THE NEUTRAL REDUCTION

of

NITRO COMPOUNDS

and

THE ACTION OF LIGHT

on

AZOXY COMPOUNDS.

A THESIS

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It is a pleasant duty for the author to express his thanks to Dr. W.M.Cumming for introducing him to this subject, and for the careful supervision which he has exercised throughout; to the Royal Technical College for the facilities which have been provided; to Messrs. Nobel Industries, Ltd., and to the Carnegie Trust for scholarships during the tenure of which this work has been carried out, and particularly to the latter for renewing their scholarship for a second year.

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Experimental

CHAPTER ONE.

The Reduction of 2-Nitronaphthalene.

Benzidine and its derivatives are of great importance in the dyestuff industry on account of the fact, discovered in 1885, that the tetrazo salts derived from them possess the property of dyeing cotton directly, without the use of a mordant. The corresponding derivatives of naphthalene, the naphthidine bases, have been in comparison somewhat neglected, and it is our intention to explore this field in the near future.

A necessary preliminary was the investigation of the methods of preparation of the substances involved, and a paper (1) has been published from this laboratory in which the reduction of 1-nitronaphthalene is described. These authors found that, while the reducing agents, (sodium amalgam, zinc dust and sodium hydroxide with or

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1. Cumming and Steel, J.C.S.,1923,123,2465

without alcohol) which are usually employed were altogether unsatisfactory in that no product other than tar or 1-naphthylamine could be obtained under conditions where any reduction at all occurred, the employment of zinc dust for the reduction of 1-nitronaphthalene in alcoholic solution in the presence of ammonium chloride was both cleanly and satisfactory.

By adjusting the quantity of zinc dust, 1:1'-azoxy-, 1:1'-azo-, or 1:1'-hydrazo-naphthalene could be obtained at will, and by reduction of 1:1'-azoxynaphthalene with stannous chloride and hydrochloric acid in acetic acid solution (a method not applicable to 1-nitronaphthalene) naphthidine could be obtained. Dinaphthaleneimine, a cyclic compound theoretically derived from naphthidine by loss of ammonia, was obtained by the action of dilute sulphuric acid on 1:1'-hydrazonaphthalene. A substance, $2NH_4Cl,5Zn(OH)_2$, obtained as a by-product in the preparation of 1:1'-azoxynaphthalene was also described.

These reagents, (zinc dust, ammonium chloride, and either water or alcohol) have frequently been employed in the preparation of N-aryl hydroxylamines (4) and occasionally (5) in the preparation of azoxy compounds. In view of the success which had attended the application of this method to 1-nitronaphthalene it was decided to test its suitability for the reduction of 2-nitronaphthalene.

Preparation of 2-Nitronaphthalene.

The preparation of 2-nitronaphthalene on a reasonable scale presents considerable difficulty. The nitration of naphthalene itself, under such diverse conditions as at-55° (6) and at 360° (7), yields 1-nitronaphthalene as practically the sole product of mononitration. The formation of traces of 2-nitronaphthalene is, of course, indicated by the occurrence of 2-naphthylamine in commercial 1-naphthylamine, and

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4. Bamberger, Ber.,1894,27,1347,1548
   Wohl, Ber.,1894,27,1452
   Bamberger and Rising, Ann.,1901,316,257, etc.
5. Wacker, Ann.,1901,317,375;1902,321,61
   Alway, Am.Ch.J.,1902,28,475
   Bamberger and Elger, Ber.,1903,36,1611,3645
   Wohl and Goldenburg,Ber.,1903,36,4153
   Duval, C.R.,1905,141,198; Bull.,1910,(iv),7,677
   Reissert,Ber.,1908,41,3921
6. Pictet,C.R.,1893,116,815.
7. Nageli, Bull.,1899,(iii),21,786

Armstrong (8) has isolated a small quantity of 2-nitronaphthalene from a sample of 1-nitronaphthalene by a laborious process of fractionation. Wynne, however, considers the matter still open to doubt (9).

In the case of derivatives of naphthalene, the nitro group also generally enters in the alpha position, the only exceptions, other than compounds containing either a second nitro group or a hydroxyl group, which are cited in "Thorpe's Dictionary of Applied Chemistry" (10), being (i) 2:4:7- and 2:4:8-nitronaphthalene disulphonic acids, formed in small quantities and accompanied by the isomeric 1-nitro derivatives, (ii) 2-amino-6-nitronaphthalene-8-sulphonic acid, which Jacchia (11) claims to have obtained by acting on 2-aminonaphthalene-8-sulphonic acid with nitric acid, and (iii) 1-acetylamino-2-nitronaphthalene prepared by Lellmann and Remy (12) together with other substances by the nitration of 2-acetylaminonaphthalene.

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8. Thorpe's Dictionary of Applied Chemistry,1912,III,580
9. " " " " " ,1922,IV,428
10. " " " " " ,1922,IV,408-514
11. Jacchia, Ann.,1902,<u>323</u>,119;Immerheiser,D.R.P.,57023
12. Lellmann and Remy, Ber.,1886,19,797;Lellmann, Ber.,1887, <u>20</u>,892.

2-Nitronaphthalene has been actually prepared (13) by dissolving 1-acetylamino-2-nitronaphthalene in alcohol and treating with ethyl nitrite in presence of sulphuric acid. The preparation of 1-acetylamino-2-nitronaphthalene is an involved and wasteful process; the nitration product consists of a mixture of a molecular compound of 1-acetylamino-2-nitronaphthalene and 1-acetylamino-4-nitronaphthalene with an excess of the 1:4 compound. After separation of this excess mechanically the double compound can be broken down by limited hydrolysis with alcoholic sodium hydroxide, the 1:4 derivative being attacked preferentially. This, the original method of preparing 2-nitronaphthalene has not been employed by subsequent authors. Methods later described in the literature include the decomposition of diazonium salts of 2-naphthylamine in the presence of cupro-cupri sulphite (14) or cuprous oxide (15,16)

These latter methods do not give good yields, and owing to the large amount of inorganic material

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13. Lellmann and Remy, Ber., 1886, <u>19</u>, 236
14. Hantsch and Blagden, Ber., 1900, <u>33</u>, 2553
15. Sandmeyer, Ber., 1887, <u>20</u>, 1496
16. Meisenheimer and Witt, Ber., 1903, <u>36</u>, 4153

necessarily employed are exceedingly tedious and impracticable. Starting with fifty grams of 2-naphthylamine, (the largest scale possible under normal laboratory conditions for these preparations), only five to six grams could be obtained on the average after not less than three weeks work, when the method of Meisenheimer and Witt (16) was used.

Accordingly a certain amount of time was spent on attempts to devise new methods for the preparation of this substance. The β-nitronaphthylaminesulphonic acid described by Immerheiser and by Jacchia appeared a possible source, but preliminary experiments indicated that fair yields of this substance were not likely to be obtained. Lack of time, and the necessity for pushing on with the main line of research has prevented us from carrying these experiments as far as we would desire. It is our intention, however, to return to this subject with a view to determining the optimum conditions for this interesting reaction.

On nitration of sodium naphthalene-2-sulphonate, the first nitro group enters one of the free alpha positions(17). Accordingly, of the possible seven mononitronaphthalene sulphonic acids only three (1-nitronaphthalene -3-,-6-,and -7- monosulphonic acids)can be obtained thus. Sodium naphthalene-1-sulphonate yields a mixture of 1-nitro -4-,-5-,and -8- naphthalene sulphonic acids with the 1:8 acid in preponderating amount.

A general reaction which is utilised in the dyestuff industry with success consists in the replacement of a sulphonic acid group by a nitro group. Dyestuffs prepared in this way include picric acid, prepared by the action of dilute nitric acid on phenol sulphonic acid, Martius Yellow (2:4-dinitro-1-naphthol) prepared by the nitration of 1-naphthol-2:4-disulphonic acid and Naphthol Yellow S (2:4-dinitro-1-naphthol-7-sulphonic acid) prepared by the nitration of 1-naphthol-2:4:7-trisulphonic acid (18). A long series of experiments were made in an attempt to induce this reaction by the action of nitrating agents on sodium naphthalene-

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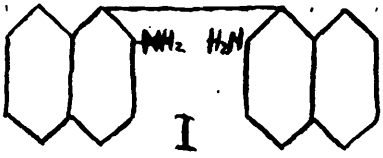
17. Cleve,Bull.,1876,26,444;1878,29,414;Ber.,1886,19,2179
    Armstrong and Wynne,Proc.C.S.,1889,17;1895,239
    Cassella,D.R.P.,67017;85058
    Erdmann and Suvern,Ann.,1893,275,330
18. Bender, Ber.,1882,22,996
    Badische, D.R.P.,10785

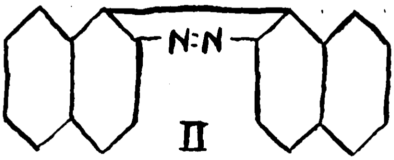
-2-sulphonate, which, while they make no claim to be exhaustive, indicate by the total lack of even traces of the desired 2-nitronaphthalene that there is little likelihood of success along this line. The 2-nitro-naphthalene required for this research was therefore prepared according to the method of Meisenheimer and Witt (13) apparently the most promising of the published methods.

Reduction of 2-Nitronaphthalene.

Meisenheimer and Witt (13) have studied the effect of varying reducing agents on 2-nitronaphthalene. They have found that zinc dust and alcoholic sodium hydroxide reacted with 2-nitronaphthalene with formation of a mixture of 2:2'-azonaphthalene, 2:2'-diamino-1:1'-dinaphthyl (I) and 1:1'-dinaphtho-o-diazin (II).

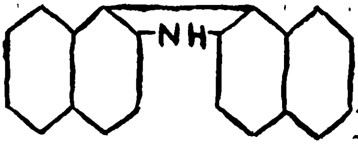


I

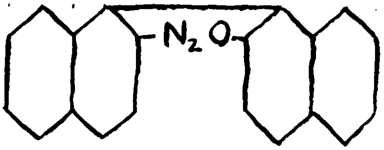


II

2:2'-Diamino-1:1'-dinaphthyl would be the compound which would be expected on causing 2:2'-hydrazonaphthalene to undergo the benzidine change, and its constitution was also proved by heating it above its melting point, when the corresponding carbazole, (III) ,1:1'-dinaphtho:2:2'-imin was formed. They also found that by very cautious reduction of 2:2'-azonaphthalene with zinc dust and sodium hydroxide 2:2'-hydrazonaphthalene could be obtained, and that this yielded 2:2'-diamino-1:1'-dinaphthyl on treatment not only with acid, but, contrary to expectation, with alkaline solutions. They also reduced 2-nitro-naphthalene with stannous chloride and sodium hydroxide, obtaining a mixture of 2:2'-azoxynaphthalene with 1:1'-dinaphtho-o-diazin oxide (IV). 2:2'-Azoxynaphthalene on reduction with zinc dust and sodium hydroxide gives 2:2'-azonaphthalene, and 1:1'-dinaphtho-o-diazin oxide the parent diazin (II).



III



IV

Jacobsen (19) has pointed out that, as both the positions para to the hydrazo group in 2:2'-hydrazo naphthalene are blocked, the substance which would have been expected would have been a "semidine" derivative such as Va, and further that it is very unusual for this transform-

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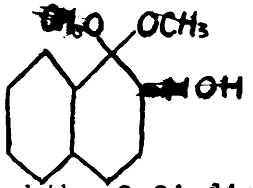
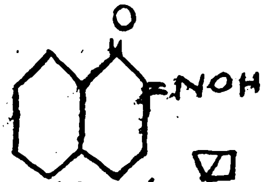
19. Jacobsen, Ann., 1922, 427, 142

-ation to take place in alkaline solution. At the same time he confirms Meisenheimer and Witt's experimental data, and has found that the same substance is formed when 2:2'-azonaphthalene is reduced with stannous chloride and hydrochloric acid in the presence of alcohol.

