An
Investigation of the Constitution
and
Properties of the Naphthidine Bases.

A THESIS

Presented by GEORGE HOWIE

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Preface.

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I N D E X.

Preparation of 1:1'-Azoxy-, 1:1'-Azo- and 1:1'-Hydrazo-naphthalenes.

Reduction Products of 1:1'-Azoxy- and 1:1'-Azonaphthalenes and the "Benzidine" Conversion of the Hydrazonaphthalenes.

Preparation of 2:2'-Diamino-1:1'-Dinaphthyl by Reduction of 2:2'-Azonaphthalene.

Constitution and Syntheses of the Naphthidine Bases.

Synthesis of Dinaphthyline(1:1'-Diamino-2:2'-Dinaphthyl)

Synthesis of 3:3'-Diamino-2:2'-Dinaphthyl

Synthesis of 4:4'-Diamino-2:2'-Dinaphthyl

Synthesis of 1:2'-Imine-2:1'-Dinaphthyl

EXPERIMENTAL.

The Preparation of 1:1'-Azoxy-, 1:1'-Azo- and 1:1'-Hydrazo-naphthalenes.

1:1'-Azoxynaphthalene.

1:1'-Azonaphthalene.

The Reduction to the Hydrazo-stage of Symmetrical and Unsymmetrical 1:1'-Azoxynaphthalenes and of 1:1'-Azonaphthalene in Neutral, Alkaline and Acid Solutions.

In Neutral Solution

In Alkaline Solution

In Acid Solution

Preparation of 2:2'-Diamino-1:1'-Dinaphthyl by Reduction of 2:2'-Azonaphthalene.

Preparation of 2:2'-azonaphthalene

Constitution and Syntheses of the Naphthidine Bases.

Naphthidine(4:4'-diamino-1:1'-dinaphthyl)

3:3'-Diamino-1:1'-Dinaphthyl.

2:2'-Diamino-1:1'-Dinaphthyl.

Dinaphthyline(1:1'-diamino-2:2'-dinaphthyl)

3:3'-Diamino-2:2'-Dinaphthyl.

4:4'-Diamino-2:2'-Dinaphthyl.

1-Amino-2:2'-Dinaphthyl.

Properties and Derivatives of the Naphthidine Bases and Imines.

Naphthidine(4:4'-diamino-1:1'-dinaphthyl)

3:3'-Diamino-1:1'-Dinaphthyl.

2:2'-Diamino-1:1'-Dinaphthyl.

Dinaphthyline(1:1'-diamino-2:2'-dinaphthyl)

1-Amino-2:2'-Dinaphthyl.

Dinaphthyleneimine(Dinaphthylcarbazole; 1:1'-imine-2:2'-dinaphthyl.

2:2'-Imine-1:1'-Dinaphthyl.

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The Reaction Between Benzyl Alcohol, Benzaldehyde and Quinoline on Azoxy- and Azobenzenes and Azoxy- and Azotoluenes.

Experimental.

The Reducing Action of Benzoin.

* *

INTRODUCTION.

Benzidine has proved a valuable dyestuffs intermediate due to the fact that it yields a wide range of direct cotton dyes. On the other hand, the naphthidines, the corresponding bases of the naphthalene series, have been little studied undoubtedly due to the difficulty of preparing them by standard means.

In the case of the diaminodiphenyls the constitutions of the known bases have been definitely established but a great deal of confusion exists both in the nomenclature and constitution of the diaminodinaphthyls isolated to date. Several investigators have concerned themselves with the preparation of diaminodinaphthyls both by direct reduction of the nitronaphthalenes and by synthetic means but their combined results still leave the problem far from complete. Moreover, some of their statements are in direct contradiction to those of others.

A typical example of much of the work done on the naphthidine bases is contained in the recent paper(J.C.S., 1931,1271) by Clemo, Cockburn and Spence who describe the preparation of naphthidine by reduction of 4:4'-dinitro-1:1'-dinaphthyl, assigning to the base a melting point of 191° "alone or mixed with an authentic naphthidine". They claim to have proved naphthidine to be the corresponding diamino-derivative, but they give no details as to how they prepared the "authentic" specimen. They cite the paper of Corbellini and Debenedetti(Gazzetta, 1929,59,391), also that of Nietski and Goll(Ber.,1885,18,3254) but make no reference to the paper by Cumming and Steel(J.C.S.,1923,123,2468). All these authors ascribe a melting point of 198° for the base. It may be mentioned that 2:2'-diamino-1:1'-dinaphthyl melts at 191° (Meisenheimer and Witte, Ber.,1903,36,4159; Cumming and Ferrier, J.C.S.,1924,125,1111).

While many others might be quoted, the above example will suffice to indicate the present state of knowledge and confusion that exists regarding the chemistry of the naphthidine bases and of the necessity of completely elucidating the problem.

The object of this research was primarily to determine the true constitution of the known diaminodinaphthyls, the preparation of further diaminodinaphthyls and an investigation of their properties, derivatives and dyestuffs formed by them.

For the preparation of the bases, the products of reduction of 1:1'-azoxy- and 1:1'-azonaphthalenes and the conversion products of the 1:1'-hydrazonaphthalenes were first examined; the reduction products of 2:2'-azoxy- and 2:2'-azonaphthalenes and the conversion of 2:2'-hydrazonaphthalene have been fully worked out by various investigators, their results being detailed later. Thereafter, synthetic means for the preparation and the establishing of the constitution of the bases were considered.

As a preliminary to the main research, methods for the preparation of 1:1'-azoxy-, 1:1'-azo- and 1:1'-hydrazonaphthalenes were investigated. New methods and a review of the methods as detailed in the literature for the preparation of 2:2'-azoxy-, 2:2'-azo- and 2:2'-hydrazonaphthalenes have already been described by Ferrier(Thesis for Ph.D., Glasgow University, January 1926).

PREPARATION of 1:1'-AZOXY-, 1:1'-AZO- and 1:1'-HYDRAZONAPHTHALENES.

1:1'-AZOXYNAPHTHALENE.

Wacker(Ann.,1902,321,63) obtained azoxynaphthalene by reducing an alcoholic solution of 1-nitronaphthalene by means of a water solution of dextrose or an alcoholic solution of phenylhydrazine both in presence of sodium hydroxide solution. After filtration, the azoxynaphthalene was precipitated by addition of water to the filtrate. This, however, caused tarring and since the product was barely capable of recrystallisation it was far from pure.

Cumming and Steel(J.C.S.,1923,123,2464), in a study of the reduction of 1-nitronaphthalene, have shown that alkaline reduction, so successful in the reduction of nitrobenzene when azoxy-, azo- or hydrazobenzene can be obtained, is not applicable to 1-nitronaphthalene since the action of the usual reducing agents(sodium amalgam or zinc dust and sodium hydroxide with or without alcohol) yielded only 1-naphthylamine and tar where any reduction took place at all. Reduction to the azoxy-, azo- and hydrazo-stages was finally effected by the method of neutral reduction. An aqueous alcoholic solution of 1-nitronaphthalene, saturated with ammonium chloride, was reduced in the heat by means of zinc dust. The reduction mixture was filtered hot and the filtrate cooled when a crystalline precipitate was thrown down, which on extraction with alcohol, yielded 1:1'-azoxynaphthalene. A further yield was obtained by concentrating, under reduced pressure, the mother liquor obtained after removal of the crystalline deposit. The method, moreover, gives a clean product no tar being produced.

The latter method being the more satisfactory was adopted for the preparation of 1:1'-azoxynaphthalene, the conditions for maximum yield being investigated.

The reduction essentially results from the interaction between zinc dust and water for the production of the necessary hydrogen. A much larger quantity of zinc dust than that required by theory is necessary and it was thought that atmospheric oxidation might be partially oxidising the azoxynaphthalene back to nitronaphthalene. To exclude all air, two reductions were carried out one in presence of carbon dioxide and the other in presence of sulphur dioxide. In the first case only a very little azoxynaphthalene was obtained, practically the whole having been reduced to 1-naphthylamine while in the latter case 1-naphthylamine was the only product. It appears, therefore, that a strictly neutral solution is necessary since the presence of even a weak acid like carbonic acid causes the production of chiefly naphthylamine and, as has been shown by Cumming and Steel, alkaline reduction yields only naphthylamine and tar.

Cumming and Eaton(J.R.T.C.,1930,<u>2</u>,191) have shown that the pH value taken at intervals during the reduction of nitro-compounds to azoxy-compounds by the method of Cumming and Steel is 6.5-7.0 that of distilled water. Despite the fact that ammonia(see later) is evolved the reduction is a neutral reduction.

The effect of replacing ammonium chloride by a number of other salts and the conditions of formation of the double zinc salts formed in the reduction were examined(Cumming and Howie, J.R.T.C.,1929,2,43).

Among these were magnesium and calcium chlorides. The use of magnesium chloride was suggested by the work of Zechmeister(Ber.,1926,59,867) who obtained azoxy-compounds by reducing nitro-compounds in presence of ammonium chloride using magnesium in place of zinc.

Calcium chloride was employed by Scheiber(Ber.,1904,37, 3057) in the production of 1-naphthylhydroxylamine, the reduction being carried out by means of zinc dust on a solution of 1-nitronaphthalene in a mixture of alcohol, ether and water containing calcium chloride.

During the reduction of 1-nitronaphthalene to the azoxy-stage, Cumming and Steel obtained an inorganic by-product of the composition $5Zn(OH)_2.2NH_4Cl$, the salt consisting of white needles insoluble in alcohol or water.

With all the salts tried no azoxynaphthalene nor double zinc compound was formed but only 1-naphthylamine or a mixture of naphthylamine and unchanged nitronaphthalene. It would appear, therefore, that the formation of such a double zinc compound is essential for the production of 1:1'-azoxynaphthalene and if the formation of this double zinc compound could be promoted the yield of azoxynaphthalene might be materially increased. For this purpose the effect of the addition of zinc chloride, which by hydrolysis would yield zinc hydroxide, as well as ammonium chloride was tried but again no azoxynaphthalene or double zinc compound were formed.

The yields at varying temperatures and in presence of a different solvent were noted.

The maximum yield of azoxynaphthalene obtained was 32% of theory.

The conditions for the preparation of large quantities of the azoxy-compound are described(p. 70).

Interaction between Zinc and Ammonium Chloride.

After the addition of each batch of zinc dust in the reduction of 1-nitronaphthalene to 1:1'-azoxynaphthalene a strong smell of ammonia was observed due probably to some reaction between zinc and ammonium chloride as simply expressed by the equation:-

$$2NH_4Cl + Zn = ZnCl_2 + 2NH_3 + H_2$$

This would explain the formation of ammonia and further the zinc chloride also formed could by hydrolysis yield zinc hydroxide and so give rise to the double zinc salt.

