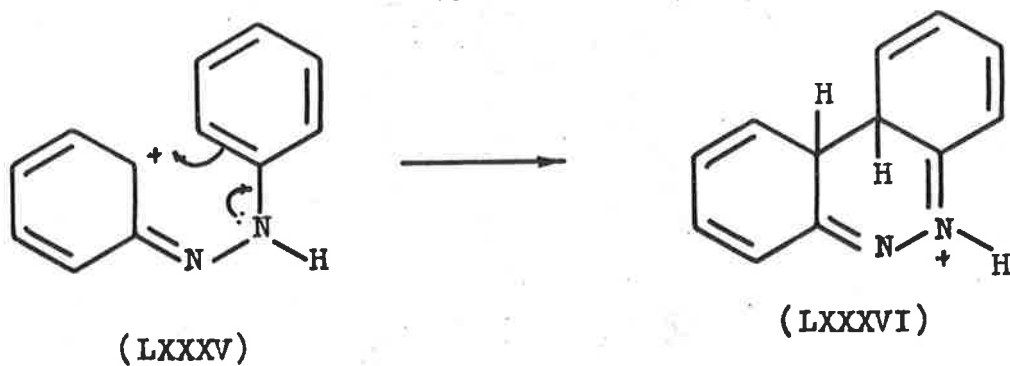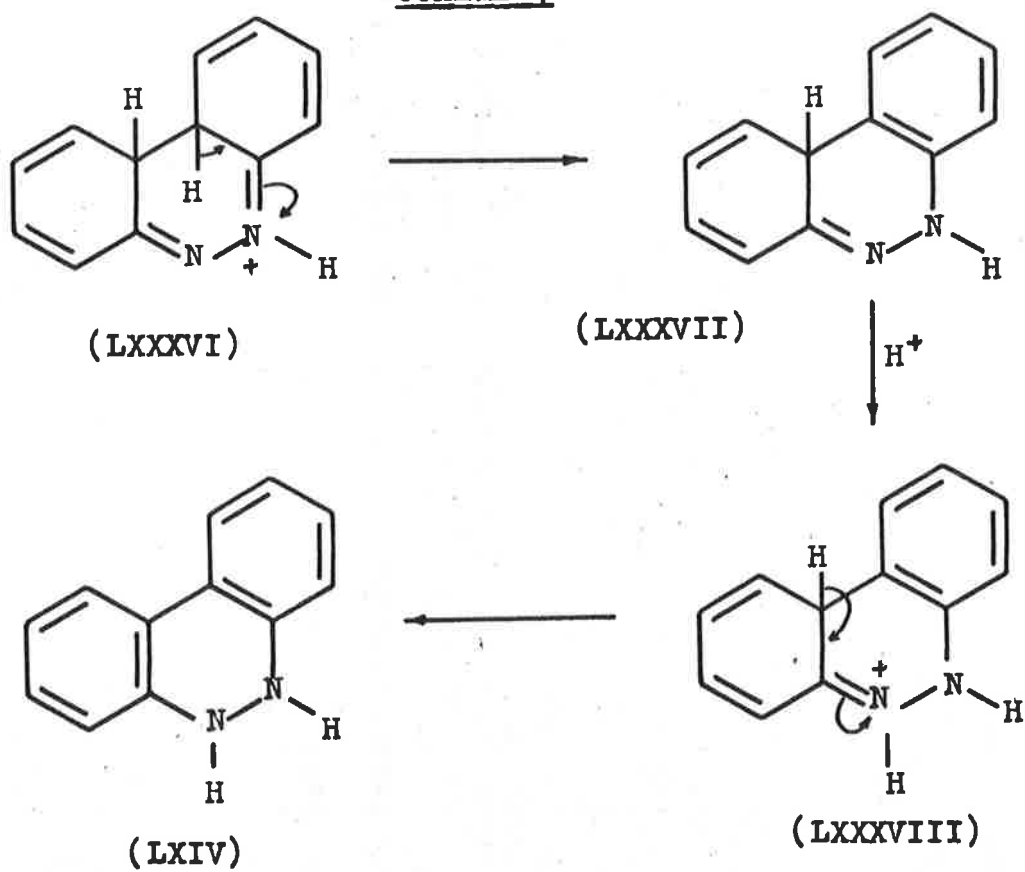
en either of the two nitrogen atoms in (LXXXV). Protonation on the sp^3 hybridized nitrogen would remove the lone pair and presumably would prevent cyclization completely. protonation on the sp^2 hybridized nitrogen would probably reduce the availability of the lone pair on the other nitrogen by an inductive effect and would thus reduce the rate of cyclization.

The probable steps which follow cyclization are shown in Scheme 7. Two hydrogen atoms are effectively transferred from the tertiary carbon atoms to the nitrogen atoms. The loss of the protons is probably fast and irreversible because of the resonance energy gained at each step. It is unlikely that the reverse of the formation of 5,6-dihydrobenzo[g]cinnoline (LXIV) would occur as protonation at the nitrogens would be much more likely than at the ring junctions which originally bore the two hydrogens. 5,6-Dihydrobenzo[g]cinnoline is known to be readily oxidized,[52] and is not isolated in the pure state because of this fact. Under the reaction conditions it would be present as a salt which would be less readily oxidized,[52] but in view of the strong oxidizing power claimed for azobenzene in strongly acidic solution,[23] it would be expected that the rate of oxidation would still be rapid.

Thus the rate determining step is almost certainly the actual photocyclization process (Scheme 6). A simple

attempt to relate the observed quantum yield, $\Phi(obs)$, to the competition caused by protonation of the intermediates gave

$$\Phi(obs) = \Phi_0 - a.10^{-H_0} \tag{4.2}$$

where Φ_0 represents the quantum yield without competition from protonation and "a" is a constant.   In no case did the data fit the above equation because the calculated competition from protonation increased too rapidly as the acid strength increased.   Because of the complex nature of the proposed competition to cyclization, it seemed of little use to attempt to explain the dependence of quantum yield on acid concentration quantitatively.

With 4-chloro- and 4-methylazobenzene the polar cyclization as described for azobenzene is more complex because there is ambiguity in the position of protonation. One nitrogen would probably be favoured but a mixture is likely on consideration of the N-oxidation of mono-substituted azobenzenes where mixtures of N-oxides can be obtained.[106]   Thus it is necessary to consider the fate of each possible species.   The probable electron redistributions leading to cyclizations are shown for 4-chloro- and 4-methylazobenzene in Schemes 8 and 9 respectively.

In structure (LXXXIX), the nett electron density at the positions ortho to the NH group would be reduced by the -I

SCHEME 8

(LXXXIX)

(XC)

SCHEME 9

(XCI)

(XCII)
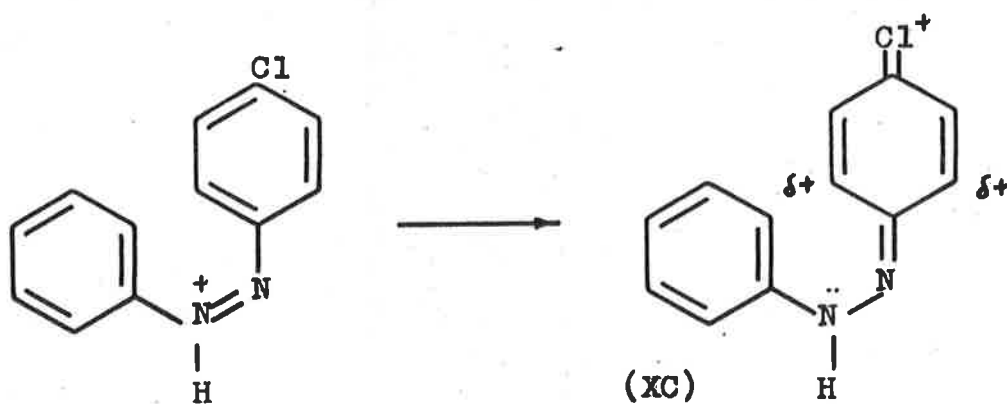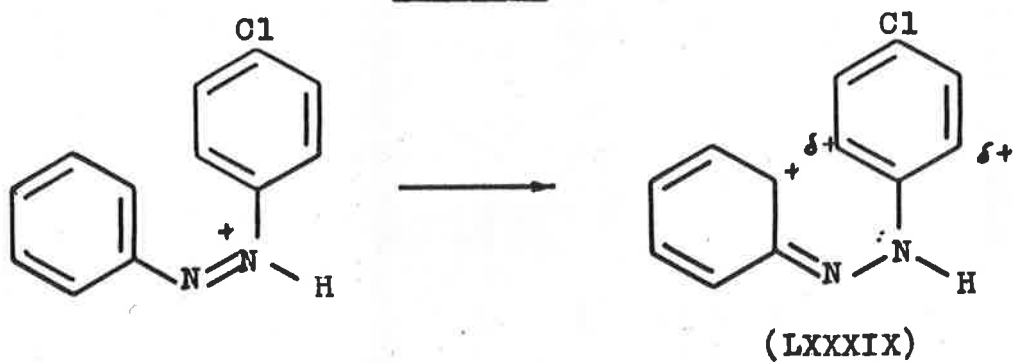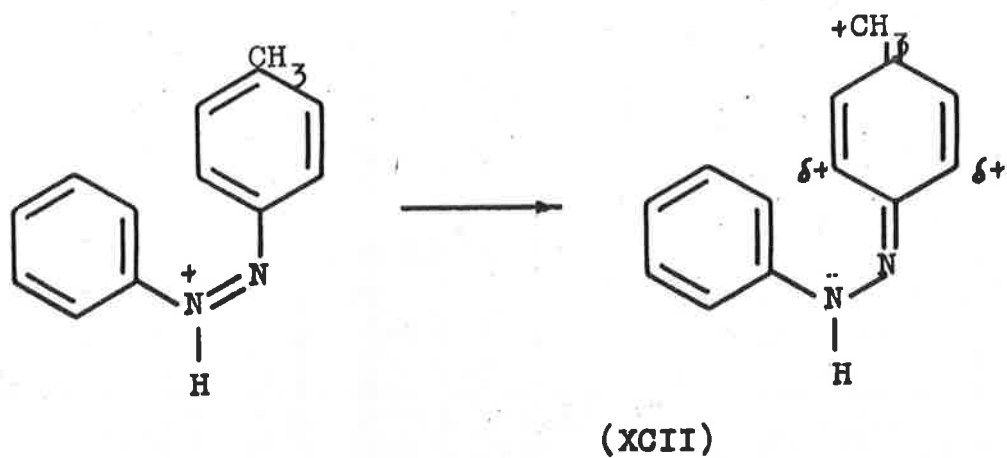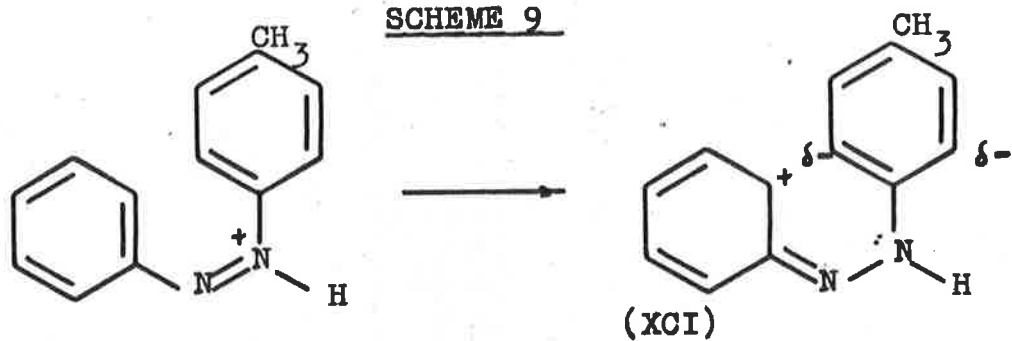
effect of the chloro group. With structure (XC) the
contribution from the resonance structure with a positive
charge on the chloro group is probably large and so the
positions ortho to the sp^2 hydridized nitrogen would be
less positive. In both cases a decrease in the rate of
cyclization of 4-chloroazobenzene compared with azobenzene
should result, and this is observed.