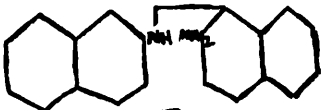
Meisenheimer and Witt (20) have also studied the action of methyl alcoholic potassium hydroxide on 2-nitronaphthalene. This reagent, when applied to most other nitro compounds, constitutes the most generally applicable method for preparing azoxy compounds, and it is interesting to note that no 2:2'-azoxynaphthalene was obtained thus, their product consisting of naphthaquinone oxime dimethylacetal (V), or its decomposition product 1-naphthaquinone-2-oxime (VI),70 per cent, 1:1'-dinaphtho-2:2'-diazin oxide (IV),15-20 per cent, and 2:2'-azonaphthalene, 8-10 per cent.



V



VI



Va.

Hantsch and Schmeidel have prepared 2:2'-azo-

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20. Meisenheimer and Witt, Ber.,1903,36,4164

-naphthalene by allowing naphthalene-2-syn-diazo sulphonate to decompose.(21). They further claim to have prepared 2:2'-hydrazonaphthalene by the reduction of 2:2'-azonaphthalene with zinc and acetic acid. The compound which they describe as 2:2'-hydrazonaphthalene melts at 168°-169° and is difficultly soluble in organic solvents. This method of reduction would almost inevitably cause intra-molecular conversion of the benzidine type, and 2:2'-hydrazonaphthalene is described by other authors as melting at 140°-141° and as readily soluble in most organic solvents. Meisenheimer and Witt (16) have pointed out that the compound described by Hantsch is most probably 2:2'-diamino-1:1'-dinaphthyl.

We have found that on reducing 2-nitronaphthalene with zinc dust and ammonium chloride in aqueous alcoholic solution either 2:2'-azoxy- or 2:2'-azo-naphthalene is formed, or a mixture of both, the proportions depending on the weight of zinc dust used. An insoluble zinc compound is produced as a by-product, and there is distinct evidence that it is formed by the dedomposition of an intermediate compound soluble in

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21. Hantsch and Schmeidel, Ber.,1897,**30**,81

alcohol. 2:2'-hydrazonaphthalene is a very unstable substance, with a strong tendency to change either (a) by oxidation to 2:2'-azonaphthalene or (b) intramolecularly to 2:2'-diamino-1:1'-dinaphthyl, the inorganic by-products of the reduction apparently acting as catalysts for this latter reaction. For this reason we have not been able, save in one doubtful case, to prepare 2:2'-hydrazonaphthalene, but we have frequently and with ease prepared 2:2'-diamino-1:1'-dinaphthyl.

On account of the inaccessibility of 2-nitro-naphthalene experiments of a similar nature were carried out using 2:2'azonaphthalene as starting material. As quantities of 2:2'-azoxynaphthalene were required for experiments described in chapter III, the oxidation of 2:2-azonaphthalene to 2:2'-azoxynaphthalene was investigated. Contrary to the experience of Cumming and Steel (in dealing with 1:1'-azonaphthalene) it was found this oxidation could not be carried out by passing a current of air through a boiling solution of 2:2'-azo-naphthalene. 2:2-Azoxynaphthalene can, however, be produced quantitatively by oxidising 2:2'-azonaphthalene with 30 per cent hydrogen peroxide ("perhydrol") in glacial acetic acid solution.

EXPERIMENTAL.

1. Preparation of 2-Nitronaphthalene.

A. Action of nitric acid on sodium naphthalene-2-sulphonate.

Nitric acid, dissolved in various solvents, was allowed to act on sodium naphthalene-2-sulphonate under varying conditions, as shown in Table I overleaf. The reaction mixture was worked up in experiments 1 to 8, and 13, by steam distillation of the neutralised reaction mixture. The only substance detected in the distillate was naphthalene. In the remaining experiments the reaction mixture was neutralised and after standing over night filtered. Both filtrate and residue were extracted with ether. The ethereal extracts on evaporation yielded only traces of colouring matter, and the aqueous residues on evaporation a yellow crystalline mixture of salts of naphthalene nitrosulphonic acids.

In view of the fact that not even a trace of unsulphonated nitronaphthalenes could be detected in any

TABLE I.

The Action of Nitrating Agents on Sodium Naphthalene-2-sulphonate

No.	Conc. HNO_3 per cent	$\frac{\text{Mols. } HNO_3}{\text{Mols. salt}}$	Temp.	Notes
(a) Nitric acid dissolved in water				
1.	15	1.4	100	
2.	15	1.4	-15	
3.	35	1.4	20	Afterwards heated 30 minutes (on water bath.
4.	68	2.1	-15	
5.	68	2.1	20	
6.	68	2.6	20	
7.	68	2.6	100	
8.	68	10.8	-15	
(b) Nitric acid dissolved in sulphuric acid.				
9.	8.3	1.1	20	Do. as 3
10.	13.9	1.1	20	Do. as 3
11.	13.9	1.1	20	) Allowed to stand over week-end before extraction.
12.	21.8	1.1	-15	)
13.	21.8	1.1	20	
(c) Nitric acid dissolved in glacial acetic acid.				
14.	8.6	1.1	20	As number 3
15.	8.6	1.1	-15	
16.	16.6	1.1	20	Do.
17.	35.0	1.1	100	
18.	17.5	1.8	100	
19.	17.0	2.5	100	

experiment, the prospect of obtaining a satisfactory yield by any further modification was seen to be small, and the method was abandoned.

B. Attempts to prepare 2-amino-8-nitronaphthalene-8-sulphonic acid.

Fifty grams of 2-naphthylamine were added to 150 grams of concentrated sulphuric acid and heated for six hours in a boiling water bath. The product was then poured into water and next morning filtered and dried. In order to separate the 2-aminonaphthalene-8-sulphonic acid from its isomers it was boiled with two equivalents of sodium ethoxide in alcoholic solution, and after cooling filtered and dried.

The product was nitrated by the method described by Jacchia (11), but no product answering to his description could be isolated.

C. The decomposition of naphthalene-2-diazonium nitrate.

The method of Meisenheimer and Witt (16) was utilised as follows:

52.5 Grams crude 2-naphthylamine were added with stirring, quickly in small portions, to a boiling mixture of 175 ccs. nitric acid (specific gravity 1.4) and 1750 ccs. of water. As soon as a clear solution was obtained it was cooled as quickly as possible to 0° in order to obtain finely divided crystals of 2-naphthylamine nitrate. After cooling it was diazotised in the usual way, and then as much sodium nitrite added as is necessary to neutralise the excess nitric acid, that is, 180 grams sodium nitrite dissolved in 800 ccs. water. If this operation is properly conducted the whole should go almost completely into solution. The solution, now smelling strongly of nitrous acid, was poured with stirring over cuprous oxide mixture, prepared by reduction of 375 grams of copper sulphate with glucose and sodium hydroxide according to the method of Sandmeyer (15), whereon a brisk evolution of nitrogen and nitric oxide set in.

Meisenheimer and Witt extract the 2-nitronaphthalene from the reaction mixture by steam distillation. We have found this to be a lengthy and impracticable method, even when superheated steam is employed. Accordingly we extracted the 2-nitronaphthalene by exhaustive extraction with a suitable solvent. As a result of comparative experiments, in which aliquot portions of the same reaction product were extracted with different solvents in a Soxhlet apparatus for six hours, it was found that the amount extracted in the same time by different solvents was represented by the figures:

Ether	10	(Standard)
Alcohol	8.8	
Benzene	5.1	

As it was found that alcohol, despite its slightly lower extractive efficiency than ether, gave a considerably cleaner product than the other two solvents, it was adopted in all further preparations.

2-Nitronaphthalene is described in the literature as yellow needles, which in the compact state seem yellowish brown. We found that on boiling a solution of 2-nitronaphthalene in aqueous alcohol (50 per cent) with animal charcoal, it can be obtained as almost colourless needles of the normal melting point, (79°). This product showed no tendency to darken on exposure either to air or light.

2. Reduction of 2-Nitronaphthalene.

A. Preparation of 2:2'-azoxynaphthalene.

One gram of 2-nitronaphthalene and two grams of ammonium chloride were dissolved in ten ccs. of 90 per cent alcohol and three ccs. of water by heating on the water bath until all the 2-nitronaphthalene had dissolved, a little of the ammonium chloride remaining undissolved. Zinc dust (1.4 grams) was then added in very small quantities, the temperature being maintained at about 75°-80°. On addition of each batch of zinc dust heat was evolved and a strong smell of ammonia could be observed. When all the zinc dust had been added the hot reaction mixture was filtered, and the residue and filtrate (A) worked up separately.

The greenish residue was extracted successively with alcohol, hot water, and again several times with hot alcohol. The first alcoholic extract yielded only a small quantity of white plates melting or decomposing at 220°-230°. By fractional crystallisation of the other alcoholic extracts five batches of crystals melting respectively at I, 155°-163°; II, 162°-164°; III, 158°-159°; IV, 152°-155°; V, 131°-133°. Batches I - IV after several crystallisations from alcohol melted sharply at 164°.

Found: N = 9.25, Calc. (for azoxynaphthalene), N = 9.39 per cent.

The filtrate (A) deposited a crystalline mass, of which more was obtained by concentrating the mother liquors. This product was extracted with water and then exhaustively with alcohol. A white crystalline powder, insoluble in water or alcohol, readily soluble in dilute hydrochloric acid, and probably identical with the compound $2NH_4Cl.5Zn(OH)_2$ described by Cumming and Steel (1) was filtered off. The isolation of this compound, which is insoluble in alcohol, from an alcoholic filtrate is regarded by us as evidence that in this reduction an intermediate compound containing zinc plays an important part. Further evidence supporting this conclusion will be considered in the experimental part of Chapter Two. The alcoholic filtrates from the zinc compound yielded further quantities of 2:2'-azoxynaphthalene on concentration.

B. Preparation of 2:2'-azonaphthalene.

The reduction was carried out precisely as in the preparation of 2:2'-azoxynaphthalene, but zinc dust was on this occasion added until the colour of the solution was completely discharged. The reaction mixture was then filtered hot, and the residue washed several times with hot alcohol. The united alcoholic filtrates, which by now had regained their red colour, were allowed to cool and filtered. On crystallising the product from alcohol, reddish orange crystals melting sharply at 204° were obtained. These were identified with 2:2'-azonaphthalene by comparison with a sample prepared by the method of Hantsch and Schmeidel (21).

On evaporating the mother liquors, two crops of crystals, yellow and red, melting at 157°-159°, and resembling crude 2:2'-azoxynaphthalene in appearance were obtained. In view of the facts (a) that the reaction passed through a colourless stage, proving the absence of azo- or azoxy- naphthalenes, (b) that we have shown (p. 23) that 2:2'-azonaphthalene is unaffected by air when in alcoholic solution, the formation of this substance is an indication that 2:2'-hydrazonaphthalene may oxidise in part directly to 2:2'-azoxynaphthalene, and not via 2:2'-azonaphthalene.