The above reaction was proved qualitatively by heating together in the dry state a mixture of zinc and ammonium chloride. When zinc and an aqueous solution of ammonium chloride were refluxed together for varying times the above reaction did not occur quantitatively nor was any double zinc salt formed. Identical results were obtained when the conditions were similar to those in the reduction process. It appears, therefore, that the presence of a nitro-compound or a reduction product of a nitro-compound is essential for the production of the double zinc salt. Conversely, the formation of the azoxy-compound takes place only in the presence of the double zinc salt.

Cumming and Ferrier(J.R.T.C.,1929,2,40) are of the opinion that the crystals of the double zinc salt are derived from an intermediate organo-zinc compound which is soluble in hot alcohol but decomposed by it.

In the case of m-nitrobenzaldehyde the azoxy-compound in combination with a zinc complex was isolated by Cumming and Eaton(loc.cit.), the formula assigned to the compound being $ZnCl_2.3NH_4Cl.2(C_{14}H_{10}O_3N_2)$. The azoxy-compound could only be isolated from this compound by treatment with acids, alkalis and certain salts.

It has been later shown that, in the neutral reduction of 1:1'-azoxynaphthalene to the hydrazo-stage, a double zinc salt corresponding to the formula $9Zn(OH)_2.4NH_4Cl.6H_2O$ is formed.

All these double zinc salts are crystalline substances insoluble in alcohol or water. They are soluble in acids, alkalis and ammonium chloride solution. From the latter they may be recrystallised unchanged. They are soluble in zinc chloride solution. On heating, water is evolved at 100° while at 130° ammonia is evolved; at higher temperatures ammonium chloride is volatalised, zinc oxide being left.

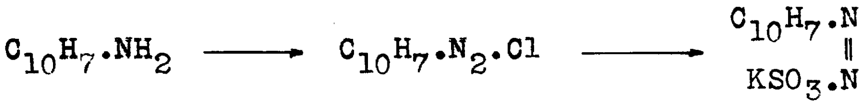
It is worthy of note that the double zinc salt, when suspended in boiling water or aqueous alcohol is not decomposed by addition of zinc dust nor will it combine with the azoxy-compound in alcoholic solution when refluxed for some hours.

1:1'-AZONAPHTHALENE.

Nietzki and Goll(Ber.,1885,18,197; 3252) prepared 1:1'-azonaphthalene by dissolving and diazotising 4-amino-1:1'-azonaphthalene in alcoholic solution and boiling the resulting diazonium solution. The azonaphthalene consisted of alizarin red needles showing a blue dichroism. Azonaphthalene obtained by us by this method consisted of orange red needles while larger crystals appeared a deeper red when viewed by direct light under a powerful lens. A bluish colour is seen in some cases when viewed under reflected light.

Cumming and Steel(loc.cit.) in the neutral reduction of 1-nitronaphthalene isolated 1:1'-azonaphthalene by continuing the reduction correspondingly farther after the azoxy-stage had been reached. The azonaphthalene so obtained consisted of red crystals; the yield was poor(private communication).

Hantzsch and Schmiedel(Ber.,1897,30,82) by diazotisation of 1-naphthylamine and treatment of the diazonium solution with potassium sulphite obtained 1-naphthalene-syndiazonium sulphonate.



$$C_{10}H_7.NH_2 \longrightarrow C_{10}H_7.N_2.Cl \longrightarrow \begin{array}{c} C_{10}H_7.N \\ \| \\ KSO_3.N \end{array}$$

which on keeping moist decomposed with formation of 1:1'-azonaphthalene.

$$2C_{10}H_7.N_2.SO_3K + H_2O = C_{10}H_7.N:N.C_{10}H_7 + KHSO_3 + KHSO_4 + N_2$$

The product is described as alizarin red greenish shimmering needles.

The method of neutral reduction was applied to 1:1'-azoxy-:naphthalene for the preparation of 1:1'-azonaphthalene. Contrary to expectations no trace of azonaphthalene was found, the reduction yielding only hydrazonaphthalene and unchanged azoxynaphthalene. The suggestion is, therefore, advanced that the azo-compound is not formed by the direct reduction of the azoxy-compound and is not an intermediate stage in the reduction to the hydrazo-compound, which is in accordance with the well known Haber scheme. Azo-compounds are formed by direct reduction of the nitro-compound or by condensation of the nitro-compound and hydrazo-compound.

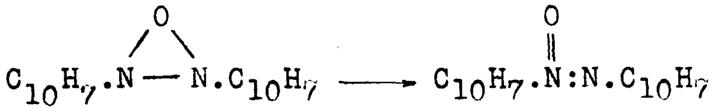
$$R.NO_2 + 2R.NH.HN.R = 2R.N:N.R + R.NHOH$$

In the alkaline reduction to the azoxy-stage of nitro-compounds- chiefly benzene solutions of halogen derivatives- Suter and Dains(J.Amer.C.S.,1928,<u>50</u>,2733) substituted higher alcoholates, both aliphatic and aromatic, for the usual methyl and ethyl alcoholates and found in many cases a greatly improved yield especially when benzyl alcohol was employed. Some of the results obtained are noted below:-

Na moles	Alcohol	C_6H_6 c.cs.	Nitro-comp. moles	Amine%	Azoxy%	Other pro-:ducts.
0.3	CH_3	450	0.15p.$C_6H_4CH_3NO_2$	1.3	..	Conds.prods
0.1	CH_3	150	0.05p.$C_6H_4ClNO_2$	3.5	4.6	H.COOH
0.1	C_2H_5	C_6H_6	p.$C_6H_4CH_3NO_2$	..	..	Less resins than with CH_3
⋮	⋮	⋮	⋮	⋮	⋮	⋮
0.1	$C_6H_5CH_2$	100	0.5 $C_6H_5NO_2$	..	Pres.	C_6H_5.COOH
⋮	⋮	⋮	⋮	⋮	⋮	⋮
0.1	$C_6H_5CH_2$	150	0.05 $2C_{10}H_7NO_2$	..	Tar	C_6H_5.COOH & C_6H_5.CHO
0.1	$C_6H_5CH_2$	150	0.05p.$C_6H_4ClNO_2$	..	100	C_6H_5.COOH
0.1	$C_6H_5CH_2$	250	0.05p.$C_6H_4ClNO_2$	..	100	C_6H_5.COOH, 73% C_6H_5.CH
0.1	$C_6H_5CH_2$	300	0.05p.$C_6H_4ClNO_2$	..	95	C_6H_5COOH
⋮	⋮	⋮	⋮	⋮	⋮	⋮
0.1	Furfural	300	0.05p.$C_6H_4ClNO_2$	..	91	...

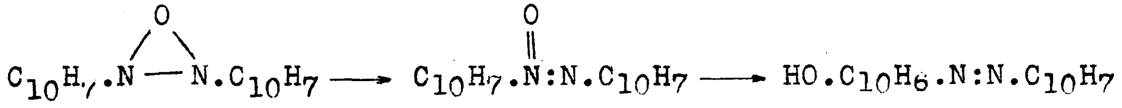
A consideration of the above results leads us to advance the view that the alcohol itself is partially responsible for the reduction, e.g. benzyl alcohol being oxidised to benzaldehyde or benzoic acid and at the same time aiding the reduction of the nitro-compound.

The result of heating together for several hours azoxynaphthalene with benzyl alcohol and benzaldehyde respectively was, therefore, examined. Under all conditions tried, the effect was to convert completely the yellow symmetrical variety, which was employed in these reactions, into the red unsymmetrical variety first isolated by Cumming and Steel(loc. cit.).



$$C_{10}H_7.\overset{O}{\overbrace{N\text{—}N}}.C_{10}H_7 \longrightarrow C_{10}H_7.\overset{\overset{O}{\|}}{N}{:}N.C_{10}H_7$$

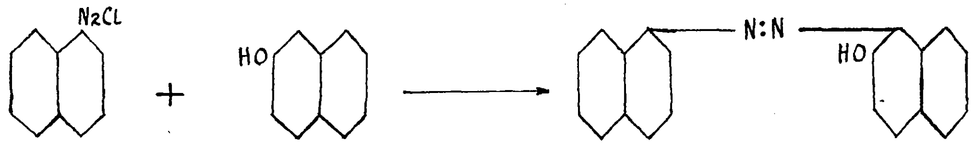
The addition of a base, quinoline, which would inhibit the formation of perbenzoic acid and so prevent any possible reoxidation to azoxynaphthalene of any azonaphthalene that might have been formed, resulted in the formation of 2-hydroxy-1:1'-azonaphthalene, m.p. 230°, as well as unsymmetrical 1:1'-azoxynaphthalene.



$$C_{10}H_7.\overset{O}{\overbrace{N\text{—}N}}.C_{10}H_7 \longrightarrow C_{10}H_7.\overset{\overset{O}{\|}}{N}{:}N.C_{10}H_7 \longrightarrow HO.C_{10}H_6.N{:}N.C_{10}H_7$$

These results should be compared with those obtained from other azoxy-compounds(p. 158).

The constitution of the hydroxyazonaphthalene was established by comparing it with a sample as prepared by the method of Meldola and Hanes(J.C.S.,1894,65,837) who obtained 2-hydroxy-1:1'-azonaphthalene by coupling 1-naphthalene diazonium chloride to 2-naphthol.



They proved identical in all respects.

Cumming and Steel(private communication and mentioned by

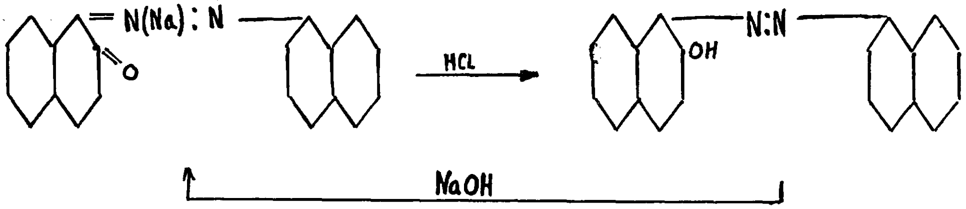
Cumming and Ferrier, J.C.S.,1925,127,2374) record the formation of an hydroxyazo-compound, m.p. 224°, by exposure of 1:1'-azoxynaphthalene to light. A recrystallisation from benzene of their specimen gave m.p. 230°. A mixed m.p. of the latter with that obtained above gave no depression. As was expected, the action of light on unsymmetrical 1:1'-azoxy:naphthalene was to convert it into 2-hydroxy-1:1'-azonaph:thalene. Continued exposure to light of 2-hydroxy-1:1'-azo:naphthalene caused no further change. The hydroxyazonaph:thalene obtained by the action of light on 1:1'-azoxynaph:thalene is, therefore, 2-hydroxy-1:1'-azonaphthalene and not 4-hydroxy-1:1'-azonaphthalene as suggested by Baudisch and Fürst(Ber.,1912,45,3426).