In structure (XCI) the electron density at the positions
ortho to the NH group would be enhanced by the inductive
effect of the methyl group and the rate of cyclization
should increase. With (XCII), hyperconjugation involving
the methyl group would probably reduce the positive charge
at the positions ortho to the sp^2 hybridized nitrogen and
the rate of cyclization should be lowered. On resonance
considerations, the basicity of the nitrogen atom furthest
from the methyl group should be higher and therefore
structure (XCII) should predominate. This allows the low
quantum yield with 4-methylazobenzene to be rationalized.
Unfortunately it is not possible to estimate the many
variables in this scheme and a qualitative treatment is all
that the present data will allow.

Quantum yields from a greater variety of substituted
azo compounds may be of assistance in testing the mechanism
outlined above. There is a limit, however, to the number
of substituents which allow cyclization in sulphuric acid,

e.g. amino, dimethylamino, hydroxy, and alkoxy substituents
prevented cyclization completely.   It is well known that
these substituents decrease the thermal stability of
cis-azobenzenes in acid solution.[107]   Collins and Jaffé[108]
studied the spectra of conjugate acids of several cis-
azobenzenes (including 4-methoxyazobenzene) in perchloric
acid-acetic acid mixtures and claimed that the cis-isomers
were stable during the period of spectral measurement.
This system may be suitable for the photochemical cyclo-
dehydrogenation of azobenzenes.

In common with cis-stilbene and cis-azobenzene,
protonated cis-azobenzene has a very broad, structureless
long-wavelength absorption maximum and so its first excited
singlet state is also likely to have a very short life. It
is not possible to say with certainty that it is this state
which cyclizes, but if this is so, the arrangement of the
substituents in the cyclised products would reflect the
conformation of the cis-azo compound in the ground state.
It should be noted that the phenyl rings in cis-azobenzene
are twisted about $56°$ out of the plane of the azo group.[109]
Thus substituents in the 3,3'-positions of a cis-azobenzene
with a conformation such as to give a 1,10-disubstituted
benzo[c]cinnoline would not interact as such in the azo
compound as in the benzo[c]cinnoline, otherwise the
1,10-disubstituted benzo[c]cinnoline would probably not form.

A similar consideration would apply with 2-substituted azobenzenes, although with 2,2'-dimethylazobenzene, the steric hindrance in the conformation with both methyl groups in the cyclization positions would probably be prohibitively great.   Also the gain in resonance energy in forming an isolated phenyl ring may not be sufficient to allow ejection of the first methyl group (see below)   Thus it is not surprising that no unsubstituted benzo[c]cinnoline was isolated from 2,2'-dimethylazobenzene.

Following the polar mechanism for cyclization, ortho substituents would be ejected as positive ions.   The energy for such a drastic process as elimination of a methyl group probably comes from the resonance energy gained on ejection of the substituent, as well as from photoactivation energy. Probably the proton is lost first in a fast, irreversible reaction.   The substituent could then be lost in a slow, irreversible reaction without affecting the overall rate of cyclization.   The resonance energy gained in the formation of the biphenyl system would greatly assist the elimination of the substituent.   The methyl carbonium ion probably attacks products and reactant to form the tars observed. Cl^+ and I^+ may form substitution products, and the species CO_2H^+ would be expected to give carbon dioxide.

It is of interest that Grellmann et al.[110] have proposed

an ionic mechanism for a photochemical reaction of
diphenylamines which apparently gave a dihydrocarbazole
(XCIV) as a transient species, _via_ the intermediate (XCIII).

(XCIII)   (XCIV)
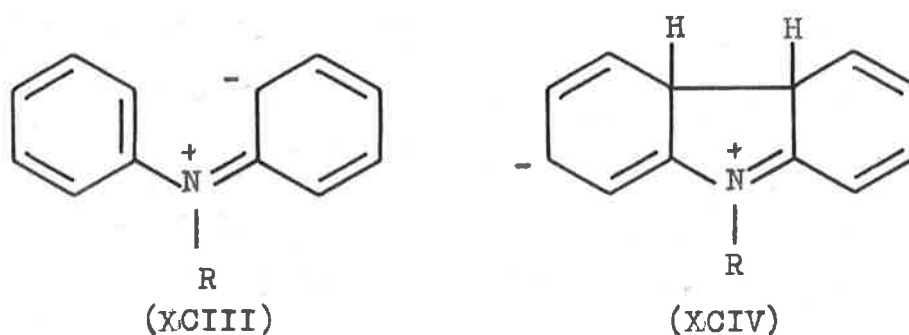
The transient species (XCIV) underwent a reaction with
oxygen to give a carbazole.   Further work[111] showed that
this species (XCIV) was formed from a triplet state of the
diphenylamine which was in turn formed from the first
excited singlet state.

If the analogy for this reaction is carried to the
photocyclization of azobenzenes, the intermediate formation
of a triplet state would mean that the excited azo molecule
would probably have time to assume a new conformation with
respect to its substituents and also a new acid base
equilibrium.   If the triplet state is represented by such
structures as (LXXXV) and similar forms, then _cis-trans_

isomerisation would also occur. Protonation of this triplet
would be sufficient to prevent its cyclization, so that if
the polar mechanism proposed earlier is true, then cyclization
of very short-lived singlet state should be involved. The
fact that monoprotonated trans-azobenzene did not photo-
cyclize could also suggest that the cyclizing species is too
short-lived to allow photoactivated trans-isomer to assume a
cis-configuration in a state capable of cyclization.

A suggested mechanism for the methyl migration in the
irradiation of 2,4,6-trimethylazobenzene is shown in Scheme
10. The only rationalization for this process is that it
avoids the ejection of a methyl group. Alternatively the
migration could occur before cyclization, by analogy with
the photomigrations of alkyl groups in alkyl benzenes,[112,113]
which have been shown to have intramolecular[112] and non-free
radical[113] mechanisms. It should be noted, however, that
the isomerizations in the alkyl benzenes were effected with
light of much shorter wavelength than that used for the
irradiation of 2,4,6-trimethylazobenzene.

It is of interest to compare the photochemical
cyclization of azobenzenes in sulphuric acid with the
cyclization in acetic acid and ferric chloride,[4] and the
thermal cyclization with aluminium chloride.[5] It is possible

124.

SCHEME 10
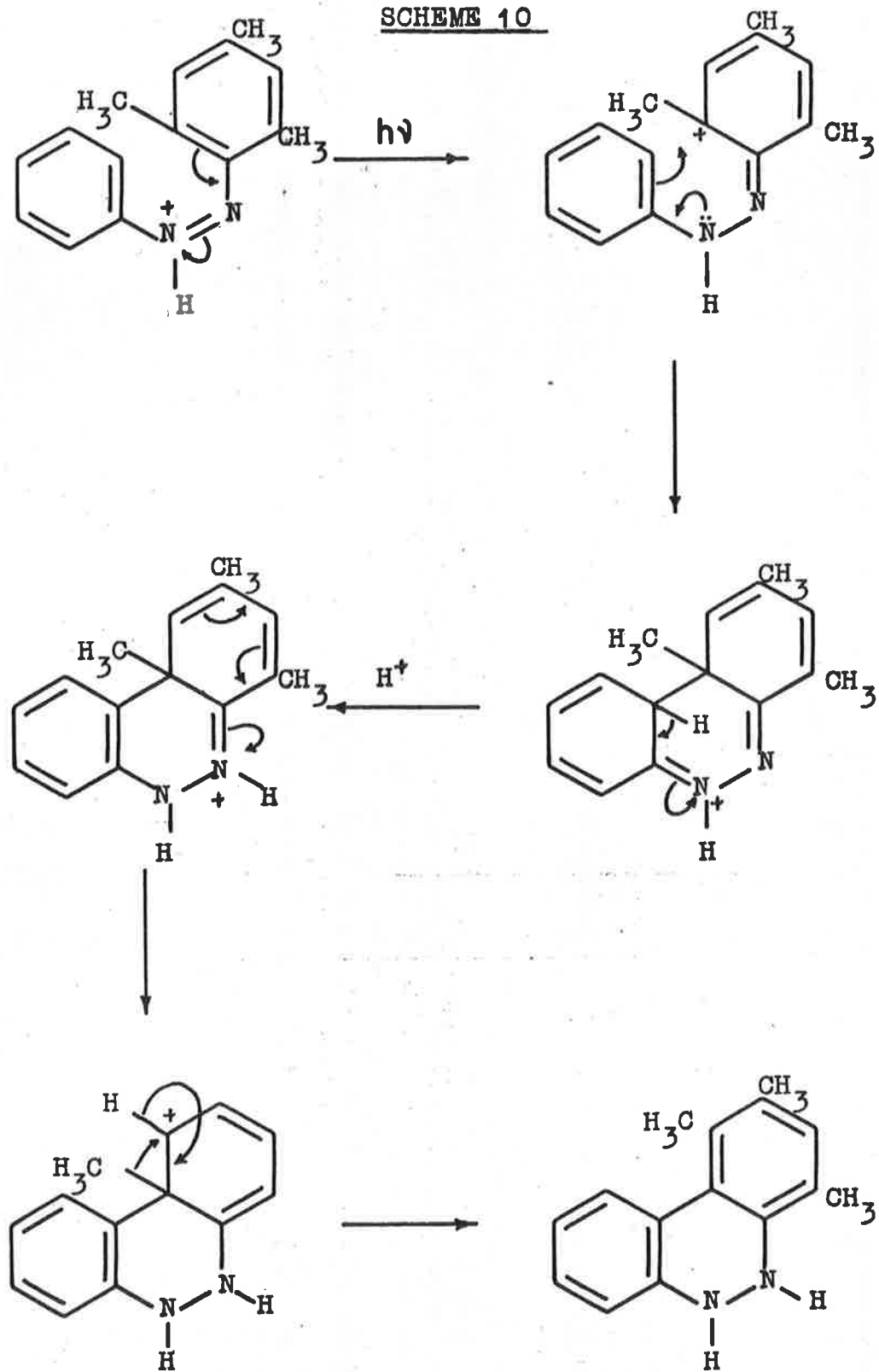
that a polar mechanism, similar to the one outlined above,
may apply, with ferric chloride or aluminium chloride acting
as Lewis acids in place of protons.   The ferric chloride
could also act as oxidizing agent.   There is, however,
insufficient evidence to speculate further on the mechanism
of these cyclizations.

In conclusion it may be said that the polar mechanism
explains most of the known characteristics of the photo-
cyclization of azobenzenes.   Further work should include
determination of quantum yields at much lower temperatures
(if this is possible) to determine the activation energy for
the cyclization step and also quantum yields should be
measured for irradiation in the other absorption bands of
cis-azobenzene at 300 and 230 mμ.[3]   Flash photolysis
techniques could be useful in the study of the cis-trans
photoisomerization; and if 5,6-dihydrobenzo[c]cinnoline
is formed, it should be possible to follow its rate of
oxidation to benzo[c]cinnoline.   At low temperatures it
also may be possible to follow the ejection of a substituent
in the cyclization of a 2-substituted azo compound.

CHAPTER V

EXPERIMENTAL

5.1 General

Melting Points

All melting points were determined in capillaries and are uncorrected.

Photochemical Reactor

Unless otherwise specified the photochemical reactions were carried out in a Pyrex reactor consisting of a Philips HPK 125W mercury lamp surrounded by a water jacket which in turn was surrounded by a jacket of 150 ml capacity containing the solution to be irradiated.

Countercurrent Distribution

Where countercurrent distribution was used to separate mixtures, a Quickfit automatic 50-tube apparatus with stationary and moving phases of 25 ml each was employed.

Spectra

Infrared spectra were determined with a Perkin-Elmer Infracord; ultraviolet spectra were determined with an Optica CF_4 recording spectrophotometer. The n.m.r. spectra were determined by Dr. T. M. Spotswood with a Varian DP60 spectrometer, using a 60 Mc/sec oscillator. Tetra-

methylsilane was used as an internal standard.

5.2 Preparation of Azo Compounds

Dimethylazobenzenes

4,4'-Dimethylazobenzene was prepared by reduction of p-nitrotoluene with zinc dust and sodium hydroxide in methanol. After three recrystallizations from ethanol, the product was chromatographed in hexane on alumina, and then recrystallized from ethanol. 4,4'-Dimethylazobenzene was obtained as orange-yellow needles, m.p. 144.5-145.5° (lit.[114] 144°).

3,3'-Dimethylazobenzene was obtained from Dr. G. E. Lewis,[84] and had m.p. 53° (lit.[114] 54°).