C. Attempted preparation of 2:2'-hydrazonaphthalene. Isolation of 2:2'-diamino-1:1'-dinaphthyl.

The method of reduction usually adopted was as follows:- 2:2'-azonaphthalene (1 part) and ammonium chloride (2 parts) were suspended in 90 per cent alcohol (100 parts) and boiled on the water bath for a few minutes. The mixture was then allowed to cool to 65°-70° and zinc dust added until the colour of the solution was completely discharged. If the temperature was below 65° the reduction proceeded exceedingly slowly and the results were unsatisfactory.

The reduction mixture was worked up by many different methods, two typical examples of which are given below:

I. Immediately after the reduction was completed, the solution was poured into a large volume of water containing a few drops of sulphurous acid (in some experiments ammonium sulphide) and filtered. The precipitate was dried in vacuo over sulphuric acid and extracted with absolute alcohol (in some experiments dry ether). The extracts on concentration yielded a product consisting essentially of 2:2'-azonaphthalene.

II. With a view to limiting the possibility of atmospheric oxidation, the reaction mixture was concentrated under reduced pressure immediately after reduction. A copious yield of white plates was obtained, which, after crystallisation from absolute alcohol and from a mixture of benzene and petroleum ether, melted at 188°-191°, and otherwise resembled in their properties 2:2'-diamino-1:1'-dinaphthyl. The same result was obtained when the reaction mixture was filtered before distillation and the colour again discharged by addition of a little zinc dust.

In one experiment a very small quantity of a crystalline product melting at 139°-140° was isolated, corresponding to 2:2'-hydrazonaphthalene (melting point 140°, Meisenheimer and Witt,16).

3. Oxidation of 2:2'-azonaphthalene

A. Action of atmospheric oxygen.

2:2'-azonaphthalene (0.5 gram) was dissolved in the minimum quantity of boiling glacial acetic acid and a brisk current of well-dried air passed through the boiling solution for two days. On cooling a crystalline mass was thrown down consisting of unchanged 2:2'-azonaphthalene, melting at 204°. The mother liquor yielded on concentration and precipitation with a few drops of water, a minute quantity of dark brown crystals melting at 131°-133°. The experiment was repeated using boiling 90 per cent alcohol as solvent with identical results.

B. Action of hydrogen peroxide.

Five grams of 2:2'-azonaphthalene were dissolved in one litre of glacial acetic acid by warming on the water-bath. Ten ccs. 30 per cent hydrogen peroxide ("Perhydrol") were added drop by drop, and the heating continued for fifteen hours, a further seventy ccs. of perhydrol being added in small quantities at a time. The solution, now pure yellow, was allowed to cool, and a small insoluble residue filtered off. The solution was then concentrated to small bulk, and crystallisation induced by the addition of a few drops of water.

A bulky reddish yellow product was obtained. This was crystallised several times from 90 per cent alcohol, and the melting point thus raised to 164°. The identity of this substance with 2:2'-azoxynaphthalene prepared by reduction of 2-nitronaphthalene was established by the method of mixed melting points.

CHAPTER TWO.

The Reduction of Nitro Compounds With Zinc Dust and Ammonium Chloride in Alcoholic Solution.

The employment of zinc dust in the presence of a neutral salt such as calcium or ammonium chloride is now a standard method for the preparation of β-aryl hydroxylamines from the corresponding nitro compounds, (4), but the application of this reducing agent to the preparation of azoxy-,(5), azo- and hydrazo- (22) compounds has been much less frequent. It has been utilised by Wacker for the reduction of certain of the nitronaphthalenes and their sulphonic acids; by Alway in the preparation of m-azoxybenzaldehyde; by Wohl and Goldenburg in that of p-azoxyphenyl acetate; by Duval in an investigation of nitro derivatives of diphenyl-

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22. v. Pechmann and Nold, Ber.,1898,31,557
    Zincke and Kuchenbecker, Ann.,1903,330,1

-methane; and by Reissert in investigating o-azoxyphenyl acetic acid. Bamberger utilises the method indirectly by preparing the N-arylhydroxylamine which is then oxidised by means of a current of air to the azoxy compound.

The application of this reducing agent to 1- and 2- nitronaphthalenes has been already discussed, and in view of the favourable results obtained it was decided to test its utility as a general method for the reduction of nitro compounds. In considering its application to the preparation of azoxy compounds, while it must be admitted that the process cannot compete, either from the point of view of convenience of working or of yield with the standard method for the preparation of these compounds consisting in the use of sodium methoxide in methyl alcohol solution, (23), yet we have found the method applicable to the

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23. Klinger, Ber.,1882,15,865
Klinger and Pitschli, Ber.,1885,18,2551
Gattermann and Ritschke, Ber.,1890,23,1738
Lachmann, J.A.C.S.,1902,24,1178
and many others

preparation of certain compounds (e.g. the azoxy naphthalenes (20), p-azoxytoluene (24)), which cannot be prepared by the standard method using methoxide.

In the case of these compounds reduction by means of zinc dust and ammonium chloride is cleaner and furnishes somewhat higher yields than methods which involve the use of strong alkali. The production of azoxy compounds appears to take place via an intermediate compound which readily decomposes with the production of an inorganic by-product, of the formula $2NH_4Cl.5Zn(OH)_2$. Reduction of p-nitrotoluene to p-hydrazotoluene is accompanied by the formation of a substance of the formula, $(CH_3.C_6H_4.NH_2)_4NH_4Cl.ZnCl_2$, and drastic reduction of nitrobenzene by the formation of the aniline zinc chloride salt ($2C_6H_5NH_2.ZnCl_2$) described by Lachowitz and Bardrowski (25).

While p-hydrazotoluene was accessible with comparative ease, considerable difficulty was

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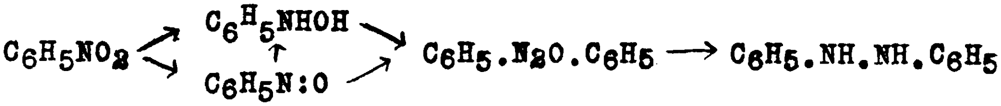
24. Klinger, Ber.,1882,<u>15</u>,865
    Fisher and Hepp, Ber.,1893,<u>26</u>,2231
25. Lachowitz and Bardrowski, Monats.,<u>9</u>,513

experienced in attempting the preparation of hydrazobenzene by direct reduction of nitrobenzene with zinc dust and ammonium chloride. This was finally traced to the following peculiarity in the course of the reaction.



$$C_6H_5NO_2 \begin{array}{c}\nearrow\\ \searrow\end{array} \begin{array}{c} C_6H_5NHOH \\ \uparrow \\ C_6H_5N{:}O \end{array} \begin{array}{c}\searrow\\ \nearrow\end{array} C_6H_5.N_2O.C_6H_5 \longrightarrow C_6H_5.NH.NH.C_6H_5$$

It is well known that in the alkaline reduction of nitro compounds, phenylhydroxylamine and nitrosobenzene are first formed. Azoxybenzene is formed by condensation of these, and hydrazobenzene by reduction of the azoxybenzene. It appears that *either* nitrosobenzene is not formed in appreciable quantities in this reduction, *or* that reduction of phenylhydroxylamine to aniline proceeds preferentially to the formation of azoxybenzene, except where nitroso benzene is in large excess.

This view has been deduced from the following data:-

1. We have found that on reduction of nitrobenzene with zinc dust and ammonium chloride in

alcoholic solution the usual products were phenyl hydroxylamine and aniline hydrochloride. Occasionally small quantities of azoxybenzene were also present.

2. Phenylhydroxylamine on similar treatment gave only aniline, in the form of a double salt with zinc chloride.

3. Azoxybenzene under the same conditions gave hydrazobenzene in nearly eighty per cent yield.

4. Nitrosobenzene also gave hydrazobenzene, but in much smaller yield. In this experiment the phenylhydroxylamine would be formed by reduction of the nitrosobenzene, which would always be in excess.

The opportunity was taken of utilising the quantity of material accumulated in the course of this research to investigate a point of some interest in the chemistry of p-azoxytoluene. Janovsky and Reimann, (26), on crystallising the product obtained by the action of zinc dust and sodium hydroxide on p-nitrotoluene, obtained, together with p-azotoluene and p-hydrazotoluene, two azoxytoluenes melting

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26. Janovsky and Reimann, Ber.,1889,22,40
Janovsky, Ber.,1889,22,1172 ;Monats.,1889,10,594

respectively at 70° and 75°. p-Azoxytoluene had previously been prepared by Melms (27) who stated its melting point to be 70°. Janovsky accordingly characterised his compounds, that which melted at 70° as "p-azoxytoluene", and that which melted at 75° as "iso-p-azoxytoluene". Janovsky also stated that the compound melting at 75° could also be obtained by oxidation of p-azotoluene with three parts of nitric acid (specific gravity 1.51). On investigating the properties of the two isomers he collected the following data: The two compounds have the same molecular weight; on reduction with zinc chloride in alcohol different compounds of the formula $C_7H_7.NH.N(OH).C_7H_7$ were formed; (this statement is made in the Monatshefte paper; in the second Berichte paper it is stated that hydrazotoluene is formed under these conditions); on sulphonation a monosulphonic acid was formed from the normal compound, a disulphonic acid from the iso- compound; nitric acid of density 1.4 was stated to act on the normal compound with production of a mononitro compound melting at 51°, on the iso compound

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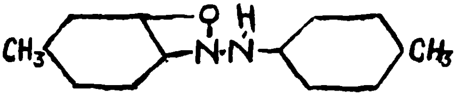
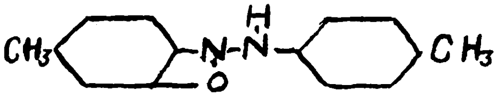
27. Melms, Ber.,1870,<u>3</u>,549

with production of a similar compound melting at 82° (but fuming nitric acid produced the same trinitro derivative, melting at 196°, from each); heating the normal compound with bromine in acetic acid causes the formation of 2-bromo-4:4'-dimethylazoxybenzene, whilst the isomer is stated to yield 3-bromo-4:4'-dimethyl-azoxybenzene, together with other substances. Janovsky on these grounds formulated the isomers as VII and VIII. Assuming the possibility of free rotation around a single bond, these formulae each represent the same substance, and it is difficult to understand exactly what meaning Janovsky ascribed to them.

VII



VIII



After exhaustive fractional crystallisation of the product obtained by the action of zinc dust and ammonium chloride on p-nitrotoluene, and later of the product obtained by following Janovsky's own methods (using zinc dust and sodium hydroxide) closely, no trace could be obtained of any substance melting at 75°, although large quantities of p-azoxytoluene melting at 70° were isolated. The action of three parts nitric acid

(1.51) does not in our hands give, as stated by Janovsky, a product melting at 75°, but a mixture of a red substance melting at 202°, probably tetranitroazotoluene (28), melting point 201°, with a white substance melting at 153°. The formation of the latter is favoured by increase in the time of nitration.