The above surprising results are important when it is considered that the only previous known method of preparing unsymmetrical azoxy-compounds in a pure state is by exposing the symmetrical variety to light, continued exposure yielding the o-hydroxyazo-compound(Cumming and Ferrier, loc.cit.).

The above experiments repeated in the dark gave the same results and hence the conversion to the unsymmetrical azoxy:naphthalene and to the hydroxyazo-compound cannot be due to light. The formation of the latter compound seems, therefore, to be brought about by the presence of the base although it was found that on heating 1:1'-azoxynaphthalene with quinoline alone, while both unsymmetrical 1:1'-azoxynaphthalene and 2-hydroxy-1:1'-azonaphthalene were formed, the yield of the hydroxyazo-compound was much poorer than when benzaldehyde was present.

In contrast to this is the well known conversion of azoxy-compounds to the corresponding p-hydroxyazo-compound by the action of concentrated sulphuric acid(Wallach and Belli, Ber., 1880,13,525); although it must be recorded that Knipscheer(Rec.Trav.Chim.,1903,22,1) by heating azoxybenzene under pressure with acetic anhydride obtained not only p-hydroxyazobenzene but also o-hydroxyazobenzene.

On addition of concentrated hydrochloric acid, an alcoholic solution of 2-hydroxy-1:1'-azonaphthalene, which is of an intense red colour, passes through a reddish violet stage(permanganate colour) and finally becomes colourless. The original red colour is restored on neutralisation by sodium hydroxide.



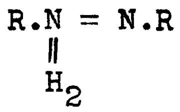
As a matter of interest and to determine if the action of benzyl alcohol, benzaldehyde and quinoline on 1:1'-azoxynaphthalene was typical of all azoxy-compounds, the effect of these reagents on azoxybenzene and azoxytoluene was investigated. The results are detailed on page 158.

1:1'-HYDRAZONAPHTHALENE.

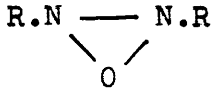
Nietzki and Goll(Ber.,1885,18,3252) obtained 1:1'-hydrazonaphthalene by reducing, with zinc dust, an alcoholic solution of 1:1'-azonaphthalene containing 1% sodium hydroxide. Crystallised from benzene it formed colourless plates of m.p. 275°.

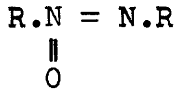
Cumming and Steel prepared 1:1'-hydrazonaphthalene by the neutral reduction of 1-nitronaphthalene by continuing the addition of zinc dust after the azo-stage had been reached until the solution had been rendered colourless. Crystallised from absolute alcohol needles, m.p. 274°, were obtained. These needles on recrystallisation from alcohol saturated with sulphur dioxide to prevent atmospheric oxidation yielded a different modification consisting of plates of m.p. 271°. A mixed m.p. gave 269.5°. The opinion was, therefore, advanced that 1:1'-hydrazonaphthalene exists in a symmetrical and unsymmetrical form corresponding to symmetrical and unsymmetrical 1:1'-azoxynaphthalenes.

R.NH - HN.R



$$\underset{\substack{\| \\ \mathrm{H_2}}}{\mathrm{R.N}} = \mathrm{N.R}$$





$$\underset{\substack{\| \\ \mathrm{O}}}{\mathrm{R.N}} = \mathrm{N.R}$$

By the neutral reduction of 1:1'-azoxynaphthalene to the hydrazo-stage and by the alkaline reduction of both 1:1'-azoxy- and 1:1'-azonaphthalenes in alcoholic solution containing 3% sodium hydroxide we have obtained colourless plates of m.p. 153°, with decomposition, turning red. From the nitrogen content they may be an hydrazonaphthalene, a "semidine" derivative or a diamino-derivative(found N = 9.92, 9.90; required N = 9.86%). On exposure to air the compound turns pale yellow while an alcoholic solution in the heat reddens somewhat when a current of air is passed through.

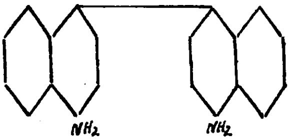
It possesses feebly basic properties being sparingly soluble in cold dilute hydrochloric acid but completely insoluble in cold or boiling oxalic acid solution. However, in a fine state of division, obtained by dissolving compound in alcohol and then precipitating by water, it dissolves readily in cold dilute hydrochloric acid. This solution has no reaction with nitrous acid and hence compound cannot be a "semidine" or a diamino-derivative. Moreover, on treatment with acids in the heat- even sulphurous acid- the base dinaphthyline, m.p. 281°, is formed. This base is identical with that obtained, along with naphthidine, by the methods of Cumming and Steel and Nietzki and Goll by treatment of their hydrazonaphthalene with dilute hydrochloric acid(Cumming and Steel and Nietski and Goll give m.p. 273° for dinaphthyline but by repeated recrystallisation from more suitable solvents of specimens obtained by their method we have raised the m.p. to 281°). The compound, m.p. 153°, must, therefore, be an hydrazo-compound and in view of its basic properties the unsymmetrical formula $C_{10}H_7.NH_2:N.C_{10}H_7$, has been assigned to it.

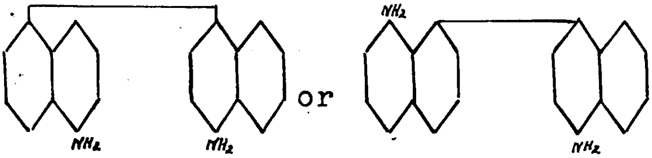
From the above it follows that the two modifications viz. needles, m.p. 274°, and plates, m.p. 271°, of 1:1'-hydrazonaphthalene, as isolated by Cumming and Steel, cannot be the symmetrical and unsymmetrical compounds respectively. In view of the fact that sulphurous acid converts unsymmetrical 1:1'-hydrazonaphthalene, m.p. 153°, into dinaphthyline, m.p. 281°, it seems probable that the above plates, m.p. 271°, obtained by treatment of an alcoholic solution of the symmetrical 1:1'-hydrazonaphthalene, m.p. 274°, with sulphurous acid, are but impure dinaphthyline. This, moreover, would explain the depression in m.p. obtained by the mixed m.p. of the plates and needles.

REDUCTION PRODUCTS of 1:1'-AZOXY- and 1:1'-AZONAPHTHALENES and the "BENZIDINE" CONVERSION of the HYDRAZONAPHTHALENES.

The action of hot mineral acid on hydrazobenzene is to cause it to undergo intramolecular change to form chiefly benzidine(4:4'-diaminodiphenyl) and a little of the isomeric diphenyline(2:4'-diaminodiphenyl). Nietzki and Goll(loc.cit.) found that 1:1'-hydrazonaphthalene, similarly to hydrazobenzene, on treatment with hot dilute hydrochloric acid, was converted into two isomeric bases. To these they assigned the nomenclature naphthidine, m.p. 198°, and dinaphthyline, m.p. 273°. Both were diamines and yielded phthalic acid on oxidation. Further, on diazotisation and boiling of the diazonium compounds in alcohol these authors claim to have obtained 1:1'-dinaphthyl from both bases. This latter statement we have been unable to verify as dinaphthyline did not yield 1:1'-dinaphthyl, m.p. 157°, but 2:2'-dinaphthyl, m.p. 187°.

The above authors found that naphthidine showed great similarity to benzidine both in appearance and in the formation of difficultly soluble salts, the free base being obtained as colourless lustrous plates and both the hydrochloride and sulphate being readily formed. Oxidation with chromic acid gave phthalic acid while on more gentle oxidation 1-naphthoquinone was formed although the quinone does not appear to have been isolated. The symmetrical formula 4:4'-diamino-1:1'-dinaphthyl (1) was, therefore, advanced as its constitution.

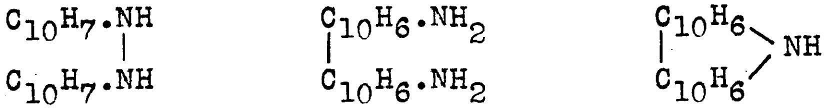
(1)


(2)


On the other hand, the alternative formulae (2) were suggested for the base dinaphthyline, the following argument being put forward in their support. Dinaphthyline is a derivative of 1:1'-dinaphthyl and hence the bond can only link the two naphthalene residues in the alternative positions as shown in formulae (2). Further, since dinaphthyline is obtained from 1:1'-hydrazonaphthalene, which itself was derived from 1:1'-azonaphthalene, the amino-groups must occupy 1:1'-positions. This latter statement is, of course, not true as was shown four years prior to the paper of Nietzki and Goll by Schultz and Strasser(Ber.,1881,14,612) in their determination of the constitution of the bases derived from the conversion of hydrazobenzene.

Unlike the corresponding benzene derivatives(Schmidt and Schultz, Ann.,1881,207,330) which yield a mixture of 4:4'- and 2:4'-diaminodiphenyls, 1:1'-azoxynaphthalene(Cumming and Steel, loc.cit.) and 1:1'-azonaphthalene(Nietzki and Goll, loc.cit.) on reduction with stannous chloride in hydrochloric acid yield only the one base naphthidine.

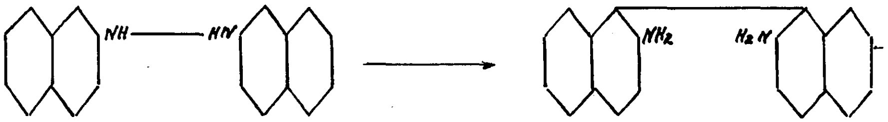
Dinaphthyline on boiling with acids, even acetic acid and picric acid, loses ammonia with formation of the corresponding imine called by Nietzki and Goll dinaphthylcarbazole. These authors assigned no constitution to this compound and indeed it is difficult to conceive of the formation of such a carbazole from an unsymmetrical diamine theoretically derived from an hydrazonaphthalene as follows:-



$$\begin{array}{l} C_{10}H_7.NH \\ \quad\quad\ | \\ C_{10}H_7.NH \end{array} \qquad \begin{array}{l} C_{10}H_6.NH_2 \\ | \\ C_{10}H_6.NH_2 \end{array} \qquad \begin{array}{l} C_{10}H_6\searrow \\ | \qquad\quad NH \\ C_{10}H_6\nearrow \end{array}$$

The same carbazole results on treatment of 1:1'-hydrazonaphthalene, m.p. 274°, with hot dilute sulphuric acid(Cumming and Steel, loc.cit.).

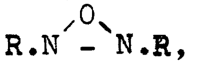
2:2'-Hydrazonaphthalene on treatment with acids is converted into 2:2'-diamino-1:1'-dinaphthyl(Meisenheimer and Witte, Ber.,1903,36,4153).



Cumming and Ferrier(J.C.S.,1924,125,1108) in an attempt to prepare 2:2'-hydrazonaphthalene by the neutral reduction of 2-nitronaphthalene failed to isolate any 2:2'-hydrazonaphthalene complete conversion having taken place to the corresponding base 2:2'-diamino-1:1'-dinaphthyl.