2,2'-Dimethylazobenzene was prepared by sodium hypobromite oxidation of 2,2'-dimethylhydrazobenzene which was obtained by reduction of o-nitrotoluene with zinc dust and sodium hydroxide. The crude azo compound was washed, dried, and chromatographed in hexane on alumina. Recrystallization of the product from methanol gave 2,2'-dimethylazobenzene as red needles, m.p. 54-55° (lit.[114] 55°).

Methylazobenzenes

4-Methyl-, 3-methyl-, and 2-methylazobenzenes, were prepared by the condensation of nitrosobenzene (5.0 g) with appropriate toluidine (5.0 g) in glacial acetic acid (20 ml). When necessary, the reaction was moderated by cooling in an

ice-water bath.   After 5-7 days water was added, the organic
product collected, washed, dried, and chromatographed in
hexane on basic alumina.   Final purification was effected
by recrystallization or distillation.   4-Methylazobenzene
was recrystallized from ethanol and formed orange plates,
m.p. 70-71.5° (lit.[115] 71-72°).   3-Methylazobenzene was
obtained as a bright red liquid, b.p. 180-185°/14 mm
(lit.[42] b.p. 175°/19 mm).   2-Methylazobenzene was obtained
as a bright red liquid, b.p. 178°/15 mm (lit.[46] b.p. 180-181°
(corr.)/20 mm).

Chloroazobenzenes

4-Chloro-, 3-chloro-, and 2-chloroazobenzenes were
prepared by condensing nitrosobenzene (5.0 g) with the
appropriate chloroaniline (6.0 g) in glacial acetic acid
(10 ml).   In the preparation of 2-chloroazobenzene it was
necessary to heat the reaction mixture at 70° for 12 hr to
effect condensation.   The crude azo compounds were
chromatographed in hexane on basic alumina.   4-Chloroazo-
benzene was obtained from ethanol as orange-red needles,
m.p. 86-87.5° (lit.[116] 87.5°).   3-Chloroazobenzene was
obtained from ethanol as orange needles, m.p. 66.5-67°
(lit.[116] 67.5°).   2-Chloroazobenzene was recrystallized
from ethanol-methanol (with cooling to -15°) and was
obtained as red prisms, m.p. 31.5° (lit.[47,117] 33°,29-31°).

4-Iodoazobenzene

This compound was obtained from Dr. G. E. Lewis, who had prepared it by condensation of 4-iodoaniline with nitrosobenzene in glacial acetic acid to give 4-iodo-azobenzene as orange plates, m.p. 106-106.5° (lit.[37] 105°).

3-Iodoazobenzene

3-Iodoaniline was prepared from m-nitroaniline by the method of Baeyer.[118]   3-Iodoaniline (5.0 g) was added to a solution of nitrosobenzene (2.5 g) in glacial acetic acid (2.5 ml), the mixture was allowed to stand overnight at room temperature, warmed to 50-60° for 1 hr, and then dissolved in benzene (100 ml).   The solution was washed with several portions of 6N hydrochloric acid (tar being filtered off), then with 1% sodium hydroxide solution, and finally with water.   The benzene was evaporated and the residue chromatographed on activated alumina, elution being effected with 10% benzene in hexane.   The first band was collected, the solvent evaporated and the orange solid (3.9 g, 56%) recrystallised from ethanol-methanol to give 3-iodoazobenzene as orange needles, m.p. 71-71.5° (lit.[119] 72-73°).

2-Iodoazobenzene

A mixture of nitrosobenzene (4.28 g) and 2-iodoaniline (8.76 g) was dissolved in glacial acetic acid (10 ml), maintained at 70-80° for 7 hr, and then set aside overnight. The mixture was shaken with light petroleum, b.p. 60-90°,

and washed with water, 18$\underline{N}$ sulphuric acid, and then water
again. The petroleum layer was evaporated and the product
chromatographed on alumina with light petroleum, b.p.
60-90°. Evaporation of the eluate of the first band gave
a deep red solid (5.76 g. 47%). Recrystallization from
ethanol and then from hexane, with cooling in dry ice-ethanol,
gave 2-iodoazobenzene as orange-red needles, m.p. 62° (Found:
C, 47.1; H, 2.9; N, 8.8%. $C_{12}H_9IN_2$ requires C, 46.8;
H, 2.9; N, 9.1%).

Azobenzene-4-carboxylic Acid

A commercial sample (L. Light) was recrystallized twice
from ethanol and formed red plates, m.p. 248-248.5° (lit.[38]
247°).

Azobenzene-3-carboxylic Acid

Ethyl 3-aminobenzoate (8.26 g) and nitrosobenzene (5.40 g)
were condensed in glacial acetic acid (6 ml). After 20 hr
the mixture was shaken with light petroleum, b.p. 60-90°, and
the solution washed with water, 5$\underline{N}$ hydrochloric acid, dilute
aqueous sodium carbonate, and water. Evaporation of the
solvent gave a dark red oil which was chromatographed on
alumina with benzene-light petroleum (1:4). Evaporation of
the solvent gave a bright red liquid which was hydrolysed
with refluxing ethanolic sodium hydroxide. The solution
was diluted with water acidified with hydrochloric acid, and
the product recrystallised from ethanol to give azobenzene-

3-carboxylic acid (4.77 g, 42%) as orange needles, m.p. 170.5-171.5° (lit.[120] 170-171°).

Azobenzene-2-carboxylic Acid

Ethyl anthranilate (12.4 g) was added to a solution of nitrosobenzene (8.0 g) in glacial acetic acid (8 ml) and the mixture warmed at 65° for 24 hr. The cooled mixture was extracted with light petroleum and the extract washed with water, 6N hydrochloric acid, dilute aqueous sodium carbonate, and water. The solvent was evaporated to give a residue which was chromatographed on alumina with benzene-light petroleum (1:4). The red oil (9.5 g) obtained from the eluate was refluxed with sodium hydroxide (1.6 g) in ethanol (50 ml) for 1½ hr; the solution was diluted with water (300 ml) and boiled to remove most of the ethanol. The cooled solution was extracted with ether (to remove non-acidic material), and the aqueous layer then acidified with hydrochloric acid. The precipitated solid was subjected to countercurrent distribution between 18N sulphuric acid and benzene; fractions near the solvent front were collected and evaporated. Recrystallization of the product from ethanol gave azobenzene-2-carboxylic acid (5.5 g, 33%) as orange prisms, m.p. 92-93° (lit.[121] 95°).

2,4,6-Trimethylazobenzene

Nitromesitylene was prepared by nitration of mesitylene,[122] and then reduced with tin and hydrochloric

acid to give mesidine which was condensed with nitrosobenzene
(equimolar proportions) in glacial acetic acid at 20° for 36
hr. The mixture was diluted with water and extracted
several times with light petroleum, b.p. $40-70^\circ$. The
extract was washed with 10% aqueous sodium hydroxide and
then 2N hydrochloric acid, and chromatographed on activated
alumina, elution being effected with light petroleum, b.p.
$40-70^\circ$. Evaporation of the eluate, gave a bright red oil
which solidified on cooling below 0°. Recrystallization
from methanol-ethanol (1:1) with cooling below 0° gave
2,4,6-trimethylazobenzene as red needles, m.p. 19.5° (Found:
C, 80.55; H, 7.15; N, 12.5%. $C_{15}H_{16}N_2$ requires C, 80.3;
H, 7.2; N, 12.5%).

5.3 Photochemical Reactions of Azobenzenes

(a) Azobenzene and p-Derivatives

Azobenzene

A solution of azobenzene (5.0 g) in 22N sulphuric acid
(120 ml) was irradiated in the mercury lamp reactor until
its ultraviolet spectrum showed the reaction to be virtually
complete (72 hr). The mixture was then partially neutral-
ized (with cooling in ice-water) with sodium hydroxide (70 g)
in water. The resulting solid was collected, washed with
dilute sulphuric acid and then ethanol, and then treated with
excess sodium hydroxide solution. Recrystallization of the

product from aqueous ethanol gave benzidine (1.71 g) as buff plates, m.p. 125° (lit. 127°), alone or admixed with an authentic specimen. Its ultraviolet and infrared spectra were identical with those of an authentic sample.

The acidic filtrate and washings were extracted with benzene, and the benzene solution washed, dried, and evaporated to give a yellow solid (2.37 g, 48%). Re-crystallization from benzene gave benzo[c]cinnoline as pale yellow needles (2.22 g, 45%), m.p. 156-156.5° (lit.[58] 156°), alone or admixed with an authentic specimen. Its ultra-violet and infrared spectra were identical with those of an authentic specimen.

4,4'-Dimethylazobenzene

A solution of 4,4'-dimethylazobenzene (3.06 g) in 22N sulphuric acid (100 ml) was irradiated in the mercury lamp reactor for 550 hr. The solution was then basified, with cooling, with concentrated aqueous sodium hydroxide, and the mixture extracted with ether. The residue obtained by evaporation of the ethereal solution was chromatographed in benzene on basic alumina. Unchanged azo compound (0.07 g) was eluted first. Evaporation of the following fractions gave 2-amino-4',5-dimethyldiphenylamine (0.14 g). On recrystallization from aqueous ethanol it formed colourless plates, m.p. 107.5-108° (lit.[31] 107°). It was characterized

by conversion into 6-methyl-2-phenyl-1-p-tolylbenzimidazole;
after three recrystallizations from aqueous ethanol this
formed light-brown plates, m.p. 187-188° (lit.[31] 185°).
Further elution of the column gave 2,9-dimethylbenzo[c]cinnoline
(1.75 g, 57%); after recrystallization from benzene-hexane
it formed pale yellow needles, m.p. 190-191° (lit.[123] 187°)
(Found: C, 81.05; H. 5.85; N, 13.4%.   Calc. for $C_{14}H_{12}N_2$:
C, 80.75; H, 5.8; N, 13.45%).   The melting point was not
depressed by admixture with an authentic specimen donated
by Dr. P. F. Holt[40] and the infrared spectra (chloroform)
of the two samples were identical.

4-Methylazobenzene

A solution of 4-methylazobenzene (3.01 g) in 22N sul-
phuric acid (135 ml) was irradiated in the mercury lamp
reactor for 105 hr.   The mixture was then partially
neutralized, with cooling, with a solution of sodium
hydroxide (80 g) in water.   The cold solution was extracted
with benzene and the benzene solution evaporated to give the
crude product (1.50 g, 50%).   Recrystallization from benzene
gave 2-methylbenzo[c]cinnoline as pale yellow prisms, m.p.
137-138° (Found: C, 80.25; H, 5.4; N, 14.55%. $C_{13}H_{10}N_2$
requires C, 80.4; H, 5.2; N, 14.4%).

After benzene extraction, the acidic solution was made
slightly alkaline with aqueous sodium hydroxide, and steam
distilled.   The residual liquors (and solid) were extracted

with ether and the ether evaporated to give a red-brown solid
(1.22 g). Recrystallization from ethanol gave
4-(4'-aminophenyl)-4-methylcyclohexa-2,5-dienone as very
pale yellow prisms, m.p. 167-168° (Found; C, 78.5; H, 6.5;
N, 7.2; O, 8.1%; mol. wt. 207. $C_{13}H_{13}NO$ requires C, 78.4;
H, 6.6; N, 7.0; O, 8.0%; mol. wt. 199). Its infrared
spectrum (chloroform) showed bands at 3500 and 3430 cm^{-1} (NH_2),
and at 1700 and 1665 cm^{-1} (C=O). Its ultraviolet spectrum
(95% ethanol) showed $\lambda_{max.}$ at 245 and 290sh mµ; in 1N
hydrochloric acid it showed $\lambda_{max.}$ at 238 and 320sh mµ. Its
n.m.r. spectrum was determined in $CDCl_3$ and showed a sharp
singlet at τ 8.38 (3 protons) assigned to a methyl group
attached to a quaternary carbon atom but not directly to an
aromatic ring, a broad singlet at τ 6.45 (NH_2), and two
quartets at τ 3.92, 3.75, 3.25, and 3.08 (4 protons, J ca.
10 c/s) assigned to the dienone protons and τ 3.52, 3.37,
3.03, and 2.88 (4 protons, J ca. 9 c/s) assigned to the
para-disubstituted aromatic ring. A diazotized solution
of the dienone coupled with a cold solution of 2-naphthol
in 10% sodium hydroxide to give a bright red dye.