A somewhat similar instance of isomerism, that reported by C.F. and R.A.Gortner (29) of azobenzene was eventually shown by Hartley and Stuart (30) to be due to the property possessed by azoxybenzene and azobenzene of forming solid solutions with one another. Two sets of mixed crystals can be formed with a eutectic temperature of 24.5° ; at this temperature crystals of azoxybenzene can dissolve about ten per cent of azobenzene molecules, whilst those of the azobenzene dissolve about forty-five per cent of molecules of azoxybenzene. Accordingly a setting point curve (Fig. 1) has been prepared. Contrary to expectation this reveals no irregularities. From the setting point, 69.95°, of the pure p-azoxytoluene

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28. Janovsky, Monats., 1888, 839
29. C.F. and R.A.Gortner, J.A.C.S., 1914, <u>32</u>, 1294
30. Hartley and Stuart, J.C.S., 1914, <u>105</u>, 309

the curve rises fairly steeply to the point corresponding to 75° and ten per cent of p-azotoluene; addition of p-azotoluene to p-azoxytoluene therefore does not

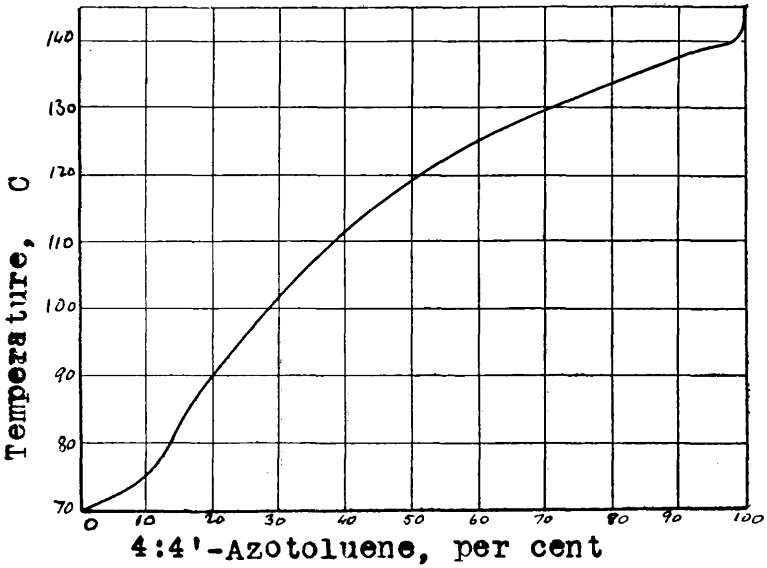

Fig. I

Melting point of mixtures of 4:4'-azoxy and -azo-toluene

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depress the setting point of the latter. The curve then rises, first with slight concavity relative to the composition axis to the point corresponding to 140° and ninety-nine per cent of p-azotoluene, and then steeply to 143.4° the setting point of pure p-azotoluene. A fifty per cent mixture has a setting point of 118.5°.

It was found that p-azotoluene resembled 2:2'-azonaphthalene in that it resisted the oxidising action of a current of air, but was readily oxidisable by "perhydrol" in acetic acid solution.

EXPERIMENTAL.

1. The neutral reduction of nitrobenzene.

(a). Isolation of zinc compound.

Nitrobenzene (25 grams) and ammonium chloride (50 grams) were dissolved in 225 ccs. alcohol containing 65 ccs. water. Forty grams of zinc dust were then added in the usual manner, the temperature being maintained between 70° and 75° and the solution mechanically stirred. On filtration of the reaction mixture a crop of white crystals appeared in the filtrate which refused to redissolve even on dilution with aqueous alcohol of similar composition and bringing to the boil. They are, in fact, almost insoluble in alcohol or in water, but are readily soluble in dilute hydrochloric acid. Adequate precautions were taken against solids passing through the filter paper, (two layers of Swedish filter paper being sometimes used), or round its edges, and no difficulty was experienced in separating the crystals from their mother liquor. Experiments were carried out with a view to discovering the conditions of formation of this substance as follows:-

1. The reaction mixture was brought to the boil and immediately filtered by suction into a flask surrounded by boiling water. Large crop of crystals.

2. The reaction mixture was allowed to cool, and to stand over-night; in the morning it was brought to the boil, and filtered under the same conditions. Large crop of crystals.

3. The reaction mixture was allowed to stand over-night and filtered cold. No crystals appeared in filtrate.

It would seem from these observations that the crystals are derived from an intermediate compound which is soluble in hot alcohol, but is decomposed by it.

<u>Analysis</u>. The compound contained zinc, ammonia, and chlorine, but no aniline.

Found, Zn.,(by pyrophosphate method)	54.83,54.87
Theory for $2NH_4Cl.5Zn(OH)_2$, Zn,	54.88 per cent

Attempts to estimate zinc by simple ignition, either over the open flame or in a muffle gave low and variable results. If specially purified mercuric oxide was added the results tended to be high.

B. Isolation of organic reduction products.

Ten grams nitrobenzene, together with twenty grams ammonium chloride were dissolved in ninety ccs. alcohol and 25 ccs water. The whole was boiled for some minutes and allowed to cool to 70°K. Sixteen grams of zinc dust was then added in small quantities so as to keep the temperature between 70° and 75°. Total time of addition, 40 minutes. When all the zinc had been added, the solution, which had developed a pronounced colour, was again decolorised. The reaction mixture was then filtered. The filtrate after concentration under reduced pressure yielded only aniline hydrochloride. The residue was separated by extraction with boiling petroleum ether into phenyl hydroxylamine (white needles, sparingly soluble in hot petroleum ether, insoluble in cold. Pronounced sternutatory properties. Melting point 76°-78°)

and aniline hydrochloride.

Yields:-		
	Phenylhydroxylamine	0.95 gram
	Aniline hydrochloride	0.97 "

2. The neutral reduction of phenylhydroxylamine.

Phenylhydroxylamine (2.8 grams) and ammonium chloride (ten grams) were dissolved in ninety ccs. of alcohol diluted with twenty-five ccs of water, and six grams of zinc added in small portions. So long as the temperature was maintained just below 75° no coloration developed, but if the temperature was allowed to rise above 75° a yellow colour appeared, which could be discharged on cooling to 75° by adding a little more zinc dust.

The reaction product was filtered, and the usual crops of inorganic material obtained. The filtrate from these was concentrated under reduced pressure, and 0.98 grams of a white crystalline compound obtained. This gave the usual analytical reactions for aniline, zinc, and chlorine, but did not contain ammonia. It was evidently the well-known aniline-zinc chloride compound, $2C_6H_5NH_2.ZnCl_2$, described by Jachowitz and Bardrowski, (25).

All crops of crystals were extracted with petroleum ether, but only traces of colouring matter were obtained.

3. The neutral reduction of nitrosobenzene.

Nitrosobenzene (8.35 grams), ammonium chloride, (20 grams), alcohol, (90 ccs.) and water (25 ccs.) were maintained at a temperature of 70° to 75° during the addition of thirteen grams of zinc dust. The solution, originally dark green in colour, passed through a red stage and eventually became colourless, a heavy white precipitate being thrown down. The reaction mixture was filtered and the filtrate allowed to cool for five minutes. A white precipitate, chiefly inorganic in nature, was filtered off, and the filtrate concentrated under reduced pressure. After standing over-night it was again filtered and evaporated to small bulk. All residues obtained thus were extracted, first three times with petroleum ether, then exhaustively with alcohol. The petroleum ether extracts deposited on standing 2.37 grams of hydrazobenzene (identified by mixed melting points and conversion to benzidine) but on concentration yielded nothing further. On concentration of the alcoholic solution 1.79 grams of hydrazobenzene was obtained. In addition a small quantity of hydrazobenzene was lost owing to the breakage of a flask. Total amount of hydrazobenzene isolated, 4.16 grams. (59.4 per cent of theory).

4. The neutral reduction of azoxybenzene.

Ten grams azoxybenzene, twenty grams ammonium chloride, ninety ccs. alcohol, and twenty-five ccs. water were heated to 70° on a water bath. The azoxybenzene did not dissolve completely in the alcohol but floated about in oily drops on the surface. On addition of zinc dust, at such a rate as to maintain the temperature between 70° and 75°, this oil gradually reddened, and the tendency for it to deposit as an incrustation on the stem of the thermometer increased. Finally the whole mass suddenly solidified, when the reaction was deemed to have reached completion. By this time twelve grams of zinc dust had been added. The reaction mixture was worked up in the usual manner and yielded 6.98 grams hydrazobenzene (76 per cent of theory) together with 0.22 grams azobenzene melting at 66°-68° and 0.21 grams of a mixture melting at 57°-58°.

The hydrazobenzene was white in colour, and was identified by its melting point, by conversion of a small portion into benzidine, and by oxidation of another portion to azobenzene (melting at 68°) by passing a brisk current of air through an alkaline alcoholic solution.

5. The neutral reduction of p-nitrotoluene.

A. To the azo-azoxy stage with zinc dust and ammonium chloride.

One part p-nitrotoluene, nine parts 90 per cent alcohol, 2.25 parts water, and two parts ammonium chloride were heated on the water bath at 70°. Zinc dust (1.5 parts) was then added at such a rate as to maintain the temperature of the solution at 70°-75°. The solution was filtered hot, the residue extracted with boiling 90 per cent alcohol, and the combined extract and filtrate cooled. An orange yellow crystalline precipitate appeared and was filtered off, further quantities being obtained by concentrating the mother liquors under reduced pressure. The crystalline product was extracted with water to remove ammonium chloride and several times with alcohol, white crystals of a zinc compound remaining undissolved. After careful and prolonged fractional crystallisation from acetic acid of the substances obtained from the combined alcoholic axtracts, the only substances isolated were p-azoxytoluene, melting at 70°, p-azotoluene, and a small quantity of unchanged p-nitrotoluene.

Yields (from twenty grams p-nitrotoluene):-

p-azotoluene	2.8 grams	14 per cent
p-azoxytoluene	5.5 "	27.5 " "

B. To the azo-azoxy stage with zinc dust and sodium hydroxide.

In case the absence of the isomeride melting at 75° should be due to the use of a different reducing agent from that employed by Janovsky, and to compare the yields obtainable by the two processes, the preparation was repeated, using Janovsky and Reimann's method as follows:-

Fifty grams of p-nitrotoluene and fifty ccs. of 25 per cent sodium hydroxide were heated together on a waterbath. Forty-five grams of zinc dust were added to the mixture in small quantities at a time, and with vigorous agitation after each addition of zinc dust, the total addition occupying in all about ninety minutes. The reaction mixture was poured on ice, and dilute hydrochloric acid solution added until it showed a neutral reaction to Congo Red. The residue was filtered off, and after washing dissolved in glacial acetic acid and fractionally crystallised as in the previous experiment. After exhaustive fractionation, the only products isolated were, as before, p-azoxy- and p-azo- toluene, together with a little p-toluidine.

(Yield, in an experiment starting with twenty grams p-nitrotoluene):-

p-azotoluene	2.5 grams	12.5 per cent
p-azoxytoluene	4.5 "	22.5 " "

C. Reduction to hydrazo stage.

The reduction was commenced as described on page 42, a further quantity of alcohol being added to dissolve the precipitated p-azotoluene, and a further quantity of zinc dust added in small portions until the colour of the solution was completely discharged. The reaction mixture was poured into ice-cold water in an Erlenmeyer flask, which was corked and shaken vigorously, to coagulate the precipitate, which was then quickly filtered and dried in vacuo. When dry, it was extracted with absolute alcohol and the extract concentrated under diminished pressure. The yellow crystalline product obtained thus was washed with hot petroleum ether. The petroleum ether solution on cooling deposited a small quantity of p-hydrazo--toluene, melting at 126°.

The substance insoluble in petroleum ether was recrystallised from absolute alcohol, when white lustrous plates melting at 250° were obtained. Ammonia and p-toluidine were obtained by the action of alkali on the substance, which also gave analytical reactions indicating the presence of zinc and of a chloride.

Found, Cl, 17.17,17.30; Zn., 10.70,10.76 per cent
Theory for $(C_7H_9N)_4.NH_4CL.ZnCl_2$, Cl, 17.23;
Zn, 10.6 per cent.

6. The oxidation of p-azotoluene.

A. By means of a current of air.

A brisk current of well-dried air was drawn through a hot solution of p-azotoluene (0.25 grams) in glacial acetic acid. On cooling, a crystalline mass of p-azotoluene was deposited, further quantities of which were obtained from the mother liquors. No other product was obtained.