The products of reduction of symmetrical and unsymmetrical 1:1'-azoxynaphthalenes and of 1:1'-azonaphthalene in acid, neutral and alkaline solutions were determined.

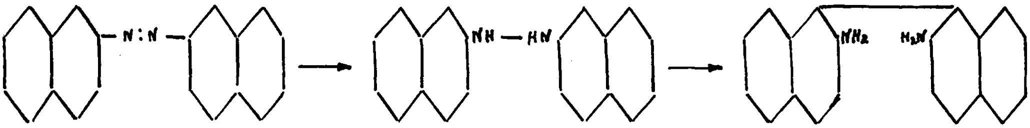
Reduction of 1:1'-azonaphthalene in acid solution employing stannous chloride proceeded easily whereas symmetrical 1:1'-azoxynaphthalene was only reduced with difficulty and unsymmetrical 1:1'-azoxynaphthalene with still greater difficulty. On the other hand, in an alkaline reducing medium unsymmetrical 1:1'-azoxynaphthalene was more readily reduced than the symmetrical compound while here again no difficulty was experienced in effecting the reduction of 1:1'-azonaphthalene. In neutral solution, the reduction of all three compounds proceeded with equal ease.

A consideration of the nature of the compounds undergoing reduction leads to an explanation of the causes governing the difference in ease of reduction depending on the medium employed. 1:1'-Azonaphthalene, R.N:N.R, is truly neutral, symmetrical 1:1'-azoxynaphthalene,  $R.N\overset{O}{-}N.R$, probably feebly acidic while unsymmetrical 1:1'-azoxynaphthalene, R.NO:N.R, is definitely acidic. It would, therefore, be expected that no matter the medium, acid, alkaline or neutral, 1:1'-azonaphthalene would be equally readily reduced but that unsymmetrical 1:1'-azoxynaphthalene would be more difficult of reduction in acid solution than symmetrical 1:1'-azoxynaphthalene, that in alkaline solution the reverse order would hold and that there would be no difference in neutral solution. As has been shown, these expectancies have been fully bourne out in practice.

It should here be noted that Nietzki and Goll and Cumming and Steel give the m.p. for naphthidine, dinaphthyline and dinaphthylcarbazole as 198°, 273° and 216° respectively. Specimens obtained by their methods on repeated recrystallisation from more suitable solvents than used by them raised the m.p. of naphthidine to 202°, dinaphthyline to 281° and dinaphthylcarbazole to 221°.

PREPARATION of 2:2'-DIAMINO-1:1'-DINAPHTHYL by REDUCTION of 2:2'-AZONAPHTHALENE.

Due to the difficulty of preparing any quantity, by synthetic means, of 2:2'-diamino-1:1'-dinaphthyl the method of Meisenheimer and Witte(Ber.,1903,36,4153) for the preparation of the base was investigated. This necessitated the preparation of 2:2'-azonaphthalene and its subsequent reduction with zinc dust and acetic acid.



(not isolated)

According to Ferrier(Ph.D. Thesis, Glasgow University, January 1926) 2:2'-azonaphthalene is best prepared by the method of Hantzsch and Schmiedel(Ber.,1897,30,82). 2-Naphthylamine is diazotised and the diazonium solution treated with potassium sulphite when 2-naphthalene-syndiazonium sulphonate is obtained. The sulphonate is, however, unstable and breaks down with formation of 2:2'-azonaphthalene.

$$C_{10}H_7.NH_2 \longrightarrow C_{10}H_7.N_2.Cl \longrightarrow \begin{array}{c} C_{10}H_7.N \\ \| \\ KSO_3.N \end{array}$$

$$2C_{10}H_7.N_2.SO_3K + H_2O \;=\; C_{10}H_7.N{:}N.C_{10}H_7 + KHSO_3 + KHSO_4 + N_2$$

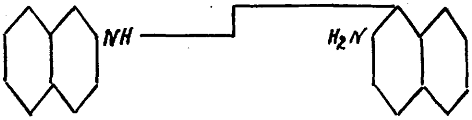
Both the preparation of 2:2'-azonaphthalene and its reduction are described.

The above method is the best available for the preparation of 2:2'-diamino-1:1'-dinaphthyl in reasonable quantity.

"BENZIDINE" CONVERSION in ALKALINE SOLUTION.

Meisenheimer and Witte(loc.cit.) by the very careful reduction of 2:2'-azonaphthalene with zinc dust and sodium hydroxide obtained 2:2'-hydrazonaphthalene. However, they observed, that if the reduction mixture be maintained at the boil for more than a few minutes the resulting product does not consist of 2:2'-hydrazonaphthalene but the corresponding base 2:2'-diamino-1:1'-dinaphthyl, conversion having taken place. The same base results on the usual treatment of the 2:2'-hydrazonaphthalene with acids.

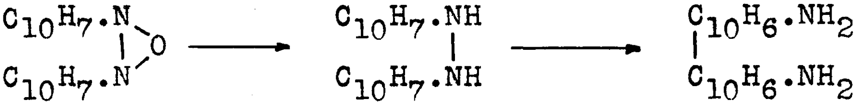
Jacobsen(Ann.,1922,427,142) has pointed out that, as both positions para to the hydrazo-group in 2:2'-hydrazonaphthalene are blocked, the substance which would have been expected would have been a "semidine" derivative such as



and further that it is very unusual for the change to take place in alkaline solution. At the same time he confirms Meisenheimer and Witte's experimental evidence and has found that the same compound is formed when 2:2'-azonaphthalene is reduced with stannous chloride and hydrochloric acid in presence of alcohol.

Cumming and Ferrier(loc.cit.) in the neutral reduction of 2-nitronaphthalene to the hydrazo-stage failed to isolate any 2:2'-hydrazonaphthalene, complete conversion having taken place to the base 2:2'-diamino-1:1'-dinaphthyl.

In the alkaline reduction of 1:1'-azoxynaphthalene a similar phenomenon was observed. Employing a 10% sodium hydroxide solution and maintaining the temperature at the boil unsymmetrical 1:1'-hydrazonaphthalene was not obtained but the base dinaphthyline.



$$\begin{array}{l} C_{10}H_7.N \\ |\;\rangle O \\ C_{10}H_7.N \end{array} \longrightarrow \begin{array}{l} C_{10}H_7.NH \\ \quad | \\ C_{10}H_7.NH \end{array} \longrightarrow \begin{array}{l} C_{10}H_6.NH_2 \\ | \\ C_{10}H_6.NH_2 \end{array}$$

Further, in the neutral reduction of 1:1'-azonaphthalene between the temperatures 70-75°, dinaphthyline was the main product although there was distinct evidence of the presence of 1:1'-hydrazonaphthalene. On the other hand, the neutral reduction of 1:1'-azoxynaphthalene at 70-75° yielded naphthidine along with unsymmetrical 1:1'-hydrazonaphthalene.

It is of interest to note that Bandrowski(Ber.,1884,<u>17</u>, 1181) in an investigation into the action of organic dibasic acids on hydrazobenzene obtained with phthalic anhydride dinaphthyldiparabenzidine $C_{28}H_{16}N_2O_4$, conversion having thus taken place.

A further interesting conversion is recorded by Clève(Bull.Soc.chim.,1886,<u>45</u>,188) who obtained benzylidenebenzidine, $C_6H_5.CH:N.C_6H_4---C_6H_4.N:CH.C_6H_5$, by the action of benzaldehyde on hydrazobenzene in presence of zinc chloride.

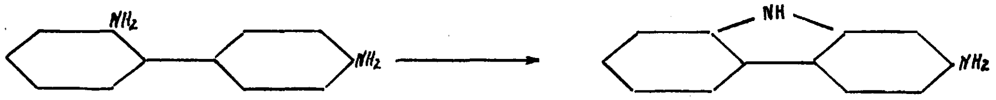
It is noteworthy that unsymmetrical 1:1'-hydrazonaphthalene and probably also the symmetrical compound are converted, in boiling alcoholic solution on treatment with even sulphurous acid, into dinaphthyline.

Thus the "benzidine" conversion can take place through a wide range in alkaline, in neutral and in weak or strong acid solution.

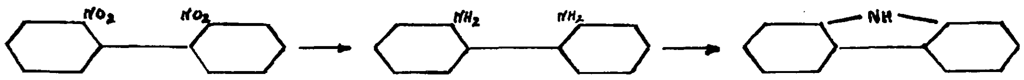
CONSTITUTION and SYNTHESES of the NAPHTHIDINE BASES.

In this connection a review of the methods employed in establishing the constitution of the corresponding diamino:diphenyls is of interest.

Shultz and Strasser(Ber.,1881,14,612) by nitration of diphenyl obtained two isomeric dinitro-compounds which they were able to prove to be 4:4'- and 2:4'-dinitrodiphenyl respectively. Reduction of the 4:4'-dinitrodiphenyl yielded benzidine while the 2:4'-dinitrodiphenyl gave diphenyline. Hence benzidine and diphenyline, the products obtained on conversion of hydrazobenzene and by the stannous chloride reduction of azobenzene(Schmidt and Schultz, Ann.,1881,207, 330) must be 4:4'-diaminodiphenyl and 2:4'-diaminodiphenyl respectively. Further, the amino-carbazole obtained by passing diphenyline over heated lime is, therefore, 4-amino-1:1'-iminediphenyl.



2:2'-Diaminodiphenyl was isolated by Tauber(Ber.,1891,24, 198) by reduction of 2:2'-dinitrodiphenyl. The corresponding carbazole was also obtained by diazotisation of the base and subsequent treatment with calcium sulphide solution.

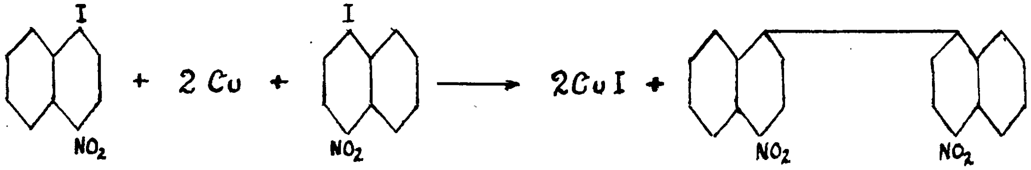


Reduction of 3:3'-dinitrodiphenyl gives rise to 3:3'-diaminodiphenyl(Brunner and Witte, Ber.,1887,20,1082).

An isobenzidine, m.p. 125°, is described by Bernthsen(Ber.,1886,19,421), and Schultz and Strasser(Ann.,1882,210, 194) claim a γ.benzidine, m.p. over 360°, but no constitution appears to have been advanced for these bases.