The above dienone (57 mg) was treated with acetic
anhydride (1 ml) and concentrated sulphuric acid (0.04 ml)
at room temperature for 10 hr.cf.34 The resulting mixture
was then refluxed with sodium hydroxide (3 g) in water (10 ml)
for 1½ hr. It was then diluted with water (20 ml), extracted
with ether (to remove non-phenolic material) and then

acidified with dilute sulphuric acid and again extracted with ether (to remove non-basic materials). Sodium carbonate was added to give pH 8.5 (indicator paper) and the mixture again extracted with ether. Evaporation of the ether gave a light brown gum. Recrystallization from benzene gave the product, presumably 4-amino-3'-hydroxy-2'-methylbiphenyl (25 mg) as pale buff needles, m.p. 122.5–123° (Found: C, 77.9; H, 6.5; N, 7.0%. $C_{13}H_{13}NO$ requires C, 78.4; H, 6.6; N, 7.0%).

Its infrared spectrum (chloroform) showed bands at 3650 cm^{-1} (OH), and 3430 cm^{-1} (NH). Its ultraviolet spectrum in 95% ethanol showed $\lambda_{max.}$ 231, 262, and 287sh mμ; in 1N hydrochloric acid it showed $\lambda_{max.}$ 240sh and 288 mμ. A diazotized solution coupled with a cold solution of 2-naphthol in 10% sodium hydroxide to give a bright red dye. The n.m.r. spectrum of the biphenyl in CDCl$_3$ showed a singlet at τ 7.85 (3 protons) assigned to a methyl group attached to an aromatic ring, a broad singlet at τ 5.55 (NH$_2$ and OH), a quartet at τ 3.38, 3.25, 3.02, and 2.90 (4 protons, J ca. 8 c/s) assigned to the para-disubstituted aromatic ring, and further partially resolved bands in the same region (3 protons) assigned to the trisubstituted aromatic ring.

4-Methylhydrazobenzene

4-Methylazobenzene was reduced with zinc dust and sodium hydroxide in boiling methanol, and the crude product was

recrystallized from cyclohexane to yield colourless plates,
m.p. 88-89° (lit.[32,124] 86-87, 91°).

Rearrangement of 4-Methylhydrazobenzene in 22N Sulphuric acid

Solid 4-methylhydrazobenzene (1.18 g) was added to 22N
sulphuric acid (25 ml) at room temperature over 5 min with
vigorous stirring.   The mixture was allowed to stand over-
night and was then worked up according to the method of
Jacobson and Lischke,[32] to give the picrate of
6-methyl-1-phenylbenzimidazole, m.p. 201-202.5° (decomp.)
(lit.[32] 198-200°).

4-Chloroazobenzene

A solution of 4-chloroazobenzene (2.50 g) in 22N
sulphuric acid (120 ml) was irradiated in the mercury lamp
reactor for 84 hr.   The resulting mixture was partly
neutralized with sodium hydroxide (80 g) in water (300 ml),
with the temperature below 35°.   The resulting precipitate
was collected and the filtrate (A) set aside.

The precipitate (1.80 g) was dissolved in concentrated
hydrochloric acid (20 ml), diluted to 100 ml with water,
shaken with benzene (20 ml), and filtered.   The solid was
washed with hot benzene (6 x 20 ml) which was then used to
extract the filtrate.   The extracts were combined and
evaporated.   The crude product, m.p. 215-216°, (1.30 g, 53%)
was recrystallized from toluene, and 2-chlorobenzo[c]cinnoline

obtained as yellow needles, m.p. 215.5-216° (lit.[24] 211°)
(Found: C, 67.05; H, 3.4; Cl, 16.7; N, 13.3%. Calc. for
$C_{12}H_7ClN_2$: C, 67.15; H, 3.3; Cl, 16.5; N, 13.05%). After
the benzene extraction, the hydrochloric acid solution was
basified with sodium hydroxide and extracted with ether.
Evaporation of the ether gave a dark crystalline product
(0.20 g) which was heated with salicylaldehyde (0.20 g) in
benzene. The resulting disalicylidenebenzidine (0.21 g)
separated from toluene (using charcoal) as orange-yellow
plates, m.p. 258.5-260.5°, alone or admixed with an
authentic specimen. The infrared spectra of the two samples
in Nujol were identical.

The filtrate (A) was basified with sodium hydroxide,
steam-distilled (to remove a small quantity of volatile
amines) and the non-volatile residue extracted with ether.
Evaporation gave a viscous oil (0.58 g) which was heated with
salicylaldehyde (0.65 g) and ethanol (10 ml) on a steam-bath
for ½ hr. The solid product was collected and washed with
methanol (yield 1.01 g). Recrystallization from benzene
with charcoal gave N,N'-disalicylidene-5-chloro-2,4'-
diaminobiphenyl as orange needles, m.p. 167.5-168° (lit.[36]
166-167°). A sample of this material (0.23 g) was boiled
with water (20 ml) and concentrated sulphuric acid (2 ml)
until no odour of salicylaldehyde could be detected. The
solution was basified with sodium hydroxide and extracted
with ether to give 5-chloro-2,4'-diaminobiphenyl as an oil

(0.11 g) on evaporation of the ether. Its dibenzylidene derivative had m.p. 105.5-106.5° (lit.[125] 104°), its diacetyl derivative, m.p. 210.5-211.5° (lit.[125] 204°), and its diformyl derivative, m.p. 192-193° (lit.[125] 194°).

4-Iodoazobenzene

4-Iodoazobenzene (3.00 g) was suspended in 22$\underline{N}$ sulphuric acid (120 ml) in a glass culture-jar (30 x 23 x 6 cm) and exposed to sunlight (summer) for 9 days. The ultraviolet absorption spectrum then indicated that virtually no azo-compound remained. The solution was diluted with water (100 ml) and partly neutralized with sodium hydroxide (75 g) in water (200 ml), the temperature being kept near 45°. The mixture was immediately shaken with benzene (500 ml), filtered to remove solid (S), and the aqueous filtrate extracted several times with benzene. The combined benzene extracts were washed with dilute aqueous sodium carbonate, but no iodine was detected with starch iodide paper upon acid-ification of the sodium carbonate solution, even though an odour of free iodine had been noticed immediately after the irradiation. The benzene solution was evaporated and the solid (1.02 g, 34%) recrystallized from benzene to give 2-iodobenzo[c]cinnoline as yellow needles, m.p. 217.5-218° (Found: C, 47.05; H, 2.4; N, 9.1%. $C_{12}H_7IN_2$ requires C, 47.1; H, 2.3; N, 9.15%).

The solid (S) was shaken with dilute aqueous sodium

hydroxide and extracted with ether. Evaporation of the ether and recrystallization of the product from aqueous ethanol gave benzidine (0.013 g, 0.4%) as buff plates, m.p. and mixed m.p. 122-123°. Its ultraviolet and infrared spectra were identical with those of an authentic specimen. The solution was basified with sodium hydroxide solution, steam-distilled to remove volatile bases, and the non-volatile residue extracted with ether. Evaporation gave crude 2,4'-diamino-5-iodobiphenyl (0.42 g, 14%) as a brown gum which was characterized as its salicylidene derivative m.p. 150.5-151.5° (lit.[37] 151°) and its p-nitrobenzylidine derivative, m.p. 215.5-216° (lit.[37] 213°).

2-Iodobenzo[c]cinnoline-N-oxide

2-Iodobenzo[c]cinnoline (61 mg) was dissolved in glacial acetic acid (6 ml) and heated with 27.5% w/v hydrogen peroxide (0.9 ml) at 60° for 2 hr. The product was precipitated with water and washed with water to give the crude product (63 mg). On recrystallization from benzene, 2-iodobenzo[c]cinnoline-N-oxide was obtained as very pale yellow needles, m.p. 221.5-222.5°, insoluble in hot sodium hydroxide solution (Found: C, 45.1; H, 2.55; N, 8.6%. $C_{12}H_7IN_2O$ requires C, 44.75; H, 2.2; N, 8.7%).

Azobenzene-4-carboxylic Acid

Azobenzene-4-carboxylic acid (2.50 g) was suspended in 22$\underline{N}$ sulphuric acid (135 ml) and irradiated in the mercury lamp

reactor for 360 hr. The resulting mixture of solid and
solution was diluted with water (250 ml) and extracted with
benzene (100 ml) to give unchanged azobenzene-4-carboxylic
acid (0.068 g), on evaporation of the benzene.

After the extraction with benzene, the strongly acidic
mixture remaining was partly neutralized with sodium
hydroxide (80 g) in water (150 ml), with cooling to keep
the temperature below 40°. The mixture was then cooled to
room temperature, the solid collected and boiled with con-
centrated hydrochloric acid (200 ml) and methanol (150 ml)
until all the methanol had been evaporated. The mixture
was then diluted with water (650 ml) and extracted with
benzene (B1). The aqueous layer was basified with sodium
hydroxide and then extracted with ether. Evaporation of
the ether gave a buff solid (0.58 g, 29%) which on re-
crystallization from aqueous ethanol gave benzidine as
buff plates, m.p. and mixed m.p. 125° (lit. 127°). Its
ultraviolet and infrared spectra were identical with those
of an authentic specimen. The aqueous layer remaining
after the ether extraction was adjusted to pH 7 with
phosphoric acid and evaporated to dryness, precipitating
the inorganic salts in stages with excess methanol. The
final residue was refluxed for 15 hr with methanol (100 ml)
containing dry hydrogen chloride; the mixture was then
diluted with a large excess of water and extracted with

benzene (B2).   The aqueous layer was again evaporated to dryness and refluxed with methanol (25 ml), containing hydrogen chloride, then diluted with water and extracted with benzene (B3).   Evaporation of the benzene extracts (B1, B2, and B3) gave the crude product (1.15 g, 44%). Recrystallization from ethanol gave methyl benzo[c]cinnoline-2-carboxylate as yellow needles m.p. 185.5° (lit.[24] 179°) (Found: C, 70.45; H, 4.35; N, 11.5%.   Calc. for $C_{14}H_{10}N_2O_2$: C, 70.6; H, 4.25; N, 11.75%).   Hydrolysis of the ester was effected with alkali.   Successive dissolution in dilute sodium bicarbonate and reprecipitation with acetic acid gave benzo[c]cinnoline-2-carboxylic acid as yellow micro-needles, m.p. 363-364° (in vacuo) (lit.[24] 362°).

(b)   m-Derivatives

3,3'-Dimethylazobenzene

A solution of 3,3'-dimethylazobenzene (2.50 g) in 22N sulphuric acid (110 ml) was irradiated in a plate glass reactor (30 x 30 x 0.1 cm) for 11 days in sunlight.   The solution was then basified, with cooling, with concentrated aqueous sodium hydroxide, and the mixture extracted with ether.   Evaporation of the ethereal solution gave a residue which was subjected to countercurrent distribution between 1-butanol and 0.5N hydrochloric acid (25 transfers).   The contents of the tubes containing the yellow benzo[c]cinnolines were combined, evaporated, and the product chromatographed

in benzene on alumina; but no significant separation was
achieved.   The solvent was evaporated and the residue
(0.79 g, 32%) submitted to countercurrent distribution
between hexane and 1.5N hydrochloric acid.   The fractions
near the starting tube gave 3,8-dimethylbenzo[g]cinnoline
(0.40 g, 16%); after recrystallization from benzene-hexane
it formed yellow needles, m.p. 188° (lit.[64] 188°) (Found:
C, 80.95; H, 5.75; N, 13.55%).   Calc. for $C_{14}H_{12}N_2$:
C, 80.75; H, 5.8; N, 13.45%).   The m.p. was not depressed
by admixture with an authentic specimen donated by Dr. P.F.
Holt,[40] and the infrared spectra (in chloroform) of the two
samples were identical.   The fractions nearer the solvent
front gave 1,8-dimethylbenzo[c]cinnoline (?) (0.18 g, 7%);
after recrystallization from hexane it formed yellow needles,
m.p. 118.5-119° (Found: C, 80.7; H, 5.9; N, 13.3%. $C_{14}H_{12}N_2$
requires C, 80.75; H, 5.8; N, 13.45%).   The fractions near-
est the solvent front were again subjected to countercurrent
distribution and gave 1,10-dimethylbenzo[g]cinnoline (0.082
g, 3%); after recrystallization from hexane it formed yellow
needles, m.p. 114.5° (lit.[40] 112-113°) Found: C, 80.8;
H, 5.85; N, 13.4%.   Calc. for $C_{14}H_{12}N_2$: C, 80.75; H, 5.8;
N, 13.45%).   The m.p. was not depressed by admixture with a
sample donated by Dr. P.F. Holt.[40]

After the removal of the benzo[g]cinnolines, the remain-
ing fractions from the butanol-0.5N hydrochloric acid separa-
tion were combined, basified, and extracted with ether.   The

ethereal solution was evaporated and the residue dissolved
in ethanol and treated with anhydrous stannous chloride
(2 g) in concentrated hydrochloric acid (6.5 ml). The
solid was collected, dissolved in water, treated with
acidified sodium sulphide solution and filtered. The
filtrate was treated with aqueous sodium sulphate and the
resulting precipitate collected and treated with excess
aqueous sodium hydroxide. The mixture was extracted with
ether and the ether evaporated to give 2,2'-dimethylbenzidine
(m-tolidine) as a colourless glass (0.30 g) which failed to
crystallize after several weeks. Its dibenzylidene
derivative had m.p. 172-173° (lit.[41] 172-173°), its
disalicylidene derivative had m.p. 201-202.5° (lit.[41]
198-199°), and its diacetyl derivative had m.p. 289°
(lit.[41] 281°).