B. By means of "perhydrol".

Ten ccs. of perhydrol were added to a hot solution of p-azotoluene (0.5 grams) in glacial acetic acid, and the mixture heated for one hour on the water bath. The lemon yellow solution on cooling and concentration yielded several crops of yellow crystals, melting after recrystallisation at 70°-71°, and identified as p-azoxytoluene by the method of mixed melting points.

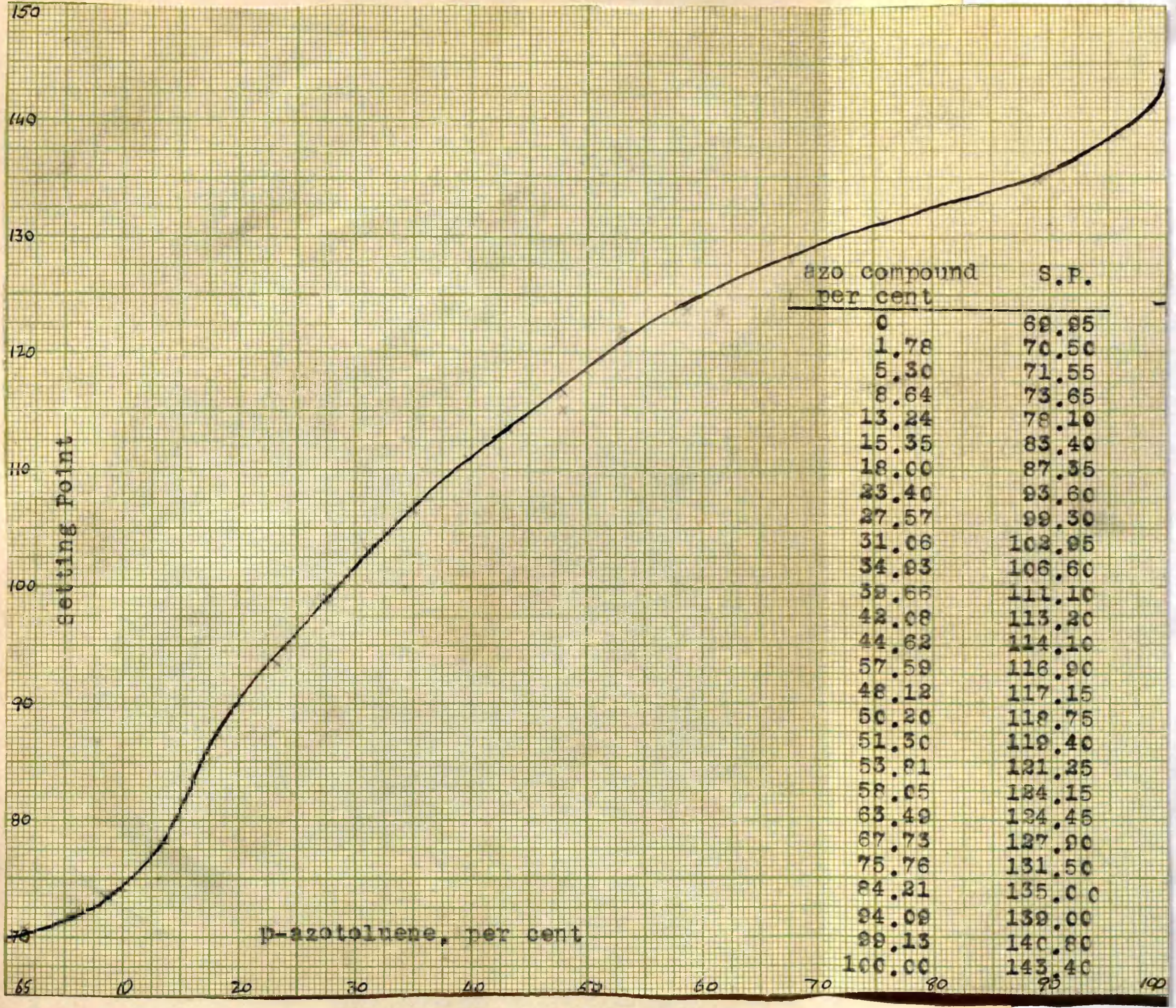
C. By means of fuming nitric acid.

p-Azotoluene (1.5 grams were added in small quantities at a time to an equal weight of nitric acid of specific gravity 1.50, contained in a flask immersed in cold water. After standing a certain time the solution was poured into water and the precipitate filtered off, washed with water, and fractionally crystallised from alcohol. Two products were isolated:-

(i) orange red crystals, melting at 202°; probably tetranitroazotoluene.

(ii) white woolly needles containing nitrogen and melting at 153°.

On nitrating for sixteen hours the product was composed chiefly of the white compound, for one hour about equal parts of each, and for five minutes wholly the red compound.



azo compound per cent	S.P.
0	69.95
1.78	70.50
5.30	71.55
8.64	73.65
13.24	78.10
15.35	83.40
18.00	87.35
23.40	93.60
27.57	99.30
31.06	102.95
34.93	106.60
38.66	111.10
42.08	113.20
44.62	114.10
57.59	116.90
48.12	117.15
50.20	118.75
51.30	119.40
53.81	121.25
58.05	124.15
63.49	124.45
67.73	127.90
75.76	131.50
84.21	135.00
94.09	139.00
99.13	140.80
100.00	143.40

SETTING POINT CURVE

of mixtures of

p-azoxytoluene and p-azotoluene

CHAPTER THREE.

The Action of Light on Azoxy Compounds.

2:2'-Azoxynaphthalene.

In the course of experiments on the preparation of 2:2'-azoxynaphthalene it was observed that this substance, either in solution or in the solid state became converted by the action of light into red crystals of slightly lower melting point and of similar chemical composition. In order to account satisfactorily for this phototropy, it will be necessary to consider the properties of the azoxy group, so far as these are at present known.

Isomerism in the azoxy series.

The occurrence of pairs of isomerides whose isomerism may be traced to some peculiarity of the azoxy group is not unknown. The somewhat doubtful case of the isomerism of the p-azoxytoluenes has been already discussed, but several better authenticated examples exist. Bamberger (31) in an investigation of the action of sodium hydroxide on nitrosobenzene isolated two isomeric o-hydroxyazoxybenzenes, $(C_6H_5N_2OC_6H_4OH)$. These apparently differed only in melting point, one melting at 75°, the other at 108°. Reissert, (32), has also succeeded in preparing by a modification of Bamberger's method an isomeric azoxybenzene melting at 81°-84°, together with the known azoxybenzene melting at 36°. He reports that isoazoxybenzene is colourless, but it must be remembered that after suitable purification ordinary azoxybenzene is also colourless. A similar isomeride of o-azoxytoluene was also obtained, melting at 80°-82°(melting point of ordinary o-azoxytoluene, 56°), but not from p-azoxytoluene. On heating the new, "iso" forms pass into the normal forms, and this transformation can also take place on adding a trace of bromine to isoazoxybenzene in chloroform solution. Reissert formulated his isomers as respectively IX and X.

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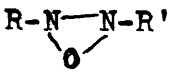
31. Bamberger, Ber.,1900,<u>33</u>,1939;1902,<u>35</u>,1614
32. Reissert, Ber.,1909,<u>42</u>,1364

He attempted to prove the open chain formula (IX) by means of phenylhydrazine and of hydroxylamine, but was unsuccessful.

$R-\underset{\underset{O}{\|}}{N}:N-R'$

IX



X

$R-N:\underset{\underset{O}{\|}}{N}-R'$

XI

These observations by Janovsky, by Bamberger, and by Reissert, although interesting, appeared sporadic, no general law being applicable to the three examples, which were not followed up further by the authors concerned. A series of papers by Angeli and his co-workers fall into a different category, and have led to the establishment of new views concerning the structure of azoxy compounds.

The first of these papers (33) dealt with the condensation of amines and nitro compounds in presence of sodium with the formation of azoxy compounds. Angeli showed that a different compound was obtained if aniline were condensed with nitronaphthalene from that obtained if nitrobenzene were condensed with 1-naphthylamine

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33. Angeli and Marchetti, Atti., 1906,(v),15,1,480

A long series of papers was subsequently published by Angeli and his school (34), in which it was shown that azo compounds could be oxidised to azoxy compounds by the use of hydrogen peroxide in glacial acetic acid solution, and, further, that in cases where the azo compound was symmetrical a homogeneous product was invariably obtained, yet in cases where the azo compound was unsymmetrical, (that is where the two aryl groups joined by the azo linkage were different) the product usually consisted of a mixture of two isomerides differing in melting point and in solubility. These two series of isomerides were not interchangeable, and gave rise to different, isomeric, derivatives by means of reactions (such as bromination) which preserved the azoxy group intact. Identical products were obtained from either isomer on reduction.

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34 Angeli and Alessandri, Atti,1911,v,20,i,896;ii,170
Angeli and Valori, Atti,1912,(v),21,i,153;1913,(v),22,i,132
Angeli, Atti,1913,(v),22,i,201,[illegible],356
Valori, Atti.,1913,(v)22,ii,125
Angeli, Gazzetta, 46,ii,67
and many others.

The Formula of Azoxy Compounds.

Basing his reasoning on this work, Angeli throws the cyclic formula (X) overboard altogether in favour of the open-chain formula (IX). It will be easily seen that with a formula of type IX isomerism is possible wherever the aryl groups R,R' are different (IX,XI), as in the compound $C_6H_5.N_2O.C_6H_4Br$, one of the first shown by Angeli to be capable of existence in two modifications.

The theory which Angeli brought forward has been confirmed in a paper by Mrs. G.M.Robinson (35) in which the same conclusion was arrived at independently on the following grounds:-

If veratrole, XII, be nitrated in acetic acid solution, no dinitro compound is obtained, but the yield of mononitroveratrole is quantitative. The dinitroveratrole can, however, be produced by the action of nitric acid of density 1.42 on the mononitroveratrole in almost theoretical yield. The azo group does

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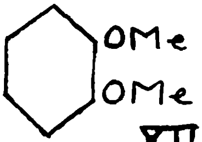
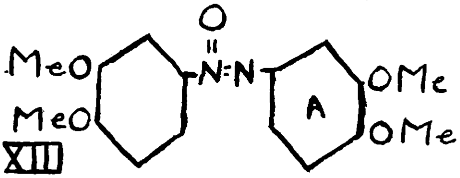
35. (Mrs.) G.M.Robinson,J.C.S.,1917;111,109

not inhibit nitration, as azoveratrole yields dinitro-veratrole on nitration in acetic acid solution. Azoxyveratrole behaves somewhat differently, as on nitration in acetic acid solution only one nucleus is attacked, the product being an unsymmetrical mononitro azoxyveratrole. Mrs. Robinson accounts for this by assigning to azoxyveratrole a formula, XIII, in which one of the veratrole nuclei is in the condition of azoveratrole, the other more or less in the condition of nitroveratrole; the nucleus marked A is the one which undergoes nitration in acetic acid solution.



XII



XIII

On the other hand, Lachmann, (36), has compared the reactivity of azoxybenzene with that of nitrosobenzene and of diphenylnitrosoamine, $(C_6H_5)_2:N.N:O$. As these compounds are much more reactive than azoxybenzene, he concludes that azoxy-benzene contains the ring structure X, but neglected the fact that, as generally formulated

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36. Lachmann, A.C.J., 1899, 21, 433; J.A.C.S., 1902, 24, 1178.

nitrosobenzene and diphenylnitrosoamine contain trivalent nitrogen only, while in the formula which he rejected for azoxybenzene, the nitrogen of the $:\overset{\cdot}{N}:O$ group is pentavalent.