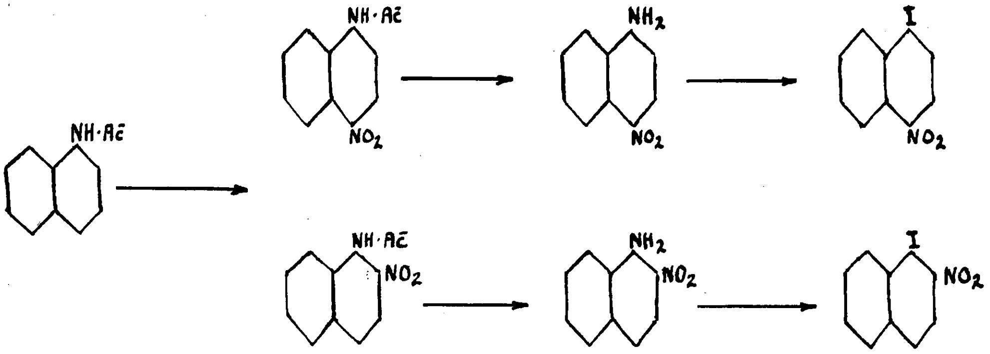
NAPHTHIDINE: 4:4'-DIAMINO-1:1'-DINAPHTHYL.

If naphthidine be 4:4'-diamino-1:1'-dinaphthyl, as suggested by Nietzki and Goll(Ber.,1885,18,3252), then it should be obtained by reduction of 4:4'-dinitro-1:1'-dinaphthyl. 4:4'-Dinitro-1:1'-dinaphthyl has been synthesised by condensation of 4-nitro-1-iodonaphthalene by fusion with copper powder(Schoepfle, J.Amer.C.S.,1923,45,1566; Chudožilov, Chem.Listy, 1925,19,187).



The yield of the dinitro-compound is, however, poor and moreover, the method, that of Meldola(J.C.S.,1885,47,519), for the preparation of the iodonitronaphthalene is both lengthy and wasteful. 1-Acetylnaphthylamine is first nitrated(Lellmann and Remy, Ber.,1886,19,796) and the 4- and 2-nitro-

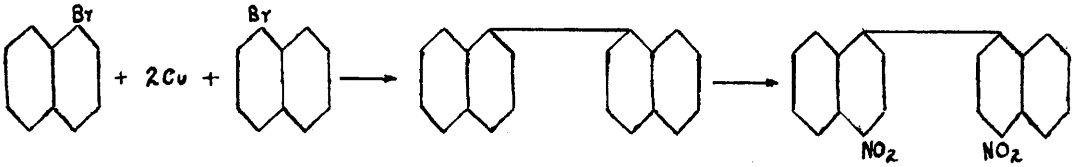
1-acetylnaphthylamines so formed separated(Morgan and Micklethwait, J.C.S.,1905,87,928). Subsequent hydrolysis of the acetyl-compounds yields the free bases which, on diazotisation and treatment of the diazonium solutions with hydriodic acid, gives rise to 4- and 2-nitro-1-iodonaphthalenes.



In the hopes of obtaining a better yield of the dinitrodinaphthyl by condensation of 4-nitro-1-iodonaphthalene, the effect of refluxing it in solution with sodium was investigated. The addition of ethyl acetate, which proved so effective in a similar condensation of 2-chloronaphthalene to 2:2'-dinaphthyl(Chattaway and Lewis, J.C.S.,1895,67,656), caused no condensation. Similarly, refluxing of the iodonitro-compound in nitrobenzene solution with copper powder caused no reaction.

Further, no condensation took place on addition of copper powder to a solution of diazotised 4-nitro-1-naphthylamine. Due to the insolubility of the free base in acid the diazotisation was carried out in solution. In alcoholic solution a strong smell of acetaldehyde was observed on addition of the copper to the diazonium solution and from the reaction mixture 1-nitronaphthalene was isolated, reduction of the diazonium solution having taken place. When acetone was used as solvent a most vigorous reaction took place and tarring resulted. As a comparison with the benzene series it is of interest to note that Niementowski(Ber., 1902,<u>34</u>,3325) by a similar condensation of diazotised o-nitraniline with copper powder obtained good yields of 2:2'-dinitrodiphenyl.

Schoepfle has, however, found that 4:4'-dinitro-1:1'-dinaphthyl is obtained in 60% yield on nitration of 1:1'-dinaphthyl which itself is obtained in 50% yield by the condensation of 1-bromonaphthalene using copper powder. The work of Schoepfle we have verified.

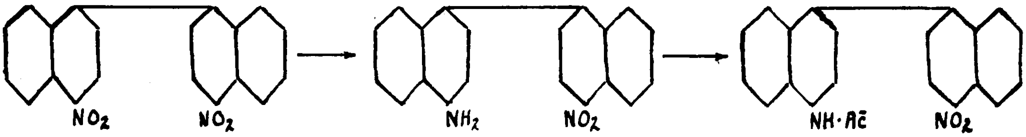


The reduction of 4:4'-dinitro-1:1'-dinaphthyl with zinc dust and glacial acetic acid yielded colourless plates, m.p. 202°. The base so formed proved identical with naphthidine, m.p. 202°, obtained in the conversion of 1:1'-hydrazonaphthalene. Naphthidine is, therefore, 4:4'-diamino-1:1'-dinaphthyl.

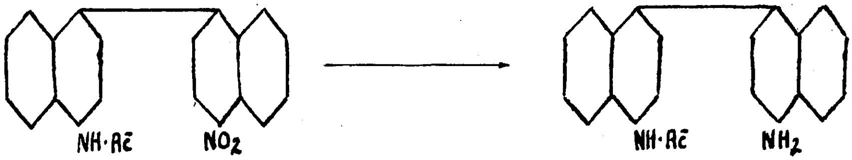
As has already been mentioned in the introduction to this thesis(p. 1) Clemo, Cockburn and Spence(J.C.S.,1931,

1271) reduced 4:4'-dinitro-1:1'-dinaphthyl and claim to have obtained naphthidine, m.p. 191° "alone or mixed with an authentic naphthidine". The source of the "authentic naphthidine" is not stated and we are unable to find in the literature any reference to naphthidine, m.p. 191°. However, on exactly repeating the method as described by Clemo and his co-workers the product obtained gave m.p. 195-196° after one recrystallisation from alcohol; a further recrystallisation from the same solvent with addition of animal charcoal gave m.p. 196-197°. The yield was so small, using the quantity of dinitro-compound(1g.) employed by them, that a further recrystallisation was practically impossible.

The reduction of 4:4'-dinitro-1:1'-dinaphthyl using sodium hydrogen sulphide was investigated when 4-amino-4'-nitro-1:1'-dinaphthyl was obtained. The nitroamine proved readily capable of acetylation to yield the corresponding acetyl-compound, 4-acetylamino-4'-nitro-1:1'-dinaphthyl.

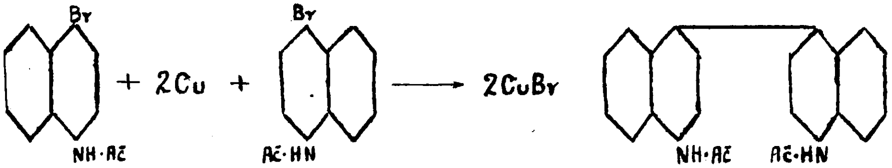


The further reduction of the acetyl-compound gave rise to 4-acetylamino-4'-amino-1:1'-dinaphthyl. However, due possibly to the ease of hydrolysis of the acetyl-compound, the base could not be obtained very pure.



Attempts were made to prepare both the diacetyl-derivative of naphthidine and naphthidine by direct condensation of the acetyl-derivative of 4-bromo-1-naphthylamine and the free base respectively.

e.g.



The following methods were tried:-

(a). Fusion with copper bronze powder.

(b). Refluxing with sodium in various solvents giving a range in temperature from 30-192°.

(c). Fusion with sodium amalgam.

(d). Refluxing in acetone solution with anhydrous aluminium chloride.

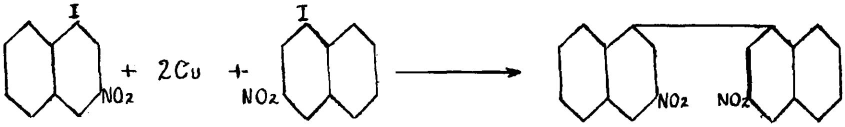
In all cases no condensation took place. It is worthy of note that, in the fusion of the acetyl-compound with sodium amalgam, the sodium partly reacted with the bromine, 1-acetylnaphthylamine being formed, the necessary hydrogen being obtained from the partial decomposition of the bromo-:acetylnaphthylamine.

It should be observed that Ullmann(Ann.,1904,<u>332</u>,60) in his work on the condensation of halogen-compounds with copper powder failed to condense the halogen-acetylphenylamines unless an acid group(e.g. a sulphonic acid group) was present.

In connection with the above, the preparation of naphthidine by Reverdin and De La Harpe(Chem.Zeit.,1893,16, 1687) by treatment in the heat of a sulphuric acid solution of 1-naphthylamine with ferric oxide, is of interest. A modification of this method for the preparation of naphthidine is described by Corbellini and Debenedetti(Gazzetta, 1929,59,391); the m.p. is recorded as 198°.

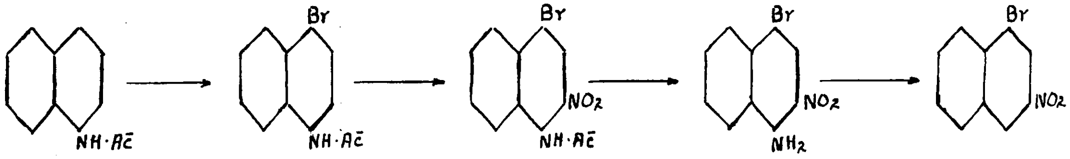
3:3'-DIAMINO-1:1'-DINAPHTHYL.

This base is not a conversion product of either 1:1'- or 2:2'-hydrazonaphthalene and was, therefore, only obtainable by reduction of the corresponding dinitro-compound. 3:3'-di:nitro-1:1'-dinaphthyl itself is not formed in the nitration of 1:1'-dinaphthyl but has been isolated by Chudožilov(Chem. Listy, 1925,19,187) by condensation of 3-nitro-1-iodonaph:thalene with copper powder.



His method for the preparation of the nitroiodo-compound is extremely involved and gives a poor yield. Since, moreover, the condensation does not run smoothly and is here again accompanied by a great loss in yield some time was spent in studying the preparation and condensation of the 1-halogen-3-nitronaphthalenes.

1-Bromo-3-nitronaphthalene is fairly readily obtained as follows by the method of Liebermann and Schiedung(Ber., 1875,8,1108). 1-Acetylnaphthylamine on bromination yields 4-bromo-2-nitro-1-acetylnaphthylamine. On hydrolysis of the acetyl-compound the free base results which on removal of the amino-group by reduction of the diazonium compound with alcohol gives rise to 1(4)-bromo-3(2)-nitronaphthalene.