3-Methylazobenzene

A solution of 3-methylazobenzene (3.00 g) in 22$\underline{N}$
sulphuric acid (135 ml) was irradiated in the mercury lamp
reactor for 89 hr. The solution was then almost neutral-
ized, with cooling, with aqueous sodium hydroxide, and the
solid collected and washed with warm dilute sulphuric acid.
The solid was then treated with excess aqueous sodium
hydroxide, and the mixture extracted with ether.
2-Methylbenzidine (1.03 g) was obtained as red-brown oil.
Its diacetyl derivative had m.p. 310° (lit.[42] 300°); its
disalicylidene derivative, m.p. 157-158.5° (lit.[42] 160°);

and its dibenzylidene derivative, m.p. 110-111° (lit.[42] 111-112°).

The acidic filtrate and washings were basified with sodium hydroxide, the mixture extracted with ether, and the product subjected to countercurrent distribution between hexane and 1N hydrochloric acid. The fractions nearer the solvent front yielded 1-methylbenzo[c]cinnoline (0.37 g, 13%). After recrystallization from cyclohexane it formed yellow needles, m.p. 117.5° not depressed by admixture with a sample provided by Dr. P.F. Holt[40] (Found: C, 80.3; H, 5.4; N, 14.2%. Calc. for $C_{13}H_{10}N_2$: C, 80.4; H, 5.2; N, 14.4%). The infrared spectra of the two compounds in chloroform were also identical. The fractions nearer the starting tube gave 3-methylbenzo[c]cinnoline (0.79 g, 27%). After recrystallization from benzene-cyclohexane it formed yellow plates, m.p. 125-125.5° (Found: C, 80.4; H, 5.3; N, 14.25%. $C_{13}H_{10}N_2$ requires C, 80.4; H, 5.2; N, 14.4%). From the "overlap" region, a mixture (0.23 g) of the two benzo[c]cinnolines was obtained, giving an overall yield of 1.39 g (47%) of benzo[c]cinnolines.

3-Chloroazobenzene

A solution of 3-chloroazobenzene (3.10 g) in 22N sulphuric acid (135 ml) was irradiated in the mercury lamp reactor for 88 hr. The product was diluted with water

(150 ml) and partly neutralised with sodium hydroxide (80 g)
in water (300 ml), with the temperature below 40°. The
cooled mixture was shaken with benzene (150 ml), filtered,
and the solid (S) washed with benzene (5 x 50 ml) which
was then used to extract the aqueous filtrate. All the
benzene solutions were combined and evaporated to give a
yellow solid (1.54 g, 50%), m.p. $141-161^{\circ}$, which was sub-
jected to countercurrent distribution between hexane and
$4\underline{N}$ hydrochloric acid. From the first fractions at the
solvent front, starting material (27 mg) was obtained.
Later fractions gave 1-chlorobenzo[c]cinnoline (cf.[24])
(0.32 g, 11%) which separated from methanol as yellow
needles, m.p. $145-146^{\circ}$ (Found: C, 67.35; H, 3.3; Cl, 16.6;
N, 13.05%. $C_{12}H_7ClN_2$ requires C, 67.15; H, 3.3; Cl, 16.5;
N, 13.05%). From the fractions nearer the starting tube,
3-chlorobenzo[c]cinnoline (cf.[24]) (1.04 g, 35%) was
obtained. Recrystallization from ethanol gave yellow
needles, m.p. $189.5-190.5^{\circ}$ (Found: C, 67.0; H, 3.45;
Cl, 16.1; N, 13.15%. $C_{12}H_7ClN_2$ requires C, 67.15;
H, 3.3; Cl, 16.5; N, 13.05%).

The solid (S) (1.98 g) was treated with aqueous sodium
hydroxide and then extracted with ether. Evaporation of
the ether and recrystallization from aqueous ethanol gave
2-chlorobenzidine (0.91 g), m.p. $101.5-102.5^{\circ}$. An
authentic specimen, prepared by reduction of 3-chloro-

azobenzene with stannous chloride and hydrochloric acid, had m.p. $101.5-102.5^{\circ}$ and the mixed m.p. showed no depression. According to the literature this compound has m.p. 113°.[43] The infrared spectra $(CHCl_3)$ and ultraviolet spectra (95%) ethanol) of the two samples were identical. The ultraviolet spectrum showed $\lambda_{max.}$ at 274 mμ (log ε 4.37).

3-Iodoazobenzene

3-Iodoazobenzene (3.00 g) was suspended in 22$\underline{N}$ sulphuric acid (120 ml) and irradiated in the mercury lamp reactor for 96 hr, during which time the mixture was warmed twice to assist the dissolution of some of the remaining azo compound. Unchanged starting material (0.85 g, 28%) was first removed. The irradiated mixture was diluted with water (100 ml) and partially neutralized with sodium hydroxide (70 g) in water (200 ml), the temperature being kept below 40°. The cold mixture was shaken with benzene (300 ml) and the solid (S) was filtered off. The aqueous layer was extracted several times with benzene (B), the aqueous layer was basified with sodium hydroxide solution, extracted with ether, and the ether evaporated to give a brown oil (0.12 g) which was not investigated further. The solid (S) was dissolved in a mixture of hot concentrated hydrochloric acid (50 ml) and water (100 ml) and the solution was extracted with several portions of benzene. These were combined with the benzene (B) and evaporated to

give a yellow solid (1.07 g) which was subjected to counter-
current distribution between benzene-light petroleum b.p.
60-90° (1:1) and 4N hydrochloric acid.   The first 100
fractions of yellow solution were collected and the rest
of the material in the machine was isolated separately,
recrystallized from ethanol, and the mother liquor was
combined with the above 100 fractions.   This combined
material was subjected to countercurrent distribution
between hexane and 4N hydrochloric acid.   From the
fractions nearer the solvent front 1-iodobenzo[c]cinnoline
(0.29 g, 10%) was obtained.   On recrystallization from
methanol it formed yellow needles, m.p. 122° (Found:
C, 47.35; H, 2.55; I, 41.2; N, 8.95%. $C_{12}H_7IN_2$ requires
C, 47.1; H, 2.3; I, 41.45; N, 9.15%).   The material
isolated from the tubes nearer the starting tube was com-
bined with the product from the above ethanol recrystalliza-
tion to give 3-iodobenzo[c]cinnoline (0.76 g, 25%).   On
recrystallization from ethanol it formed yellow needles,
m.p. 193-193.5° (Found: C, 47.4; H, 2.45; I, 40.9; N, 8.95%.
$C_{12}H_7IN_2$ requires C, 47.1; H, 2.3; I, 41.45; N, 9.15%).

After benzene extraction, the hydrochloric acid solution
was basified with sodium hydroxide solution and extracted
with ether to give a brown gum (0.92 g, 31%) on evaporation
of the ether.   The gum failed to crystallize and was
characterized as a benzylidene derivative by refluxing

with benzaldehyde in ethanol for 10 min.   Recrystalliza-
tion of the product from ethanol gave N,N'-dibenzylidene-
2-iodobenzidine as very pale yellow plates, m.p. 157-157.5°
(Found: C, 64.0; H, 4.15; N, 5.45%. $C_{26}H_{19}IN_2$ requires
C, 64.2; H, 3.95; N, 5.75%).

Azobenzene-3-carboxylic Acid

A solution of azobenzene-3-carboxylic acid (3.00 g) in
22$\underline{N}$ sulphuric acid (120 ml) was irradiated in the mercury
lamp reactor for 72 hr, then diluted with water (100 ml)
and partly neutralized with sodium hydroxide (70 g) in
water (250 ml), with the temperature below 40°.   The
mixture was cooled to room temperature, the precipitate
collected, and the aqueous layer extracted with ethyl
acetate.   The solid was digested in hot concentrated
hydrochloric acid (120 ml), then diluted with water (300 ml),
extracted with ethyl acetate (totalling 1 l.), and the
aqueous layer set aside (A).   Evaporation of all the
abovementioned ethyl acetate extracts gave a yellow solid,
sparingly soluble in ethyl acetate, which was dissolved
in concentrated hydrochloric acid (60 ml) and diluted with
water (60 ml).   The mixture of solid and solution was
subjected to countercurrent distribution between benzene
and 6$\underline{N}$ hydrochloric acid.   After a clear separation of
two yellow colour regions, the products were isolated.
From the region nearer the solvent front the product was

isolated from the acid layer by evaporation of most of the
acid, dilution with water, and extraction with several
portions of ethyl acetate.   Evaporation of the extract
gave a yellow solid which was recrystallized from n-butyl
acetate to give 1-hydroxybenzo[c]cinnoline-10-carboxylic
acid lactone (0.31 g, 10%) as yellow needles, m.p. 329-
330° (Found: C, 70.3; H, 2.7; N, 12.3; O, 14.4%. $C_{13}H_6N_2O_2$
requires C, 70.3; H, 2.7; N, 12.6; O, 14.4%).   The infrared
spectrum ($CHCl_3$) showed a very strong band at 1740 cm^{-1}
(lactone C=O), a strong band at 1125 cm^{-1} (lactone C-O-),
but no maxima in the 4000-2000 cm^{-1} region, except for a
sharp band at ca. 3000 cm^{-1} (C-H).   It was insoluble in
cold 10% sodium hydroxide, but dissolved on boiling to
give a red solution and was recovered unchanged on
acidification of the solution.   From the countercurrent
tubes at and near the starting tubes a solid acidic sub-
stance was obtained which was dissolved in hot dilute
sodium carbonate solution and reprecipitated with acetic
acid.   The resulting pale fawn solid (0.42 g) was too
insoluble for recrystallization.   A portion (0.32 g) was
refluxed for 11 hr with methanol (50 ml) containing dry
hydrogen chloride, then diluted with water (250 ml), and
the mixture extracted with benzene.   Evaporation of the
benzene gave a yellow solid which was recrystallized from
ethanol to give methyl benzo[c]cinnoline-3-carboxylate

(0.24 g) as pale yellow plates, m.p. 177° (Found: C, 70.55; H, 4.5; N, 11.5%. $C_{14}H_{10}N_2O_2$ requires C, 70.6; H, 4.25; N, 11.75%).

The aqueous hydrochloric acid solution (A) was concentrated by boiling to 5 ml, diluted to 50 ml, and clarified with charcoal. The filtrate was treated with sodium acetate (5 g) in water (10 ml) and the resulting benzidine-2-carboxylic acid (0.73 g, 24%) obtained as very pale buff micro-needles, m.p. 271.5-272.5° (in vacuo) with no decomposition (lit.[38] 269° decomp.). The mixed m.p. (also in vacuo) showed no depression, and the infrared spectra (Nujol) of the two specimens were identical.