The Semi-polar Double Bond Formula.

Recent work in physical chemistry has also thrown doubt on the possibility of Angeli's formula for azoxy compounds. According to the Lewis-Langmuir octet theory, it is impossible for nitrogen to exert five co-valencies, the two possibilities open to it being either the exercise of three co-valencies, or the simultaneous exercise of four covalencies and one electrovalency.

Neither of these alternatives at first sight appear to fit the case of azoxybenzene, as formulated by Angeli, or of compounds such as nitrobenzene or the amine oxides. Lowry has recently advanced a theory in which he postulates that in organic chemistry compounds containing a double bond generally react as if the double bond were composed of one co-valency and one electro-valency.(36a)Although this theory has

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36a. Lowry, J.C.S.,1923,<u>123</u>,822

since been restricted, in its application to ethylenic and carbonyl bonds, to "activated" molecules considered at the moment of chemical union, yet special evidence has been brought forward recently to justify its application to S:O and $:\overset{\prime}{N}:O$ bonds. Sugden (37) has recently investigated the relation between chemical composition and a new combination of physical properties which he calls the "parachor", and which may be defined as the molecular volume at constant surface tension. It is very consistently additive in its nature. Definite values are obtained for the atoms of any alement, and if these values be substituted in the empirical formula of a compound, the value of the parachor may be obtained to a close approximation. If the compound contains a double bond, a sum of 23.3 units must be added to the value otherwise obtained. In these cases, however, where of the two atoms linked by the double bond, one at least is either nitrogen or sulphur, that is, in these cases where it would be necessary to assume a semi-polar double bond in order that the formula could be expressed

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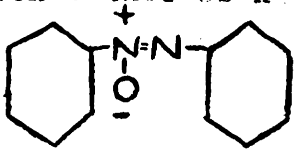
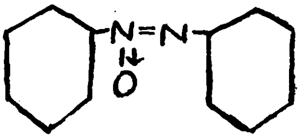
37. Sugden, Reed, and Wilkins, J.C.S.,1925,127,1525

in terms of the Lewis Langmuir theory, Sugden found that this increment did not require to be supplied, but that instead it was necessary to make a small subtraction. Sugden's formula for azoxybenzene can be written either as XIV or XV.

XIV





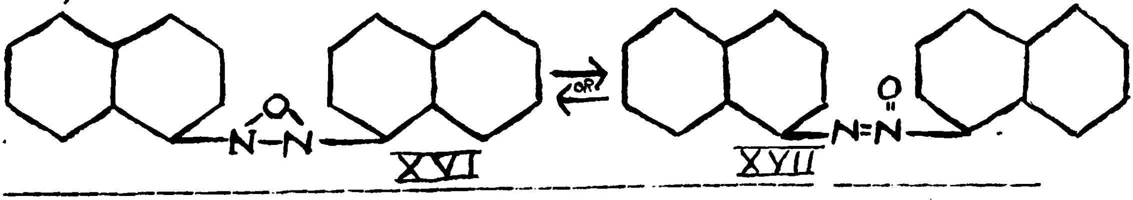
XV

Reactions of Azoxy Compounds.

Cumming and Steel (1) found that $1:1'$-azoxy naphthalene on exposure to light became transformed to a red isomeride of identical melting point. This change was alo noted by Wacker (38) and by Baudisch and Furst (39), who ascribe the change to formation of an azo-naphthol:

$C_{10}H_7.N_2O.C_{10}H_7$ $C_{10}H_7.N:N.C_{10}H_6.OH$

Cumming and Steel express the change as being due to an intramolecular change of the type XVI, XVII or vice versa.



XVI

XVII

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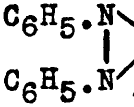
38. Wacker, Ann., 1901, 317, 375
39. Baudisch and Furst, Ber., 1912, 45, 3426

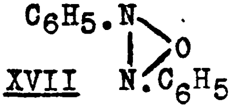
Apart from simple oxidation and reduction, the only general reaction of azoxy compounds is the transformation which they undergo (40) to the isomeric hydroxyazo compound by the action of concentrated sulphuric acid. Knipscheer (see p. 61) has shown that a similar change takes place on exposing certain azoxy compounds to light.

$$C_6H_5.N_2O.C_6H_5 \longrightarrow C_6H_5.N{:}N.C_6H_4.OH$$

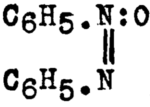
According to the Hantsch-Werner theory of geometrical isomerism it should be possible for azoxy compounds, whether they possess formulae IX or X to exist in stereoisomeric forms. It is possible



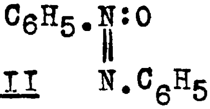
XVI



XVII



XVIII



that Reissert's isomers form an example of this type. XIX.

Accordingly there are three possible explanations of the phototropy:

I. Geometrical isomerism of the type XVI, XVII or XVIII, XIX.

II. Structural isomerism of the type XVI, XVIII

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40. Wallach and Belli, Ber., 1880, 13, 1180
Wallach and Kiepenhaeur, Ber., 1882, 14, 2617
Lachmann, J.A.C.S., 1902, 24, 1178 and many others

III. Intramolecular change from the azoxy naphthalene to the azo naphthol.

Analogy with such other azoxy compounds as have been investigated from the point of view of phototropy tended to favour the third hypothesis, and this has been experimentally verified.

Although the red form is slightly soluble in sodium hydroxide (and reprecipitated by hydrochloric acid) attempts to characterise it as an azonaphthol by means of the Schotten Baumann reaction and by methylation according to the method of Charrier and Ferrari (41) were unsuccessful, red oils being formed in both cases. Support is however given to this characterisation by comparison of the absorption spectra of each form with that of *2-hydroxy-1:2'-azonaphthalene prepared by the method of Nietzki and Goll (42). It will be seen (Fig. 2) that both the red form and the azo-naphthol show a band in common with its head at a frequency of approximately 1950 units

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41. Charrier and Ferrari, Gazzetta,1912,<u>42</u>,ii,117
42. Nietzki and Goll,Ber.,1887,<u>19</u>,1282

* No unsubstituted hydroxy 2.2'-azonaphthalene appears to have been prepared.

which is not shown by 2:2'-azoxynaphthalene and that the absorption characteristic of 2:2'-azoxynaphthalene are not shown by the red substance. The dissimilarity between the absorption spectra of the red substance and of 2:2'-azoxynaphthalene disposes of the hypothesis of geometrical isomerism, as Hartley and Dobbie (43) have shown that the absorption spectra of geometrical isomers are identical.

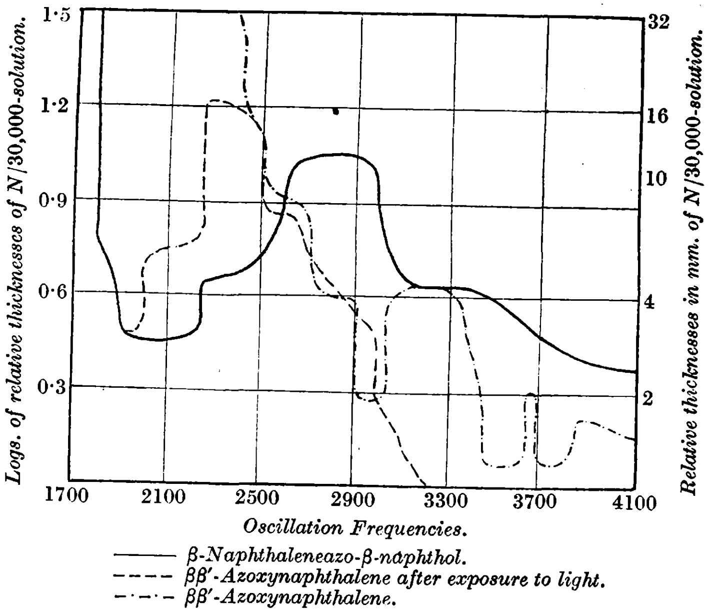

Fig II

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43. Hartley and Dobbie, J.C.S.,1900,77,509

It is of interest that Cumming and Steel (44) have since found that on continued exposure of 1:1'-azoxynaphthalene to light an azonaphthol melting at 224° is produced, almost insoluble in sodium hydroxide, and which does not yield acetyl or benzoyl derivatives. The non-reactivity of the azo-naphthols from 1:1'- and 2:2'- azoxynaphthalenes would indicate that in both cases the hydroxyl and azo groups were ortho to one another.

Other Azoxy Compounds.

An investigation by Knipscheer (45) into the phototropy of azoxy compounds has already been mentioned. The method he described consisted of soaking up a benzene solution of the azoxy compound with sheets of filter paper which were exposed to sunlight for five weeks. By this means 10.3 per cent of the azoxybenzene were transformed into o-hydroxyazobenzene and 39.7 per cent lost through vaporisation. Under similar conditions m-m'-dichloroazoxybenzene was transformed into a mixture

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44. J.K.Steel, priv. comm., 29,6,25
45. Knipscheer, Rec.trav.chim., 1903, 22, 1

of phenols of unknown constitution, and m-m'-dinitro-azoxybenzene did not react. As a result of experiments with benzene and toluene solutions, Knipscheer concluded that the transformation took place best in the solid state.

In view of the fact that the azophenol formed is only accessible with difficulty by the usual methods, the reaction appeared worthy of further investigation, especially as Knipscheer's statement that the transformation only takes place in the solid state did not agree with observations made in this laboratory (1,2), and as it seemed probable that the loss of starting material through vaporisation could be greatly reduced by carrying out the transformation in solution.

By exposing solutions in quartz vessels of azoxybenzene in various solvents to the light of the mercury vapour lamp for fifty hours, o-hydroxyazo-benzene was obtained in quantities varying from 28.0 per cent (of azoxybenzene initially present) with absolute alcohol as solvent to 7.7 per cent with benzene as solvent. The total loss of material where a reflux condenser was employed was usually about six to seven per cent. Where no reflux condenser was employed the loss was considerably greater. By increasing the time of exposure to one hundred hours the yield of hydroxyazobenzene was approximately doubled, but this rate of increase was not maintained on increasing the time of exposure to two hundred hours. Increase of temperature only slightly raised the yield of o-hydroxyazobenzene, and materially increased the loss of azoxybenzene through volatilisation. The transformation also takes place in sunlight, but cannot be effected by ordinary electric light.

Hydroxyazo compounds were also obtained from 2:2'-,3:3'-, and 4:4'- azoxytoluenes, 4:4'-dichloro--azoxybenzenes and 2:2'-diamino-4;4'-azoxytoluene under similar conditions. 4:4'-azoxyanisole, 4:4'-azoxyphenetole, and 4:4'-dinitroazoxybenzene reacted slightly or not at all. 2:2'-azoxytoluene gave products of widely different melting point if the transformation were carried out in benzene or alcohol solution respectively.

In all cases where we were able to determine the orientation of the product, the hydroxyl group appeared to enter the benzene nucleus in one of the positions ortho to the azo group.

EXPERIMENTAL.

1. The action of light on 2:2'-azoxynaphthalene.

A solution of 2:2'-azoxynaphthalene (0.1 per cent) in alcohol rapidly changed colour on exposure to sunlight or to the rays of a mercury vapour lamp from pale yellow to deep red, and on concentration deposited red crystals melting sharply at 162°(melting point of 2:2'-azoxynaphthalene 164°.) A mixture of the red crystals with yellow 2:2'-azoxynaphthalene melted at 157°-159°.