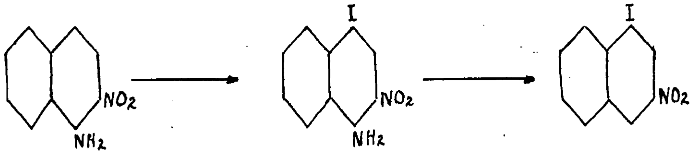
By modification of the above authors' experimental details an 18% yield of theory of the bromonitro-compound was obtained.

No condensation of the bromo-compound by refluxing in solution with either sodium or copper powder could be effected. By fusion with copper powder a reaction did take place but the high temperature(300°) necessary caused complete decomposition.

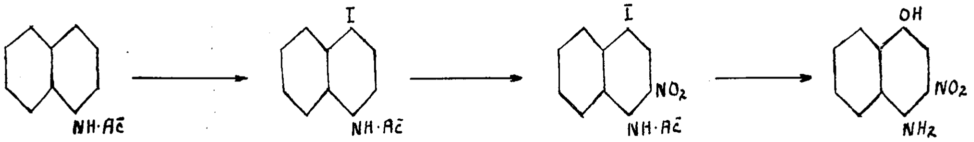
It appears, therefore, that the more reactive iodo-compound is required and attention was next turned to methods of preparing 1-iodo-3-nitronaphthalene.

Attempts to replace the bromine by iodine in 3-nitro-1-bromonaphthalene both by fusion and refluxing in solution with sodium iodide failed, the bromo-compound being completely recovered.

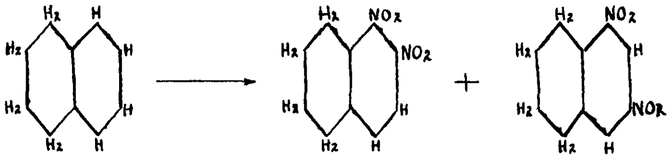
By action of iodine monochloride on 1-amino-2-nitronaphthalene(for preparation see p. 28) an iodoaminonitronaphthalene, m.p. 192-193°, was obtained(found I = 40.60; required I = 40.45%). On diazotisation of the base and reduction of the diazonium compound with absolute alcohol 1-iodo-3-nitronaphthalene, m.p. 147°, was formed. The latter compound was identified by comparing it with a sample of 1-iodo-3-nitronaphthalene, m.p. 147°, prepared by the method of Chudožilov(see later). Hence it follows that the intermediate iodoaminonitronaphthalene is 1(4)-iodo-3(2)-nitro-4(1)-aminonaphthalene. The iodine in this compound is, however, but loosely attached and even under the most careful conditions much decomposition of the iodo-compound took place in the reduction of the diazonium compound by alcohol.



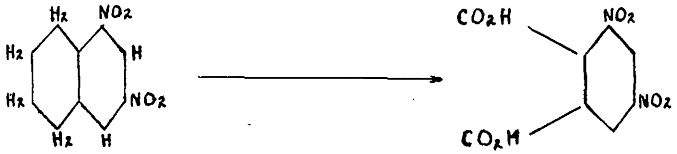
In connection with the above it is of interest to note that Meldola and Streatfield(J.C.S.,1895,67,907) having shown that 1-acetylnaphthylamine could not be directly iodated found that the action of iodine monochloride on the acetyl-compound yields 4-iodo-1-acetylnaphthylamine. This on nitration gives 4(1)-iodo-2(3)-nitro-1(4)-acetylnaphthylamine. Under no circumstances could the free base be isolated, as the action of the hydrolysing agent was to remove the iodo-group as well as the acetyl-group. The inability to prepare the free base prevented them from synthesising 1-iodo-3-nitronaphthalene by this method.



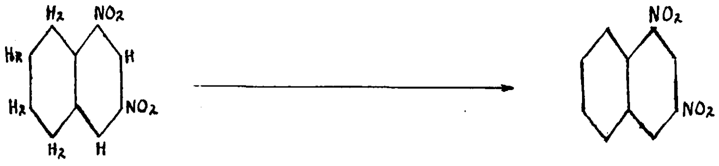
Chudožilov in his preparation of 1-iodo-3-nitronaphthalene employed tetrahydronaphthalene as the starting material. By dinitration(Schroeter, Ann.,1922,426,43) a mixture of 1-2- and 1-3-dinitrotetrahydronaphthalenes is obtained, the isomers being readily separated by fractional recrystallisation from concentrated sulphuric acid.



Schroeter established the constitution of the 1-3-isomer by oxidising it with nitric acid when 3-5-dinitrophthalic acid was obtained.

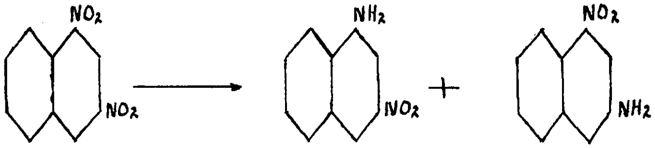


The 1-3-dinitrotetrahydronaphthalene is next oxidised by bromine(Veselý and Dvořák, Bull.Soc.chim.,1923,33,326) when 1-3-dinitronaphthalene results.

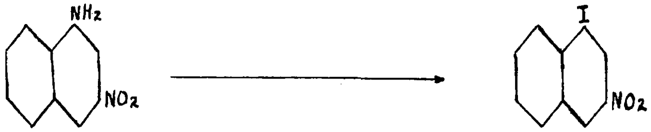


By reduction of 1-3-dinitronaphthalene(Veselý and Dvořák, loc.cit.) employing ammonium hydrogen sulphide or stannous chloride, a mixture of 1-amino-3-nitro- and 3-amino-1-nitronaphthalenes is obtained in which the 1-amino-3-nitronaphthalene predominates. A separation giving pure 1-amino-3-

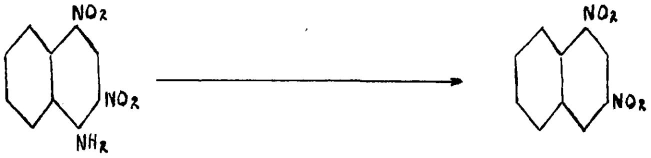
nitronaphthalene is readily effected by fractional recrystallisation of the hydrochlorides.



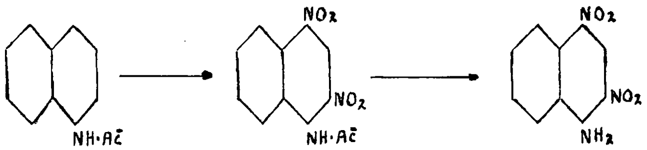
Chudožilov(loc.cit.) by diazotisation of the 1-amino-3-nitronaphthalene and treatment of the diazonium solution with potassium iodide finally obtained 1-iodo-3-nitronaphthalene.



The intermediate 1-3-dinitronaphthalene has been prepared by Liebermann(Ann.,1876,183,274) by elimination of the amino-group in 1-3-dinitro-4-naphthylamine.



Whilst the dinitronaphthalene is readily obtained by the method of Morgan and Evans(J.C.S.,1919,115,1126) who prepared it by hydrolysis of 1-3-dinitro-4-acetylnaphthylamine, the dinitration product of 1(4)-acetylnaphthylamine,



it was found that even under the most careful conditions the reduction of the diazonium compound with alcohol involved excessive tarring in consequence of which a very poor yield of 1-3-dinitronaphthalene resulted.

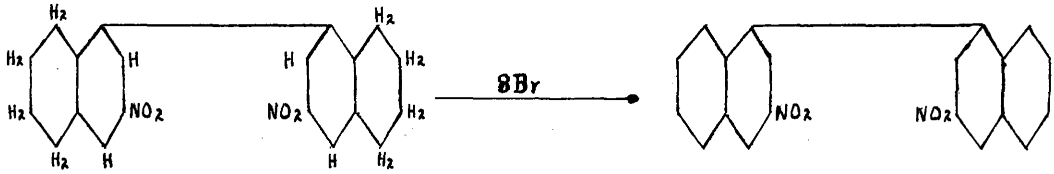
The table below gives the percentage yields, based on the starting material employed, as obtained in the above described preparations.

Method	Starting material.	Compound prepared.	% Yield.
Prep. of 1-iodo-3-nitro-4-aminonaphthalene and elimination of amino-group.	1-Acetylnaph:thylamine.	1-Iodo-3-nitro:naphthalene	2.5%
Chudožilov	Technical tetrahydro:naphthalene. Fraction of b.p.208-212°.	1-Iodo-3-nitro:naphthalene.	1.1%
Veselý and Dvořák	Ditto	1-3-Dinitro:naphthalene	7.4%
Liebermann	1-Acetylnaph:thylamine.	Ditto	5.1%

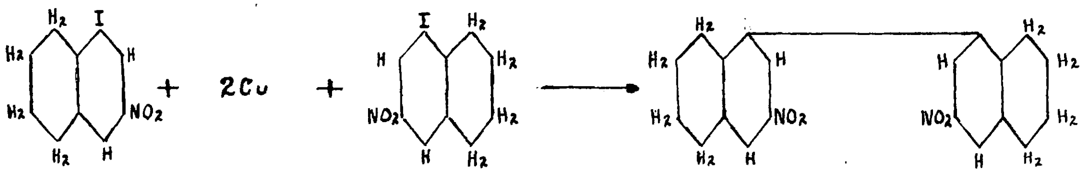
In the preparation of 1-iodo-3-nitronaphthalene, the method of Chudožilov, despite the fact that it gives a poorer yield than the alternative method indicated, was finally adopted as being both quicker and much cheaper. By starting with 496g.(3 mol) tetrahydronaphthalene, the largest practical laboratory scale, nearly 10g. 1-iodo-3-nitronaphthalene can be obtained at the end of a week's work.

As has already been mentioned Chudožilov, by condensation of the 1-iodo-3-nitronaphthalene with copper powder, isolated 3:3'-dinitro-1:1'-dinaphthyl. The difficulty of the condensation seriously affects the yield only 10% of theory being obtained.

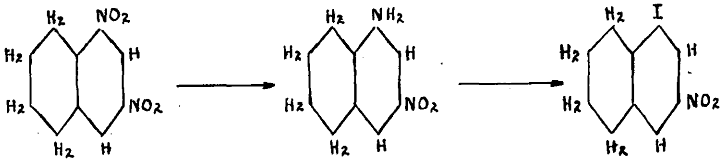
In the hopes of obtaining a better yield of 3:3'-dinitro-1:1'-dinaphthyl by oxidation of the corresponding dinitroditetrahydrodinaphthyl



the preparation of 3:3'-dinitro-1:1'-ditetrahydrodinaphthyl was attempted by the condensation of 1-iodo-3-nitrotetrahydronaphthalene.