(c)   o-Derivatives

2,2'-Dimethylazobenzene

A solution of 2,2'-dimethylazobenzene (4.0 g) in 22N sulphuric acid (120 ml) was irradiated in the mercury lamp reactor for 104 hr. The solution was partially neutralized, with cooling, by the addition of sodium hydroxide (70 g) in water. Some tar was observed in the mixture, but was not investigated. The cold solution was filtered and the filtrate extracted with benzene. The solid (S) was dissolved in 3N hydrochloric acid and the solution extracted with benzene. The combined benzene extracts were chromatographed in benzene on basic alumina. The first fractions

gave 4,7-dimethylbenzo[c]cinnoline (0.39 g, 10%); after
recrystallization from hexane it formed yellow needles,
m.p. 169-170° (Found: C, 80.6; H, 5.75; N, 13.5%.
$C_{14}H_{12}N_2$ requires C, 80.75; H, 5.8; N, 13.45%).   A
mixture of benzo[g]cinnolines was then eluted.   This was
subjected to countercurrent distribution between hexane
and 1N hydrochloric acid.   The fractions nearest the
starting tube gave 4-methylbenzo[c]cinnoline (0.76 g, 19%);
after recrystallization from cyclohexane it formed yellow
needles, m.p. 129°, alone or admixed with a specimen pre-
pared from 2-methylazobenzene.   The infrared spectra of
the two specimens were identical.   The fraction nearer
the solvent front gave a small quantity of a
dimethylbenzo[g]cinnoline, m.p. 128.5-129.5° (Found:
C, 80.2; H, 5.8; N, 13.35%. $C_{14}H_{12}N_2$ requires C, 80.75;
H, 5.8; N, 13.45%).   Its n.m.r. spectrum in $CDCl_3-CCl_4$
(1:1) showed two sharp singlets at τ 6.93 and 6.83 (3
protons each) assigned to two non-equivalent methyl groups,
a sharp singlet at τ 2.33 (ca. 2 protons), a quartet at
τ 2.38, 2.27, 2.22, and 2.10 (ca. 2 protons), and a quartet
at τ 1.43, 1.38, 1.33, and 1.28 (2 protons).   The peaks
from τ 2.38 to 2.10 integrated for 4 protons exactly.

After benzene extraction of the solution of the solid
(S), the remaining aqueous acidic solution was basified,
and the mixture extracted with ether.   The solid (0.85 g,
21%) obtained by evaporation of the ether was recrystallized

from aqueous ethanol to give 3,3'-dimethylbenzidine
(o-tolidine)[44] as fawn needles, m.p. 126-128° (lit.[126]
129°).   Its dibenzoyl derivative had m.p. 268-270°
(lit.[127] 265°), and its disalicylidene derivative had
m.p. 206-206.5° (lit.[126] 202°).

A solution of 4,7-dimethylbenzo[c]cinnoline (26 mg)
in 22N sulphuric acid (5 ml) was irradiated in a Pyrex
flask in sunlight for 3 days.   The solution was then
basified with sodium hydroxide solution (with cooling),
extracted with ether, and the ether evaporated to give a
yellow solid (25 mg), m.p. 166-168°, not depressed by
admixture with pure 4,7-dimethylbenzo[c]cinnoline.

4,7-Dimethylbenzo[c]cinnoline-5-oxide

4,7-Dimethylbenzo[c]cinnoline (50 mg) was heated with
glacial acetic acid (3 ml) and 27.5% w/v hydrogen peroxide
(0.8 ml) at 70° for 7 hr.   The mixture was diluted to 10 ml
with 1N hydrochloric acid and the product collected.   Re-
crystallization from benzene gave 4,7-dimethyl-
benzo[c]cinnoline-5-oxide (47 mg) as pale yellow needles,
m.p. 214-214.5° (Found: C, 74.95; H, 5.3%. $C_{14}H_{12}N_2O$
requires C, 75.0; H, 5.4%).   It was insoluble in boiling
10% aqueous sodium hydroxide.

2-Methylazobenzene

A solution of 2-methylazobenzene (3.01 g) in 22N
sulphuric acid (135 ml) was irradiated in the mercury lamp

reactor for 76 hr. The solution was then basified (with cooling) with concentrated aqueous sodium hydroxide, the mixture extracted with ether, the ethereal solution washed, dried, and evaporated, and the residue subjected to counter-current distribution between hexane and 1N hydrochloric acid. The fractions nearer the solvent front gave 4-methyl-benzo[c]cinnoline (0.68 g, 23%). After recrystallization from cyclohexane it formed yellow needles, m.p. 129° (Found: C, 80.25; H, 5.2; N, 14.5%. $C_{13}H_{10}N_2$ requires C, 80.4; H, 5.2; N, 14.4%). The fractions nearer the starting tube gave benzo[g]cinnoline (0.32 g, 11%); on recrystallization from benzene it formed yellow needles, m.p. 155.5-156°, alone or admixed with an authentic specimen, and its infra-red spectrum was identical with that of an authentic specimen. From the "overlap" region a mixture (0.033 g) of the two benzo[g]cinnolines was obtained. Some tar was observed in the starting tube, but was not investigated.

The contents of the first few tubes of the counter-current machine were combined, basified, and extracted with ether. Evaporation of the ether gave a residue which was dissolved in ethanol and treated with anhydrous stannous chloride (2 g) in concentrated hydrochloric acid (6.5 ml). The resulting stannous chloride double salt[46] was collected, dissolved in water, and treated with acidified sodium sulphide (to remove the tin). The filtrate was then treated

with concentrated aqueous sodium sulphate and the
precipitate collected. It was suspended in water, the
solution basified, and then extracted with ether. Evap-
oration of the ether gave a light brown oil (0.33 g) which
was identified as 3-methylbenzidine by formation of its
dibenzylidene derivative, m.p. 134.5-135° (lit.[46] 134°).

2-Chloroazobenzene

A solution of 2-chloroazobenzene (3.00 g) in 22$\underline{N}$
sulphuric acid (120 ml) was irradiated in the mercury lamp
reactor for 182 hr. The mixture was diluted with water
(250 ml), partly neutralized with sodium hydroxide (70 g)
in water (300 ml), with the temperature below 40°, shaken
with benzene (150 ml), and filtered. The solid (S) was
washed with benzene (4 x 50 ml) which was then used to
extract the aqueous filtrate. Evaporation of the benzene
gave a yellow solid (1.58 g), m.p. 155-167° which was sub-
jected to countercurrent distribution between light pet-
roleum, b.p. 60-90°, and $\underline{N}$ hydrochloric acid. The fractions
somewhat behind the solvent front gave 4-chloro-
benzo[c]cinnoline (1.10 g, 37%). Recrystallization from
1-butanol gave yellow needles, m.p. 191-192° (Found:
C, 66.95; H, 3.35; Cl, 16.7; N, 13.3%. $C_{12}H_7ClN_2$ requires
C, 67.15; H, 3.3; Cl, 16.5; N, 13.05%). The fractions
nearer the starting tube gave benzo[g]cinnoline (0.29 g,
12%), m.p. 155-155.5° alone or admixed with an authentic

specimen.

The solid (S) was treated with aqueous sodium hydroxide and extracted with ether. Evaporation gave a gum (0.91 g) which was recrystallized from aqueous ethanol and then from benzene-hexane to give 3-chlorobenzidine as pale yellow needles, m.p. 74.5-75° (lit.[47] 75°). Its infrared spectrum in chloroform showed bands at 3500 and 3430 cm^{-1} (NH_2), and at 1620 and 1490 cm^{-1} (aromatic ring); its ultraviolet spectrum in 95% ethanol showed $\lambda_{max.}$ 286 mμ (logϵ 4.46) ($\lambda_{max.}$ for benzidine, 285 mμ). A portion of the crude 3-chlorobenzidine and residues from its recrystallization were chromatographed on silica-gel with benzene-ether in varying proportions as eluate, and also subjected to countercurrent distribution between 2% aqueous acetic acid and benzene-light petroleum, b.p. 60-90° (1:4). No product other than 3-chlorobenzidine was isolated.

In a separate experiment, a solution of 2-chloro-azobenzene (0.20 g) in 22$\underline{N}$ sulphuric acid (15 ml) was irradiated in sunlight (winter) until the ultraviolet spectrum of the solution showed the reaction to be complete (7 weeks). The solution was then diluted with distilled water (100 ml), extracted with benzene, and the benzene evaporated. Thin-layer silica-gel chromatography (using ether-benzene (1:10)) showed that the product mainly con-

sisted of 4-chlorobenzo[c]cinnoline but contained some
unsubstituted benzo[c]cinnoline. The aqueous acidic layer
gave a negative halide test with silver nitrate; addition
of a trace (<1 mg) of potassium chloride to the tested
solution produced a definite precipitate.

2-Iodoazobenzene

A mixture of 2-iodoazobenzene (3.00 g) and 22N sul-
phuric acid (120 ml) was irradiated in the mercury lamp
reactor for 200 hr, during which time the mixture was heated
twice for a short time to aid dissolution of the azo compound.
The mixture was diluted with water (100 ml), partially
neutralized with sodium hydroxide (70 g) in water (200 ml),
the temperature being kept below 40°, immediately shaken
with benzene (B) (300 ml), and filtered to give a solid (S).
The aqueous layer of the filtrate was extracted with benzene
until the former was almost colourless; it was basified with
sodium hydroxide solution, extracted with ether and the
ether evaporated to give a brown gum (0.11 g, 4%) which was
not investigated further. The solid (S) was boiled with
concentrated hydrochloric acid (50 ml), diluted with water
(100 ml), and extracted with benzene until the extracts
were colourless. These extracts and the benzene extracts
(B) were combined and evaporated to give a yellow solid
which was subjected to countercurrent distribution between
benzene and 6N hydrochloric acid. On evaporation, the

fractions at the solvent front gave a solid (0.67 g, 22%),
which, on recrystallization from ethanol, gave
2-iodoazobenzene as red needles, m.p. and mixed m.p. 61°.
After 550 transfers a clear separation of two yellow
regions had occurred. The faster-moving component
(0.87 g, 29%) was recrystallized from benzene to give
4-iodobenzo[c]cinnoline as yellow needles, m.p. 193.5-
194° (lit.[81] 190.5-191.5°) (Found: C, 47.0; H, 2.3;
N, 8.95%. Calc. for $C_{12}H_7IN_2$: C, 47.1; H, 2.3; N, 9.15%).
From the tubes nearer the starting tube benzo[c]cinnoline
(0.086 g, 5%) was obtained. On recrystallization from
benzene-hexane it formed yellow prisms, m.p. 154.5-155°
alone or admixed with an authentic specimen.

After the benzene extraction, the hydrochloric acid
layer was basified with sodium hydroxide solution, extracted
with ether, and the ether evaporated to give a brown gum
(0.90 g, 30%). On recrystallization from aqueous ethanol
3-iodobenzidine was obtained as colourless needles, m.p. 70°
(Found: C, 46.5; H, 3.7; H, 8.75%. $C_{12}H_{11}IN_2$ requires
C, 46.5; H, 3.6; N, 9.0%).

Azobenzene-2-carboxylic acid

Azobenzene-2-carboxylic acid (3.00 g) was dissolved in
warm 22N sulphuric acid (120 ml), irradiated in the mercury
lamp reactor for 140 hr, diluted with water (150 ml), and
partly neutralized with sodium hydroxide (70 g) in water

(200 ml), with the temperature below 40°. The mixture was well cooled in an ice-water bath, shaken with benzene (100 ml), and the solid collected. The aqueous layer was extracted several times with benzene and all the benzene extracts combined (B). The solid was boiled with concentrated hydrochloric acid (50 ml), diluted with water (300 ml), shaken with benzene (100 ml), and filtered to remove the solid (S). The aqueous portion of the filtrate was extracted with several portions of benzene to leave an aqueous layer (A). The benzene extracts were combined with the previous extracts (B), and extracted with dilute sodium carbonate solution until the aqueous extracts were colourless. The benzene layer was evaporated and the resulting yellow solid was chromatographed on a short column of basic alumina; the green fluorescent band was eluted with 20% ether-in-benzene. Evaporation of the eluate gave benzo[g]cinnoline (0.14 g, 6%) as yellow needles, m.p. 154-155° alone or admixed with an authentic specimen (lit.[58] 156°). The infrared spectra of the two samples in chloroform were identical. The sodium carbonate extract was made slightly acidic with acetic acid, boiled down to half its original bulk, and extracted with ethyl acetate until the aqueous layer was colourless. After evaporation of the ethyl acetate, the residue was combined with the solid (S), dissolved in hot sodium carbonate solution, filtered, and acidified with acetic acid. The

solid was collected and washed with a little ether to give
the crude product (1.05 g, 35%).   On recrystallisation
from 1-butanol and then toluene, benzo[c]cinnoline-4-
carboxylic acid was obtained as yellow needles, m.p.
283.5-285° (in vacuo) (Found: C, 69.85; H, 3.85; N, 12.4;
O, 14.7%. $C_{13}H_8N_2O_2$ requires C, 69.65; H, 3.6; N, 12.5;
O, 14.3%).