Found, N, 9.39; Calculated, for $C_{20}H_{14}N_2O$, N, 9.39 per cent.

The product was slightly soluble in sodium hydroxide solution, and was reprecipitated on acidification with hydrochloric acid. Attempts to prepare benzoyl and methoxy derivatives were unsuccessful.

Absorption Spectrum Photographs.

The photographs were taken by means of a Hilger spectrograph, using an iron arc as source of light. Solutions of the pure substance in spectroscopically pure alcohol were made up to a concentration of exactly N/30,000. The absorption spectrum of various thicknesses of this solution were then photographed. Ten ccs. of the solution were then diluted to one hundred ccs. with spectroscopically pure alcohol and treated similarly.

An aliquot portion of each solution was exposed to the light of the mercury vapour lamp and its absorption spectrum also photographed.

A sample of 2-hydroxy-1:2'-azonaphthalene was prepared (42) by coupling 2-naphthol with diazotised 2-naphthylamine. After washing with alcohol and recrystallising twice from ether it melted sharply at 178°. A photograph of the absorption spectrum of this substance was taken under identical conditions.

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42. Nietzki and Goll, Ber.,1887,19,1282

The alcohol used as solvent was purified by treating ordinary absolute alcohol with sodium and distilling until satisfactory photographs of the iron arc could be obtained through a ten cm. thickness of the alcohol.

Absorption Spectra

2:2'-Azoxynaphthalene (before exposure to light).

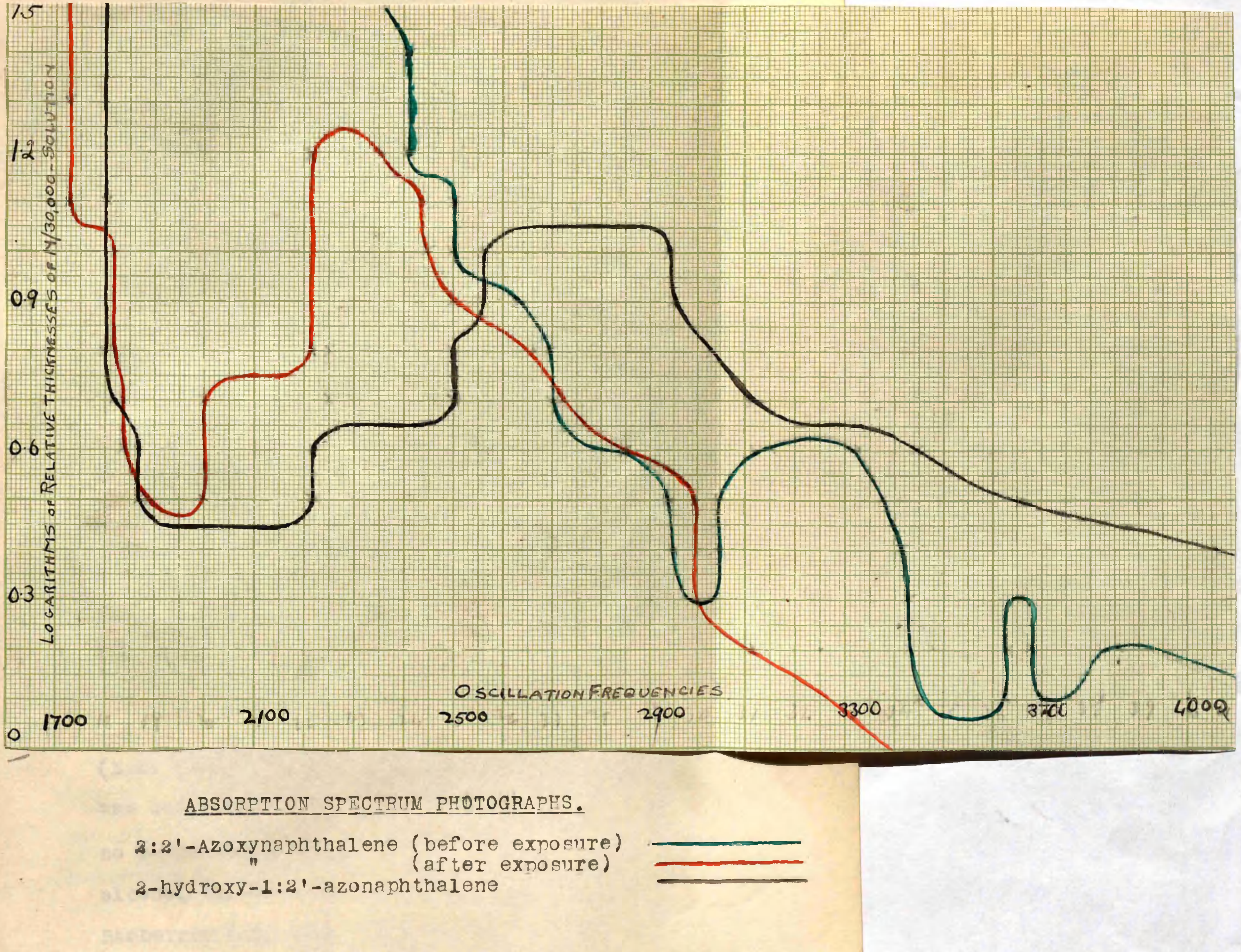
Log. length of tube	Bands	Limit of transmission frequency
1.5		2361
1.4		2410
1.3		2410
1.2		2410
1.1		2500
1.0		2500
0.9		2632
0.8		2695
0.7		2703
0.6	2849 - 3115	3333
0.5	2941 - 3040	3378
0.4	2941 - 3040	3413
0.3	2849 -3030 ; 3430 - 3650	3663
0.2	3436 -3636 ; 3676 - 3824	3861
0.1	3448 -3635 ; 3704-- 3824	4219

2:2'-Azoxynaphthalene (after exposure to light).

Log. length of tube	Bands	Limits of trans- -mission freq.
1.5		1724
1.4		1724
1.3		1724
1.2	1724 - 2222	2353
1.1	1724 - 2222	2439
1.0	1818 - 2222	2439
0.9	1818 - 2222	2500
0.8	1818 - 2222	2667
0.7	1835 - 2000	2717
0.6	1835 - 2000	2857
0.5	1887 - 2000	2994
0.4		2985
0.3		2985
0.2		3058
0.1		3125

2-hydroxy-1:2'-azonaphthalene.

Log. length of tube	Bands	Limits of trans- -mission
1.1		1802
1.0	1802 - 2564	2941
0.9	1802 - 2564	2941
0.8	1802 - 2432	3030
0.7	1818 - 2494	3115
0.6	1869 - 2222	3448
0.5	1869 - 2222	3663
0.4		4065
0.3		4090
0.2		4202
0.1		4274



ABSORPTION SPECTRUM PHOTOGRAPHS.

2:2'-Azoxynaphthalene (before exposure) —
" (after exposure) —
2-hydroxy-1:2'-azonaphthalene —

2. Action of light on azoxybenzene.

A. Effect of ultra-violet light.

Five grams of azoxybenzene dissolved in 85 per cent alcohol (500 ccs) contained in a quartz flask and placed under a reflux condenser to reduce loss from volatilisation was exposed for fifty hours to the light of a mercury vapour lamp. After exposure the solution, which had assumed a deep red colour, was concentrated and the red, crystalline residue dissolved in ether and extracted with eight per cent sodium hydroxide solution until the ethereal layer was almost colourless (two litres). The red alkaline solution after acidification with hydrochloric acid (the point of neutralisation was sharply indicated by a change in the colour of the solution from red to yellow), allowed to stand overnight and filtered. A yellow powder (1.05 grams) was obtained which melted at 76°-78° and was completely volatile in steam (hence containing no p-hydroxyazobenzene) and after crystallisation from alcohol formed beautiful red needles melting at 82°-83°. Bamberger (46) states that o-hydroxyazobenzene melts

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46Bamberger, Ber.,1900,33,1939

at 82.5°-83°.

The compound was further characterised by the formation of the copper salt described by Bamberger, who does not, however, give details of the method by which it may be prepared. We found that this can best be done by mixing equivalent amounts of an alcoholic solution of cupric chloride with a sodium ethoxide solution of the dyestuff. The salt melted at 223°. Bamberger states the melting point to be 225°-226°.

A control experiment was carried out by allowing a similar solution of azoxybenzene to stand in the dark for fourteen days. It was worked up similarly, and pure azoxybenzene recovered quantitatively.

A sample of o-hydroxyazobenzene in alcoholic solution was exposed to the lamp for 125 hours, and the product fractionally crystallised from alcohol. No change was apparent.

The yields obtained by altering the conditions of illumination are given below:-

Solvent.	Time.	Conditions.	Yields (per cent)		
			azo-phenol	azoxy-benzene	loss.
1.85% EtOH	50 hrs.	Room temperature	20.5	73.0	6.5
2. " "	100 "	" "	44.0	40.0	14.0
3. " "	200 "	" "	63.3	-	-
4.Abs. EtOH	50 "	" "	28.0	59.7	12.3
5.85% EtOH	50 "	B.P.of alcohol	22.3	48.0	29.7
6. " "	50 "	0.5% solution, R.T	26.0	67.0	7;0
7. " "	50 "	" " "	24.6	64.2	11.2
8. MeOH	50 "	Room temperature	24.0	54.0	22.0
9. PrOH	50 "	" "	26.3	-	-
10. C_6H_6	50 "	" "	7.7	-	-

Experiments 1,3,5,8, were carried out with five grams of azoxybenzene dissolved in 500 ccs. of solvent, experiments 6 and 7 with five grams of azoxybenzene dissolved in one litre of solvent and the solution distributed between two 500 ccs. quartz flasks, the remainder with three grams dissolved in 300 ccs. of solvent.

"Room temperature" implies the temperature to which the flask was heated by the radiations from the lamp.

B. Effect of sunlight.

On 24th. June, 1924, a solution of eighteen grams of azoxybenzene in 1300 ccs. of 85 per cent alcohol was divided between (1) a quartz flask (500 ccs.), (2) a glass flask of approximately the same dimensions as (1) but with thinner walls, and (3) a thick glass reagent bottle, in the proportions indicated. The flasks were corked, and the joints luted with sealing wax. They were then clamped to a retort stand in such a way as to ensure equal illumination, and exposed on the roof of the College until 24th. Sept-ember, 1924, when they were taken in and the contents worked up in a similar manner to the other experiments. The yields in the three experiments were as follows:

Solution in quartz flask:	Azophenol	1.56 gms.	31.2 %
	Azoxybenzene	3.06	61.2
	Loss	0.38	7.6
Solution in glass flask:	Azophenol	1.86	37.2
	Azoxybenzene	2.75	55.0
	Loss	0.39	7.8
Solution in glass bottle:	Azophenol	1.00	33.3
	Azoxybenzene	1.74	58.0
	Loss	0.26	8.7

In view of the nature of these results, the experiment was tried of exposing two solutions of azoxybenzene, each containing five grams azoxybenzene dissolved in 500 ccs. of 85 per cent alcohol, but one contained in the quartz flask, the other in the glass flask above mentioned, simultaneously to the rays of the mercury vapour lamp. After exposure of the two solutions for approximately fifty hours, (the exact time of exposure cannot be given owing to an accidental failure of the light at a time when it was unattended; both solutions were exposed side by side, and therefore for the same time), the yields obtained were as follows:-

Solution in quartz flask:	Azophenol	0.87	gms.	17.4%
	Azoxybenzene	3.85	"	77.0
	Loss	0.28		5.6
Solution in glass flask:	Azophenol	0.41		8.2
	Azoxybenzene	4.19		83.6
	Loss	0.40		8.0

One inference from these experiments would therefore seem to be that very little ultra-violet light appears to penetrate the Glasgow atmosphere.