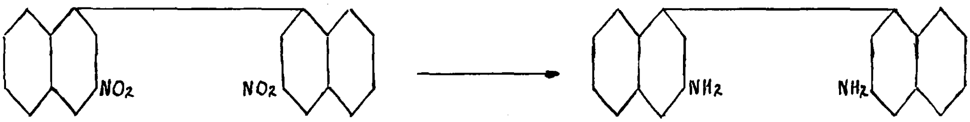


The 1-iodo-3-nitrotetrahydronaphthalene was obtained by the replacement by iodine of the amino-group in 1-amino-3-nitrotetrahydronaphthalene, the latter compound being prepared by the stannous chloride reduction of 1:3-dinitro-:tetrahydronaphthalene(Schroeter, loc.cit.).



Condensation did take place but the high temperature necessary(260°) caused complete decomposition.

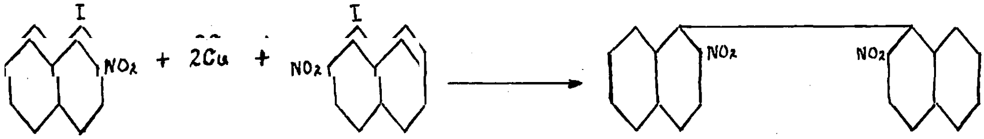
By reduction of 3:3'-dinitro-1:1'-dinaphthyl, using zinc dust and glacial acetic acid, 3:3'-diamino-1:1'-dinaphthyl was obtained as colourless plates, m.p. 270°, from benzene.



Due to the difficulty of preparing the base in sufficient quantity no derivatives could be prepared. The hydrochloride, which was extremely soluble in water, on diazotisation and coupling with various compounds, gave dyestuffs, the colours of the solutions being noted on p. 150.

2:2'-DIAMINO-1:1'-DINAPHTHYL.

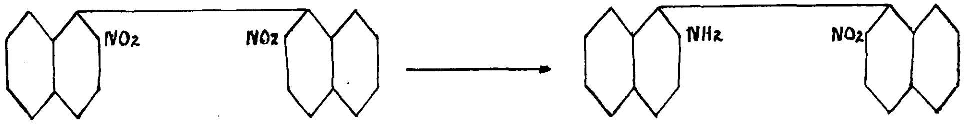
The constitution of this base, obtained by Meisenheimer and Witte(Ber.,1903,36,4153) and Cumming and Ferrier(J.C.S., 1924,125,1108) by the conversion of 2:2'-hydrazonaphthalene, was definitely established by Chudožilov(Chem.Listy, 1925,19, 187) who obtained it by reduction of 2:2'-dinitro-1:1'-dinaph:thyl using sodium amalgam. For the preparation of the 2:2'-dinitro-1:1'-dinaphthyl, 1-iodo-2-nitronaphthalene, obtained by Meldola's method(see p. 29), was condensed with copper powder. A nearly theoretical yield resulted.



It has been found that the condensation of the nitroiodo-compound by refluxing in nitrobenzene solution with copper powder does not proceed too well, much decomposition taking place. As in the case of the previous nitroiodo-compounds, refluxing in solution with sodium failed to cause condensation.

By reduction of 2:2'-dinitro-1:1-dinaphthyl in acid solution, using acetic acid and zinc dust, 2:2'-diamino-1:1'-dinaphthyl was obtained.

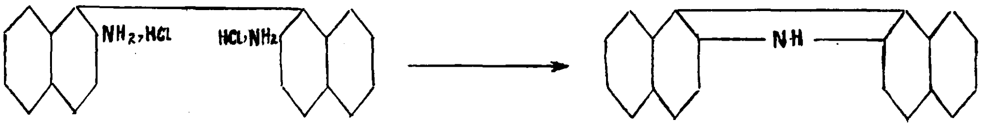
Reduction of the dinitro-compound with sodium sulphide gave 2-amino-2'-nitro-1:1'-dinaphthyl.



The nitroamine, due undoubtedly to steric hindrance, proved incapable of either acetylation or diazotisation. The failure to prepare 2-acetylamino-2'-nitro-1:1'-dinaphthyl has prevented the study of its reduction to the monacetyl-derivative of 2:2'-diamino-1:1'-dinaphthyl.

As in the case of naphthidine, attempts were made to synthesise 2:2'-diamino-1:1'-dinaphthyl directly by condensation of both the acetyl-derivative of 1-bromo-2-naphthylamine and the free base. The methods previously tried were employed but no condensation could be effected. The reaction between sodium amalgam and the acetyl-compound, similarly to that with 4-bromo-1-acetylnaphthylamine, resulted in the removal of bromine and the formation of 2-acetylnaphthylamine.

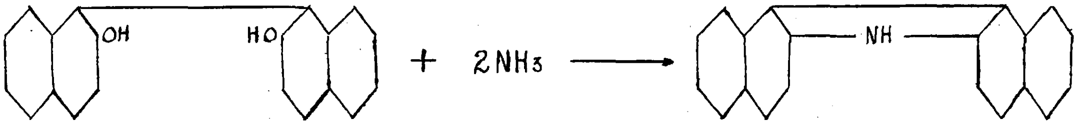
On maintaining at a temperature above 240° for a few minutes, 2:2'-diamino-1:1'-dinaphthyl hydrochloride is converted into the corresponding carbazole 2:2'-imine-1:1'-dinaphthyl(Meisenheimer and Witte, loc.cit.).



We have found that the same imine is also formed by re-

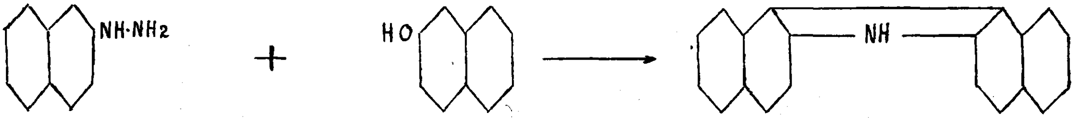
:fluxing the base in acid solution.

2:2'-Imine-1:1'-dinaphthyl has been synthesised, in small quantities, by Walder(Ber.,1883,16,2173) by heating 2:2'-dinaphthol in a sealed tube with zinc ammonium chloride. No yield is mentioned.

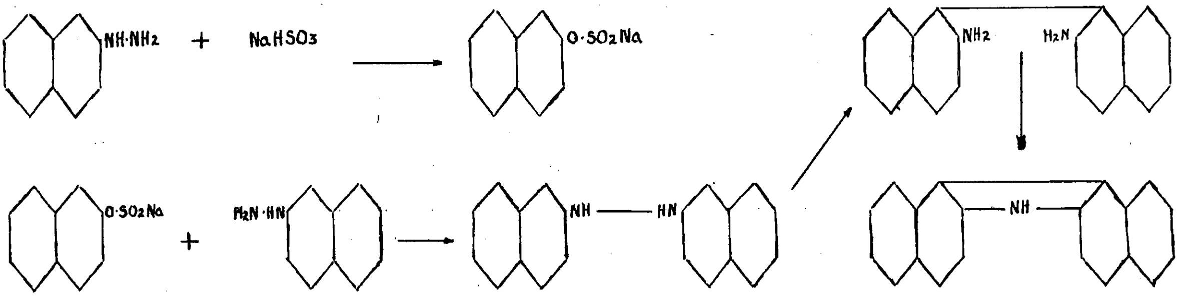


An attempt to carry out the amidation of 2:2'-dinaphthol in an autoclave was made but the product so obtained consisted of a charred mass from which no diamine or imine was isolated. Further, the graph obtained by plotting temperature against pressure consisted of a smooth curve showing that no reaction had taken place.

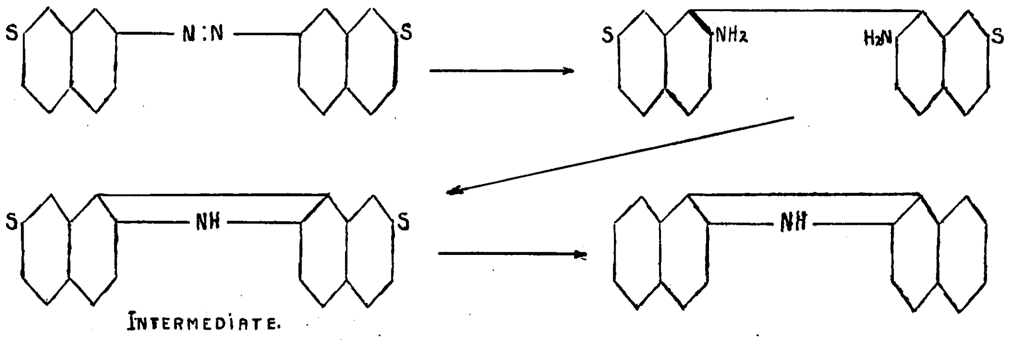
The same imine results on condensing together 2-naphthol and 2-naphthylhydrazine(Japp and Maitland, J.C.S.,1903,83, 273).



Bucherer and Schmidt(J.pr.Chem.,1909,79,369) in the reaction between sodium hydrogen sulphite and 2-naphthylhydrazine obtained, as by-products, both 2:2'-diamino-1:1'-dinaphthyl and 2:2'-imine-1:1'-dinaphthyl.

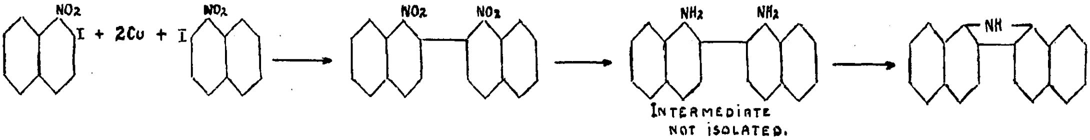


Kalle & Co., Akt.-Ges.(D.R.-P.343149) by reduction of 2:2'-azonaphthalene-7:7'-disulphonic acid obtained 2:2'-diamino-1:1'-dinaphthyl-7:7'-disulphonic acid and this on heating with mineral acid yielded 2:2'-imine-1:1'-dinaphthyl with intermediate formation of 2:2'-imine-1:1'-dinaphthyl-7:7'-disulphonic acid.



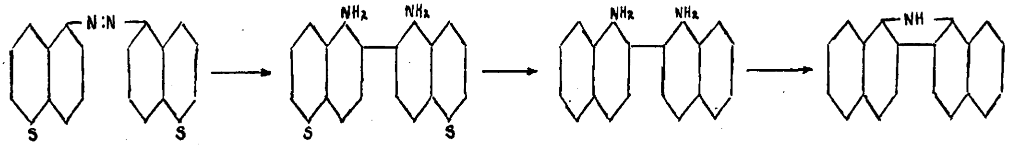
DINAPHTHYLINE: 1:1'-DIAMINO-2:2'-DINAPHTHYL.