The hydrochloric acid solution (A) was concentrated by
boiling, basified with sodium carbonate, and extracted with
ether.   After evaporation of the ether, benzidine (0.14 g,
6%) was obtained as fawn plates which, on recrystallization
from aqueous ethanol, had m.p. 123-124° alone or admixed
with an authentic specimen (lit. 127°).   The infrared
spectra ($CHCl_3$) of the two samples were identical.   After
the ether extraction, the aqueous layer was slightly acid-
ified with acetic acid to precipitate the crude product
(0.92 g, 31%), m.p. 202-204° (in vacuo).   This was purified
by dissolution in hot dilute hydrochloric acid, treatment
of the solution with charcoal, and addition of excess sodium
acetate to the filtered solution.   Benzidine-3-carboxylic
acid was obtained as pale fawn needles, m.p. 205-206°
(in vacuo), alone or admixed with an authentic specimen
(lit.[38] 207-208° decomp.).   The infrared spectra (Nujol)
of the two samples were identical.

(d) 2,4,6-Trimethylazobenzene

2,4,6-Trimethylazobenzene (3.00 g) was dissolved in
20.5N sulphuric acid (145 ml) and irradiated in the mercury
lamp reactor for 213 hr.   The resulting solution was
diluted to about 300 ml with water and partially neutral-
ized with sodium hydroxide (90 g) in water (250 ml), with
cooling, so that the temperature did not rise above 40°.
The cooled mixture was extracted with benzene (600-700 ml)
in several portions so that no more yellow colour was
extracted into the benzene.   During the benzene extractions
a black tar was filtered off.   This tar (0.96 g) was
precipitated during the partial neutralization, but was
not investigated.   Evaporation of the benzene extract
gave a brownish-yellow solid (0.94 g) which was subjected
to countercurrent distribution between hexane and 1N
hydrochloric acid.   Fractions nearer the solvent front
were re-subjected to countercurrent distribution between
light petroleum, b.p. 40-70°, and 1.5N hydrochloric acid.
From the fractions nearer the starting tube in both dis-
tributions a yellow solid (0.57 g, 20%) was obtained.
Recrystallization from hexane gave 2,4-dimethyl-
benzo[c]cinnoline as yellow needles, m.p. 121.5° (Found:
C, 80.85; H, 5.8; N, 13.2%. $C_{14}H_{12}N_2$ requires C, 80.75;
H, 5.8; N, 13.45%).   Its ultraviolet spectrum (cyclohexane)
showed $\lambda_{max.}$ at 235sh, 258, 307, 318, 350, 367, and 409 mμ,

and was characteristic of a benzo[c]cinnoline. From the
second distribution, fractions nearer the solvent front
yielded 1,2,4-trimethylbenzo[c]cinnoline (0.056 g, 2%) as
yellow needles, m.p. 146.5-147.5° on recrystallization from
hexane (Found: C, 81.55; H, 6.35; N, 12.4%. $C_{15}H_{14}N_2$
requires C, 81.05; H, 6.35; N, 12.6%). Its ultraviolet
spectrum (cyclohexane) showed $\lambda_{max.}$ at 253 (log$\mathcal{E}$ 4.62),
274sh (4.22), 317 (4.00), 327 (4.02), 357 (3.26), 374sh
(3.16), 403sh mμ (2.61); in 2$\underline{N}$ hydrochloric acid it showed
$\lambda_{max.}$ at 259 (4.52), 269sh (4.43), 292sh (3.88), 383 (4.04),
and 445 mμ (3.69). Its n.m.r. spectrum was determined in
$CDCl_3$-CCl_4 (1:1) and showed three sharp singlets at τ 7.50,
7.25, and 6.98 (3 protons each) assigned to methyl groups
in the 2-, 4-, and 1-positions respectively, a sharp singlet
at τ 2.58 (1 proton) assigned to a proton in the 3-position,
and two multiplets at about τ 2.25 and 1.35 (2 protons each)
assigned to protons in the 8-, 9- and 7-, 10-positions
respectively.

After the benzene extraction, the partially neutralized
aqueous layer was basified with sodium hydroxide solution
and steam distilled until no amines could be detected in
the distillate (about 1 l.). Ether extraction of the
distillate gave a brown oil (0.21 g), which presumably
contained aniline and mesidine (fission bases), which was
not investigated further. The residue from the steam

distillation was extracted with ether to give a black tar
(0.89 g) on evaporation of the ether. Chromatography of
this tar on 100-mesh silica gel, and elution with benzene
and then up to 30% ether-in-benzene, gave minute quantities
of many compounds. The main component was eluted with 10%
ether-in-benzene and was shown to be 4-(4'-aminophenyl)-2,4,6-
trimethylcyclohexa-2,5-dienone (0.50 g, 17%). On re-
crystallization from aqueous ethanol it formed colourless
needles, m.p. 133.5-134° (Found: C, 79.2; H, 7.7; N, 6.2%
(average). $C_{15}H_{17}NO$ requires C, 79.25; H, 7.55; N, 6.15%).
Its ultraviolet spectrum (95% ethanol) showed $\lambda_{max.}$ at 248
and 292 mμ; in 1N hydrochloric acid it showed $\lambda_{max.}$ at 248
mμ. Its infrared spectrum (CCl_4) showed bands at 3480 and
3380 (NH_2), and at 1665 cm^{-1} (dienone C=O). Its n.m.r.
spectrum (CCl_4) showed a sharp singlet at τ 8.47 (3 protons)
assigned to a methyl group in the 4-position, a sharp
singlet at τ 8.17 (6 protons) assigned to a methyl group in
the 2- and 6-positions, a broad singlet at τ 6.35 (NH_2),
a quartet at τ 3.63, 3.47, 3.15, and 3.00 (J ca. 10 c/s)
assigned to a p-disubstituted benzene ring, and a sharp
singlet at τ 3.48 assigned to the 3- and 5-dienone protons.
The peaks at τ 3.63, 3.48, and 3.47 integrated for 4 protons,
and those at τ 3.15 and 3.00 for 2 protons. A diazotised
solution of the dienone coupled with a solution of
2-naphthol in cold 10% sodium hydroxide to give an orange-
red dye.

Dienone-Phenol Rearrangement

The above dienone (96 mg) was treated with a mixture
of acetic anhydride (2.5 ml) and concentrated sulphuric
acid (0.1 ml) at room temperature for 24 hr.[cf. 34.] The
whole mixture was then refluxed with sodium hydroxide
(6 g) in water (30 ml) for 2 hr, acidified with hydro-
chloric acid, the acidity adjusted to pH 8 with sodium
carbonate solution (indicator paper), and the solution
diluted to 100 ml, and extracted with ether. A brown
solid (87 mg) was obtained after evaporation of the ether.
Recrystallization from benzene gave 4-amino-3'-hydroxy-
2',4',6'-trimethylbiphenyl as buff needles, m.p. 163°
(Found: N, 6.1%. $C_{15}H_{17}NO$ requires N, 6.2%). Its infra-
red spectrum (CHCl$_3$) showed bands at 3600 (OH), 3470sh and
3380 (NH$_2$), and 1620 cm^{-1} (aromatic ring). Its ultraviolet
spectrum (95% ethanol) showed $\lambda_{max.}$ at 239 and 283 mμ; in
1N hydrochloric acid it showed $\lambda_{max.}$ at 283 mμ. Its n.m.r.
spectrum (CDCl$_3$) showed a sharp singlet at τ 8.05 (6 protons)
assigned to methyl groups in the 2'- and 6'-positions
twisted into the shielding region of the aminophenyl ring,
a sharp singlet at τ 7.75 (3 protons) assigned to the methyl
group in the 4'-position, a singlet at τ 6.10 (3 protons)
assigned to the NH$_2$ and OH protons, and a complex multiplet
at τ 3.15 (5 protons) assigned to the five aromatic protons.
A diazotized solution of the phenol coupled with a solution
of 2-naphthol in cold 10% sodium hydroxide to give a bright

red dye.

5.4 Preparation of cis-Azobenzenes

All manipulations of the cis-isomers were carried out in diffuse light from a sodium vapour lamp, under which the cis-isomers appeared colourless. A solution of the trans-azo compound in benzene-light petroleum, b.p. 60-90°, (1:4) was irradiated in the mercury lamp reactor for about 1 hr while the solution was stirred magnetically. The solution was run through a short column of activated alumina and the trans-isomer was eluted with benzene-light petroleum (1:4) and re-irradiated in the reactor. This process was repeated several times to accumulate cis-isomer on the top of the column. All traces of trans-isomer were then eluted from the column with benzene-light petroleum (1:4) and the cis-isomer was eluted with ether. The ethereal solution was evaporated rapidly under reduced pressure and the product recrystallized to constant m.p. from light petroleum, b.p. 40-70°, with cooling in an ice-salt bath. cis-Azobenzene was obtained as red prisms, m.p. 71-71.5° (lit.[128] 71°); cis-4-chloroazobenzene was obtained as red prisms, m.p. 36-37° (lit.[129,130] 32, 38°); cis-4-methylazobenzene was obtained as orange needles, m.p. 36.5-37.5° (lit.[128] 42-45°).

APPENDIX I

A Photochemical Rate Equation where there is no Competitive Absorption by Reaction Products

For a simple photochemical reaction in which a single reactant undergoes a unimolecular photochemical change to give products, let it be assumed that the rate of disappearance of reactant is proportional to the number of quanta absorbed per unit time by the reactant. If the reactant is the only absorbing species, then for constant illumination with monochromatic light

$$-\frac{dA}{dt} = K'(1-T) \qquad (A\ I.1)$$

where A is the number of moles of reactant, t is the time of irradiation, K' is a rate constant with units moles. $time^{-1}$, and T is the transmittance at the irradiation wavelength. If Beer's law is obeyed then

$$-\frac{dA}{dt} = -\frac{dD}{dt} \cdot \frac{v}{\mathcal{E}l} \qquad (A\ I.2)$$

where D is the optical density of the absorbing system defined as $-D = \log_{10}T$, v is the volume of the system (l.), $\mathcal{E}$ is the molar decadic extinction coefficient of the reactant, and l is the path of the reaction cell (cm). Thus

$$-\frac{dD}{dt} = K(1-10^{-D}) \qquad (A\ I.3)$$

where $K = K'\ l/v$ and has units $time^{-1}$. This equation

(A I.3) is similar to equation (3.8) in the paper by Kling
et al.[91].   Integration of equation (A I.3) gives

$$\log_{10}(10^{D_o}-1)-\log_{10}(10^{D}-1) = Kt \qquad (A\ I.4)$$

where D_o is the initial optical density.

If the initial assumptions are correct, a graph of
$-\log_{10}(10^{D}-1)$ against time should give a straight line with
slope K.

APPENDIX   II

A Photochemical Rate Equation where there is Competitive Absorption by Reaction Products

In the photochemical cyclization of azobenzenes as
described in Chapter III, the products absorbed in the regions
of irradiation.   For constant irradiation with monochromatic
light, let it be assumed that the rate of cyclization is
proportional to the rate of absorption of quanta by the
reacting species, which is assumed to be the cis-isomer.
The quantity b(cis) may be defined as the fraction of light
absorbed by the cis-isomer, relative to the total light
absorbed by cis- and trans-isomers; b(cis) is given by
equation (A II.1), cf.131

$$b(cis) = D^c/(D^c + D^t) \qquad (A\ II.1).$$

where D^c and D^t are the optical densities of cis- and trans-
isomers respectively at the wavelength of irradiation.   The

fraction of the total light absorbed which is in turn
absorbed by *cis*-isomer would be $b(cis).(D^c + D^t)/D$, where
D is the total optical density (including products) at the
wavelength of irradiation. Because the *cis*-*trans*
isomerization is much faster than cyclization, the general
equation for the rate of disappearance of azobenzenes in
sulphuric acid is given by

$$-\frac{d(D^c + D^t)}{dt} = \frac{k \cdot b(D^c + D^t)}{z \quad D}(1-10^{-D}) \qquad (A \ II.2)$$

where k is the rate constant $(time^{-1})$ for the actual cycliza-
tion process and z is the yield fraction of the cyclization
reaction. Equation (A II.2) may be rewritten as

$$-\frac{d(A^c + A^t)}{dt} = \frac{k' \ \mathcal{E}^{c+t}l}{zv} \cdot \frac{b(D^c + D^t)}{D}(1-10^{-D}) \quad (A \ II.3)$$

(cf. equation A I.2), where $(A^c + A^t)$ is the total molar
concentration of azo compound, k is the rate constant for
the cyclization reaction $(moles. \ time^{-1})$, $\mathcal{E}^{c+t}$ is the molar
extinction coefficient for the *cis*-*trans* composition, l is
the cell path (cm), and v is the volume of the solution $(l.)$.