C. Effect of electric light.

A metal filament lamp was immersed in a solution of seventy-five grams of azoxybenzene in 750 ccs. of alcohol and illuminated for fifty hours. The solution by this time had only slightly changed colour, and on working up yielded pure azoxybenzene quantitatively.

3. Action of light on 2:2'-azoxytoluene.

Three grams of 2:2'-azoxytoluene dissolved in 300 ccs. of 85 per cent alcohol and illuminated for fifty hours by means of the mercury vapour lamp were worked up as described in the azoxybenzene experiments. Although the solution had changed colour from yellow to red, nothing was extracted by sodium hydroxide. The ethereal solution was concentrated, and the red, crystal--line product added to a solution containing five grams of 2:2'-azoxytoluene in 500 ccs. of alcohol, which had also been previously illuminated for fifty hours. The whole was then fractionally crystallised from alcohol. The less soluble fractions were identified as 2:2'-azoxytoluene. The more soluble fractions after purification and distillation under reduced pressure (boiling point 164° @ 3 mm.) melted at 47.5°-48.5° and formed orange red needles giving a deep red solution in alcohol.

Found, N, 12.39; $C_{14}H_{14}N_2O$ requires N, 12.39 per cent.

Sixteen grams of 2:2'-azoxytoluene were dissolved in 650 ccs. of benzene and illuminated for fifty hours. The solution, which had turned deep-red was concentrated, and extracted with eight per cent sodium hydroxide solution to which it yielded nothing. After removing the benzene, and shaling the solid with sodium hydroxide solution for three days (with negative results) the product was fractionally crystallised from alcohol. Together with unaltered starting material, a very small quantity of red needles, closely resembling in appearance the other hydroxyazo compounds was obtained. This substance melted at 92°-93°, but was not obtained in sufficient quantity for analysis.

4. Action of light on 3:3'-azoxytoluene.

The 3:3'-azoxytoluene was prepared by the method of Buchka and Schachtebeck (47). This method consists of boiling m-nitrotoluene with methyl alcoholic sodium hydroxide, removal of alcohol by distillation, and of unchanged nitrotoluene by steam distillation. The azoxytoluene is extracted from the residual oil with ether. We found this method of purification unsatisfactory in practice, owing to the difficulty of separating the azoxytoluene from traces of nitrotoluene which were sufficient to prevent crystallisation. The following modification over--comes this difficulty and was found much more reliable:- After removal of as much as possible of the ether by distillation, the product was dissolved in absolute alcohol, and the last traces of ether removed by heating on the water-bath. On dilution with a few drops of water, and cooling in a freezing mixture, crystals of 3:3'-azoxytoluene separated out. Further purification by crystallisation from 85 per cent alcohol presented no difficulty.

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47. Buchka and Schachtebeck, Ber., 1889, <u>22</u>, 834

Two flasks containing respectively five grams and 1.55 grams of 3:3'-azoxytoluene dissolved in 500 ccs. of 85 per cent alcohol were illuminated for fifty-two hours. After working up in a similar manner to illuminated azoxybenzene, 0.38 grams and 0.17 grams were obtained respectively. After recrystallisation from alcohol red needles melting at 61.5°-62.5° were obtained.

Found, N, 12.58; $C_{14}H_{14}N_2O$ requires N, 12.39 per cent

3:3'-dimethyl-4-hydroxyazobenzene melts at 115° (48).

3:3'-dimethyl-6-hydroxyazobenzene melts at 95° (49).

Therefore this substance is probably 3:3'-dimethyl-2-hydroxyazobenzene.

5. The action of light on 4:4'-azoxytoluene.

4:4'-azoxytoluene (4.72 grams), prepared

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48. Jacobsen and others, Ann., 1895, 287, 185
49. Jacobsen and Piepenbrink, Ber., 1894, 27, 2703

by the reduction of p-nitrotoluene by means of zinc dust and ammonium chloride was dissolved in 85 per cent alcohol (500 ccs) and illuminated for fifty-four hours. The alcohol was removed by distillation, the residue dissolved in ether, and extracted with six litres of sodium hydroxide solution. On acidification 0.47 grams (equivalent to a yield of 10 per cent) of 3-hydroxy-4:4'-azotoluene was obtained as a yellow powder. After crystallisation from alcohol it formed red needles melting at 150 -151° and otherwise answering to the description given by Macpherson and Boord (50) who prepared this compound by another method.

6. Action of light on 4:4-azoxyanisole.

4:4'-Azoxyanisole (4.34 grams) dissolved in alcohol (500 ccs.) was illuminated for fifty hours, the solution being kept boiling to retain the sparingly soluble azoxy compound in solution. On cooling

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50. Macpherson and Boord, J.A.C.S.,1911,33,1531

3.21 grams of pure azoxyanisole (melting point after recrystallisation 116.7°, clearing point 134°) separated out. The united mother liquors were evaporated down and the residues dissolved in ether and extracted with one litre of sixteen per cent sodium hydroxide solution. An orange alkaline extract was obtained which turned red on acidification (a reversal of the usual order of colour changes) depositing a minute crop of red crystals. These melted after recrystallisation at 121°, but were obtained in too small quantity for further examination. On evaporation of the ethereal solution a further quantity (0.5 grams)of 4:4'-azoxy-anisole was obtained.

In a previous experiment a curious effect was observed, whereby a solution, which had been illuminated for seventeen hours was observed to to have assumed a a deep coloration. The flask and contents appeared perfectly black, but on holding to the light, a little green light was transmitted.. On illumination for a further period of eleven hours this colour was found to have faded to a pale orange.

7. The action of light on 4:4'-azoxyphenetole.

Five grams of 4:4'-azoxyphenetole were dissolved in 500 ccs. of alcohol and illuminated for fifty hours. On account of the sparing solubility of azoxyphenetole in cold solvents this operation was carried out at the boil. On fractionally crystallising the product from alcohol 4.88 grams of 4:4'-azoxyphenetole (melting at 137°-138°, clearing point 164°) was obtained, together with a small quantity of a black substance which was obviously impure, and probably contained still some 4:4-azoxy anisole.

8. The action of light on 4:4'-dichloroazoxybenzene

The starting material was prepared by the action of alcoholic alkali on p-chloronitrobenzene (51) The reaction product is black and tarry, but if purified by Laubenheimer's method (boiling with acetic acid

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51. Heumann, Ber., 1872, 5, 911
Laubenheimer, Ber., 1875, 8, 1686

containing a trace of nitric acid) it becomes yellow and crystalline. The yield is excellent.

4:4-Dichloroazoxybenzene (five grams) dissolved in 500 ccs. of boiling 85 per cent alcohol was exposed to the lamp for fifty hours, the solution being kept boiling to retain the sparingly soluble azoxy compound in solution. After illumination, the solution was allowed to cool and a quantity of unchanged dichloroazoxybenzene removed by filtration. The mother liquor was concentrated and the mixed batches of crystals dissolved in ether and extracted with four litres of eight per cent sodium hydroxide solution, in small portions. A marked colour change from yellow to red took place on mixing the ethereal solution with the first batch of sodium hydroxide. On acidification a flocculent precipitate was obtained, which on crystallisation gave beautiful red needles melting at 171°-172°. Yield 11.4 per cent.

Found, N, 9.79; $C_{12}H_8ON_2Cl_2$ requires N, 9.53 per cent.

9. Action of light on 4:4'-dinitroazoxybenzene.

A. Preparation of 4:4'-dinitroazobenzene.

Twenty grams of azobenzene was added in small portions to eighty ccs. of fuming nitric acid, in a vessel surrounded by a freezing mixture. After thirty minutes the mixture was poured into cold water, thoroughly shaken, and allowed to stand overnight. The crystalline product was filtered off, washed, and extracted with ether. After recrystallisation several times from acetic acid, and finally from acetone, red needles of 4:4'-dinitroazobenzene, (52), melting at 220°, were obtained.

Found, N, 20.80, 20.72; $C_{12}H_8O_4N_4$ requires N, 20.59 %

The product obtained from the acetic acid mother liquors and the ether extract was found on fractional crystallisation to contain a little of the p-dinitroazobenzene mixed with yellow needles of a mononitroazobenzene, melting at 141°-142° (53)

Found, N, 18.30, 18.44; $C_{12}H_9O_2N_3$ requires N, 18.50 %

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52. Werner and Stiasny, Ber., 1899, 32, 3272 cf. also "Berichtigungen, loc. cit., 4085
53. Laurent and Gerhardt, Ann, 75, 73

The influence of time of nitration on the yield of 4:4'-dinitroazobenzene is as follows:-

Reagents in contact.	Yield of 4:4'dinitroazobenzene.
75 mins.	2.5 grams
17 hours	4.35 "
65 "	3.62 "

B. Oxidation to 4:4'dinitroazoxybenzene.

4:4'-Dinitroazobenzene (5.6 grams) were dissolved in 1000 ccs. glacial acetic acid containing eighty ccs. perhydrol by heating, and heating over water bath continued for two days, further quantities of perhydrol being added from time to time. The golden yellow solution was then concentrated and crystallisation induced by addition of a few drops of water. The product melted at 189.5° after recrystallisation from acetic acid. Yield quantitative.

C. Action of light on 4:4'dinitroazoxybenzene

Five grams of 4:4'-dinitroazoxybenzene, dissolved in 500 ccs. of boiling 85 per cent alcohol were exposed to the mercury vapour lamp for fifty hours. Considerable difficulty was experienced in the working up of the product owing to the insolubility of 4:4'-dinitroazoxybenzene in all cold solvents. Fractional crystallisation from alcohol or from acetic acid gave purely negative results. The procedure finally adopted was to allow the reaction mixture to cool, filter off the precipitated 4:4'-dinitroazoxybenzene and concentrate the alcoholic solution. The crystals obtained from the concentrated mother liquors were dissolved in a large volume of ether and extracted with sixteen per cent sodium hydroxide solution. Only a minute quantity of reddish precipitate was obtained on acidification.

10. The action of light on 2:2'-diamino-4:4'-azoxytoluene.

Three solutions of 2:2'-diamino-4:4'-azoxy--toluene were illuminated, a solution of the base in alcohol, a solution of the hydrochloride in water, and a solution of the hydrochloride in water containing a excess of hydrochloric acid. In each case the product of illumination was much contaminated by tarry matter. After removal of this by boiling the product in alcoholic solution with animal charcoal, small quantities of red needles melting at 210°. were obtained by fractional crystallisation from alcohol. Graeff (54) obtained by the action of sulphuric acid on 2:2'-diamino-4:4'-azoxytoluene a hydroxyazotoluene melting at 212°.

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54. Graeff, Ann., <u>229</u>,346

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CONTRACTIONS.

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Proc.C.S.	Proceedings of the Chemical Society
Ber.	Berichte der Deutschen chemischen Gesellschaft
Ann.	Justus Liebig's Annalen der Chemie
Am.Ch.J.	American Chemical Journal
J.A.C.S.	Journal of the American Chemical Society
C.R.	Comptes rendus des Seances de l'academie des Sciences
Bull.	Bulletin de la Societe chimique de France
D.R.P.	Deutsches Reichs-Patent
Gazz.	Gazzetta chimica italiana
Rec.trav.chim.	Recueil des travaux chimiques des pays-Bas
Monats.	Monatshefte fur chemie und verwandte Teile anderer Wissenschaften
Atti.	Atti della Reale Accademis Nazionale dei Lincei