Let the optical density of the products at the wavelength
of irradiation at time t be x, and let the hypothetical
initial optical density for *cis*-*trans* photoequilibrium be
D_o^h. The term "hypothetical" is used because irradiation
experiments were commenced with pure *trans*-isomer, and not
with a *cis*-*trans* photoequilibrium composition. While the
optical density due to azo compound decreases to zero, that

of the products increases to the final value, D_∞. Thus

$$\frac{dx}{dt} = -\frac{d(D^c + D^t)}{dt} \cdot \frac{D_\infty}{D_o^n} \ . \qquad\qquad (A\ II.4)$$

The rate of change of the total optical density (D) is given by

$$\frac{dD}{dt} = \frac{d(D^c + D^t)}{dt} + \frac{dx}{dt} \ . \qquad\qquad (A\ II.5)$$

A combination of equations (A II.2,4 and 5) gives

$$-\frac{dD}{dt} = \frac{bk}{z} \cdot \frac{D^c + D^t}{D}\left(1-\frac{D_\infty}{D_o}\right)(1-10^{-D}) \ . \qquad (A\ II.6)$$

The functions $(D^c + D^t)$ and x are related by equations (A II.7 and 8).

$$D_o - (D^c + D^t) = xD_o / D_\infty \qquad\qquad (A\ II.7)$$

$$D = x + (D^c + D^t) \qquad\qquad (A\ II.8)$$

Thus

$$D^c + D^t = D_o(D-D_\infty)/(D_o-D_\infty) \qquad\qquad (A\ II.9)$$

and equation (A II.6) becomes

$$-\frac{dD}{dt} = \frac{bk}{z} \cdot \left(1-\frac{D_\infty}{D}\right)(1-10^{-D}). \qquad\qquad (A\ II.10)$$

Equation (A II.10) is similar to equation (2.7) in the paper by Kling et al.[91]

An additional refinement which could be made involves a correction for the light reflected back into the solution by the rear wall of the reaction cell. The differential equation would then become

$$-\frac{dD}{dt} = \frac{bk}{z}(1 + r10^{-D})\left(1-\frac{D_\infty}{D}\right)(1-10^{-D}) \qquad (A\ II.11)$$

where r is the fraction of the transmitted light reflected

back into the cell.[132] The value of r changes with wave-
length and solvent, but for a quartz cell filled with water,
r = 0.06 from 436 to 366 mμ.[132] In this work, however,
the actinometer cell and reaction cell were identical and
the average absorption of actinometer and azo solutions
was similar. Thus the error due to back reflection would
have almost cancelled out.

APPENDIX III

Composition at cis-trans Photoequilibrium

At first sight it might be thought that the initial
hypothetical optical density (D_o^h) for the cis-trans photo-
equilibrium composition could have been determined by
extrapolation (to zero time) of the linear portion of
the graph of

$$-\int_3^D \frac{dy}{(1-\frac{D_\infty}{y})(1-10^{-y})}$$

against time (Fig. 5). From the intercept on the Y-axis,
the corresponding value of D could have been obtained from
the table of integrals. This method, however, neglects
the fact that the rate of cyclization for pure trans-azo
compound was found to be zero, or very nearly so (see Chap-
ter III). If an extrapolation method were to be used, one
would have to determine a time (t') such that the amount of
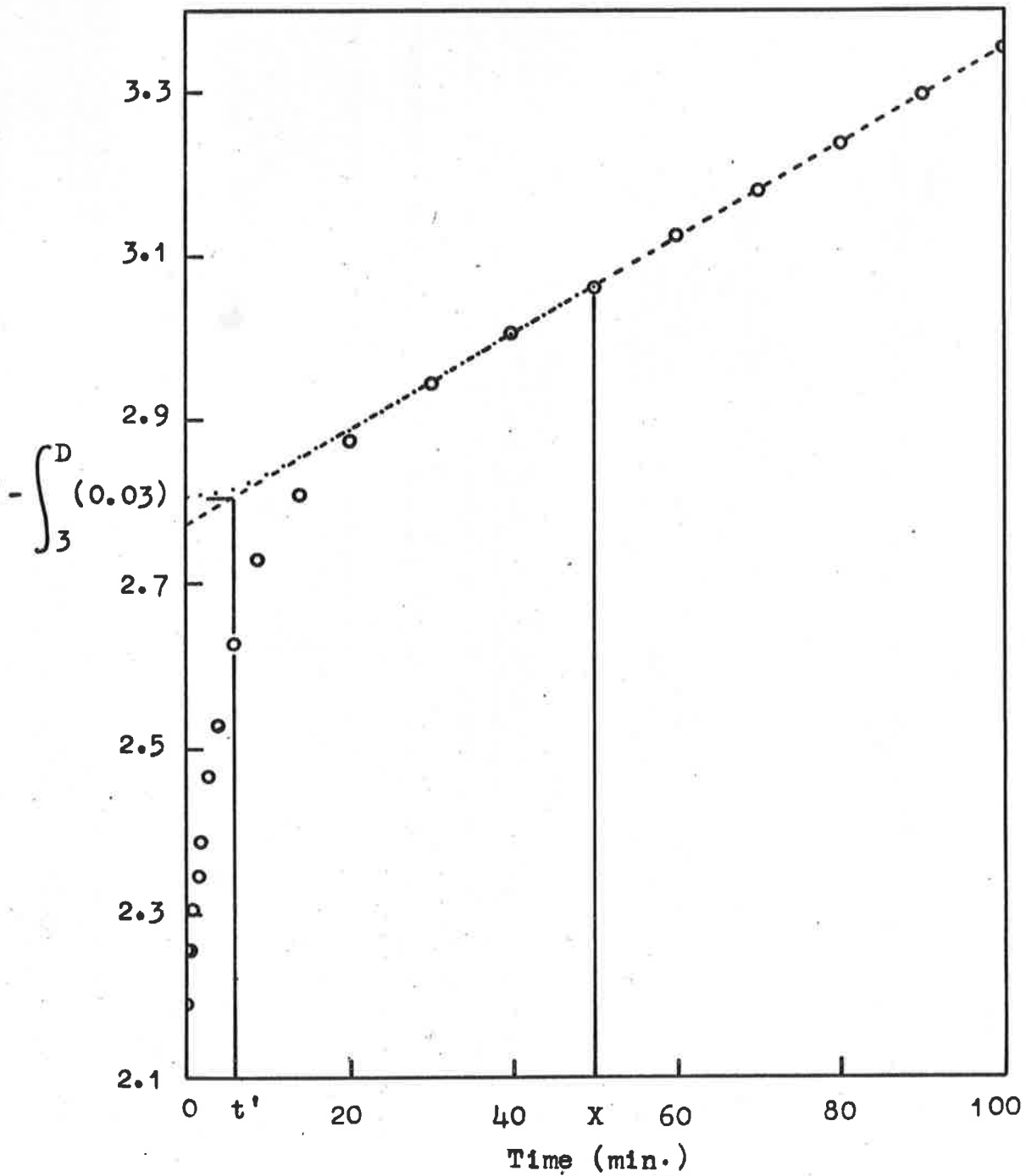cyclization which occurred from time = 0 to t' was equal

Fig. 5. —— Graph of integral against time (c.f. Fig. 3, p. 88): calculated integral, ...; experimental points, o; experimental linear extrapolation, -----.

to the "deficiency" in the amount of cyclization (relative
to cis-trans equilibrium conditions) which occurred from
time $= t'$ to the point at which cis-trans photoequilibrium
was reached.   The value of the integral at this time t',
obtained by extrapolation, would give D_o^h, using the tables
of integrals.   Accurate determination of t' seemed to be
a difficult problem, and so a different approach was used.

The rate of the cyclization process presumably was
directly proportional to b(cis) which for pure trans-
isomer, was zero at zero time, and increased to its
equilibrium value during irradiation.

The aim of the procedure was to calculate the rate of
reaction from an equation for b(cis) and a rough estimate of
D_o^h, obtained by visual estimation of t' from the graph of
the integral against time (e.g. see Fig. 5).   For any
cis-trans composition b(cis) may be calculated from

$$b(cis) = \frac{\mathcal{E}^c}{\mathcal{E}^t - \mathcal{E}^c}(\frac{\mathcal{E}^t C}{D} - 1) \qquad (A\ III.1)$$

where $\mathcal{E}^c$ and $\mathcal{E}^t$ are the extinction coefficients of cis- and
trans-azo compound respectively, C is the total molar con-
centration of azo compound, and D is the total optical
density of cis- and trans-isomers.   The equilibrium value
of b(cis) was thus calculated with $D = D_o^h$ and $C = C_o$, where
C_o is the initial concentration of the pure trans-isomer.

Equation (A III.1) may be derived as follows.   For any mixture of cis- and trans-isomers, the extinction coefficient $(\mathcal{E})$ for the mixture at a given wavelength is given by

$$\mathcal{E} = \frac{D}{C} = f\mathcal{E}^c + (1-f)\mathcal{E}^t \qquad \text{(A III.2)}$$

where f is the mole fraction of cis-isomer, and thus $f = (\mathcal{E}^t-\mathcal{E})/(\mathcal{E}^t-\mathcal{E}^c)$.   It has already been stated that $b(cis) = D^c/D$ (cf. equation (A II.1) where $D = D^c + D^t$).   Since $D^c = \mathcal{E}^c.D.f$, $b(cis)$ is given by

$$b(cis) = \frac{\mathcal{E}^c}{D} C. \frac{(\mathcal{E}^t-\mathcal{E})}{\mathcal{E}^t-\mathcal{E}^c} \qquad \text{(A III.3)}$$

which may be rewritten as equation (A III.1).

From the slope of the linear portion of the graph of the integral against time (Fig. 5) a tentative value of k/z was calculated, because slope = $b(cis).k/z$.   The rate of the cyclization process could then be calculated from $b(cis).k/z$ at any time if $b(cis)$ could be determined, i.e. from equation (A III.1) if values of C were known for measured values of D.   The initial contribution of cyclization products to D was small and was neglected in this discussion.

A stepwise procedure was used to calculate $b(cis).k/z$ as a function of time, with an I.B.M. 1620 Computer.   Small time increments (e.g. 0.4 min) were taken.   At time Δt, $b(cis)$ was calculated from equation (A III.1) with $C = C_o$,

and a value of D obtained by interpolation between experimental values. The method of interpolation was suggested by Mr. R. Lamacraft and involved the fitting of a parabola to each group of three adjacent experimental values of D; the average was taken where two parabolas had two points in common. The calculated value of $b(cis).k/z$ was plotted for the value of Δt and the small piece of curve so generated was integrated with respect to time by the computer. This small integral was added to the integral corresponding to D_o^h (obtained from the tables of integrals), and from the sum of the two integrals, the corresponding value of $D_{\Delta t}^h$ was found from the tables. The concentration at time Δt, i.e. $C_{\Delta t}$, was obtained from

$$C_{\Delta t} = D_{\Delta t}^h .C_o/D_o^h . \qquad\qquad (A\ III.4)$$

To calculate the value of $b(cis)$ for the next point at $t = 2\Delta t$, the value of C used was $C_{\Delta t}-r(C_o-C_{\Delta t})$, i.e. the difference between consecutive values of C was assumed to be approximately the same. This was found to be nearly correct, but the factor r (where $r = 0.99$) was introduced to prevent over-correction for the decrease in C with irradiation time. This cyclic process was repeated until the calculations reached a specified point $(t = X)$ within the cis-trans photoequilibrium region. A comparison was then made between the calculated value of $b(cis).k/z$ and the experimental value. A high estimate of D_o^h was found to give a high calculated

value of $b(\underline{\sigma i \sigma}).k/z$. The error was used to correct the
initial value of D_o^h, with a convergence factor, and the
whole cycle was repeated with the new D_o^h, until D_e^h was
obtained to the desired accuracy (± 0.0002). The com-
parisons of $b(\underline{\sigma i \sigma}).k/z$ corresponded very closely with
matching the position of the calculated integral curve with
the linear portion of the experimental graph. A calculated
integral curve is shown in Fig. 5.

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II. PHOTOCHEMICAL CYCLODEHYDROGENATIONS OF METHYL- AND DIMETHYLAZOBENZENES

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