Veselý(Ber.,1905,38,136) in a study of 1-nitro-2-naphthylamine prepared 1-nitro-2-iodonaphthalene and this on heating with copper powder in nitrobenzene solution yielded 1:1'-dinitro-2:2'-dinaphthyl. The 1:1'-dinitro-2:2'-dinaphthyl on reduction with zinc dust and acetic acid did not yield the corresponding base but the dinaphthylcarbazole of Nietzki and Goll. The base, due to its instability in acid solution, would not be expected but must have been formed as an intermediate to yield the carbazole. This synthesis, therefore, shows dinaphthyline to be 1:1'-diamino-2:2'-dinaphthyl and dinaphthylcarbazole to be 1:1'-imine-2:2'-dinaphthyl.

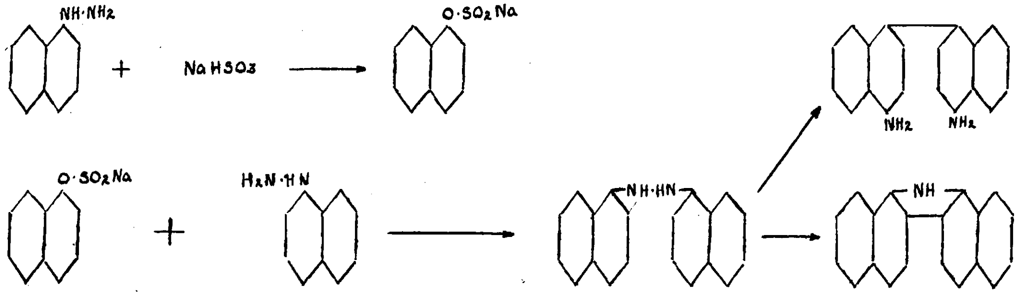


Chudožilov(loc.cit.) by the very careful reduction of 1:1'-dinitro-2:2'-dinaphthyl using sodium amalgam obtained the base but in rather an impure state(m.p. 253-259°); Cumming and Steel and Nietzki and Goll give for dinaphthyline a m.p. of 273° although as has already been stated we determined it to be 281°.

Kalle & Co., Akt.-Ges.(D.R.-P.343149) on reduction of 1:1'-azonaphthalene-5:5'-disulphonic acid obtained 1:1'-diamino-2:2'-dinaphthyl-5:5'-disulphonic acid and this on treatment with weak sodium amalgam yielded 1:1'-diamino-2:2'-dinaphthyl. According to expectations, the base gave 1:1'-imine-2:2-dinaphthyl on treatment with acids.



Bucherer and Schmidt(J.pr.Chem.,1909,79,369) by treat:ment of 1-naphthylhydrazine with sodium hydrogen sulphite obtained as by-products both naphthidine and 1:1'-imine-2:2'-dinaphthyl.



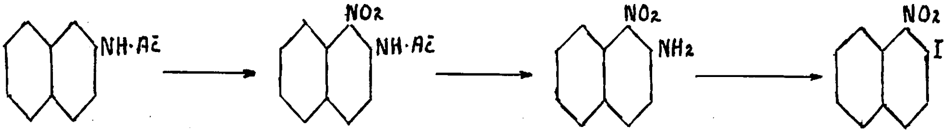
These syntheses show dinaphthyline to be a derivative of 2:2'-dinaphthyl and not of 1:1'-dinaphthyl as was shown by Nietzki and Goll who claim to have obtained 1:1'-dinaphthyl by diazotisation of dinaphthyline and subsequent boiling of the diazonium compound in alcohol. However, as has already been mentioned, on repeating their work we did not obtain 1:1'-dinaphthyl(m.p. 157°) but 2:2'-dinaphthyl(m.p. 187°).

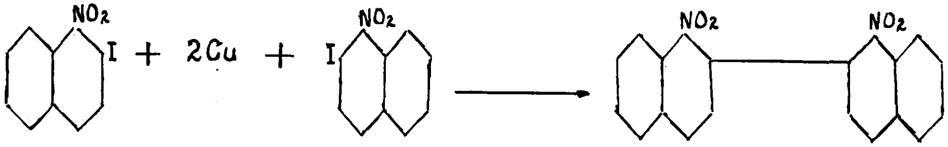
Chudožilov(loc.cit.) prepared his 1:1'-dinitro-2:2'-dinaphthyl by fusion of 1-nitro-2-iodonaphthalene with copper powder, the yield being theoretical. Veselý(loc.cit.)

refluxed the nitroiodo-compound in nitrobenzene solution with copper powder, the yield so obtained being but slightly poorer than by the fusion method.

The effect of refluxing 1-nitro-2-iodonaphthalene in solution with sodium was noted but again no condensation was effected even as before in the presence of ethyl acetate.

1-Nitro-2-iodonaphthalene for use in the condensation to yield 1:1'-dinitro-2:2'-dinaphthyl is prepared as follows:- 2-Acetylnaphthylamine on nitration forms chiefly 1-nitro-2-acetylnaphthylamine(Veselý and Jakeš, Bull.Soc.chim.,1923, 33,942). The free base, obtained by hydrolysis of the acetyl-compound, is diazotised and the diazonium solution treated with hydriodic acid when 1-nitro-2-iodonaphthalene is obtained(Meldola, J.C.S.,1885,47,519).



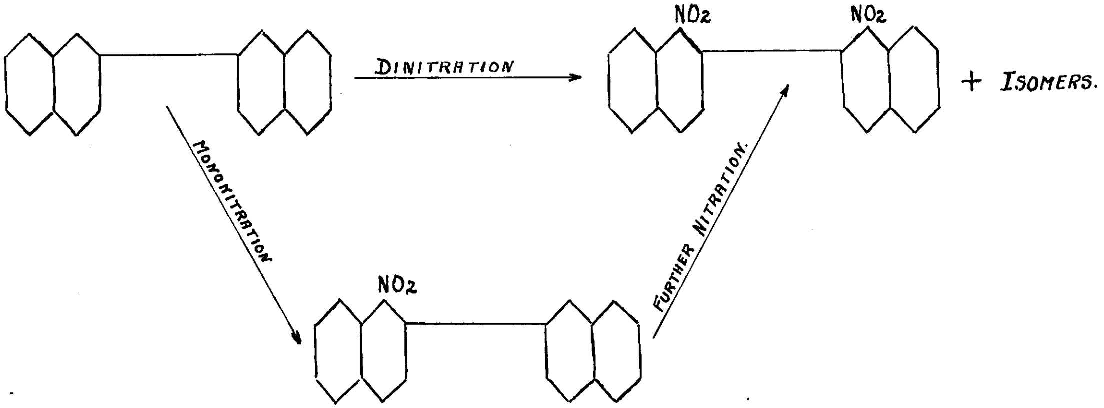


To avoid this lengthy process and in the hopes of preparing the dinitrodinaphthyl directly, the nitration of 2:2'-dinaphthyl was studied.

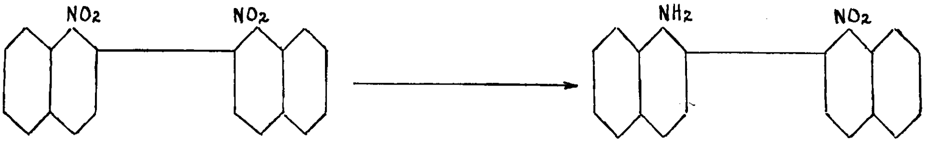
2:2'-Dinaphthyl is readily obtained in 67% yield by the condensation of 2-iodonaphthalene using copper powder(Ullmann, Ann.,1904,332,50).

2:2'-Dinaphthyl on nitration yielded first a mononitro-derivative, m.p. 179°(found N = 4.83, 4.64; required N = 4.67%). On further nitration of the mononitro-compound a mixture of isomeric dinitro-compounds, m.p. 198-208°, was obtained(found N = 8.05, 8.10; required N = 8.08%). No separation could be effected by fractional recrystallisation. Even after five recrystallisations from glacial acetic acid the m.p. was 210-220°. The same mixture resulted on treatment of 2:2'-dinaphthyl with a large excess of fuming nitric acid. The mixed dinitro-isomers on reduction gave a mixture of the corresponding diamino-isomers and here again no separation could be effected by fractional recrystallisation. However, on prolonged boiling of the diamines in acid solution a white crystalline compound gradually separated. This on removal and recrystallisation from glacial acetic acid formed colourless leaflets, m.p. 221°, which proved to be dinaphthylcarbazole(1:1'-imine-2:2'-dinaphthyl). Since the carbazole is obtained from the base dinaphthyline(1:1'-diamino-2:2'-dinaphthyl) the mixed diamino-isomers must have contained some dinaphthyline. Hence it follows that the dinitration of 2:2'-dinaphthyl and the further nitration of the mononitrodinaphthyl gives rise to 1:1'-dinitro-2:2'-dinaphthyl along with other isomers. The mononitro-product of 2:2'-dinaphthyl is, therefore, 1-nitro-2:2'-dinaphthyl.

It is our intention to attempt the separation of the dinitro-isomers by other means and if possible identify the products formed.



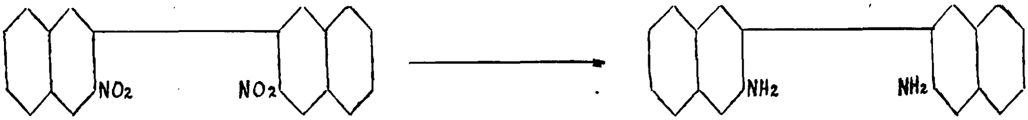
Reduction of 1:1'-dinitro-2:2'-dinaphthyl with sodium sulphide gives 1-amino-1'-nitro-2:2'-dinaphthyl.



As in the case of 2-amino-2'-nitro-1:1'-dinaphthyl, again due undoubtedly to steric hindrance, 1-amino-1'-nitro-2:2'-dinaphthyl could neither be acetylated or diazotised. The monacetyl-derivative of 1:1'-diamino-2:2'-dinaphthyl, therefore, could not be prepared by this method.

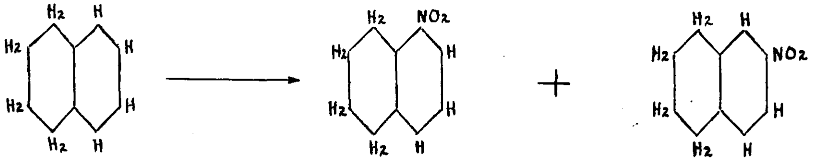
3:3'-DIAMINO-2:2'-DINAPHTHYL.

The synthesis of this base, which also is not formed in the conversion of the hydrazonaphthalenes, was attempted by the preparation and subsequent reduction of 3:3'-dinitro-2:2'-dinaphthyl.



As the dinitro-compound cannot be obtained by the direct nitration of 2:2'-dinaphthyl and 2-iodo-3-nitronaphthalene cannot be obtained from 2-amino-3-nitronaphthalene, since no method is available for the preparation of the latter compound, considerable difficulty was experienced in the isolation of the dinitrodinaphthyl and in consequence the yield was extremely poor.

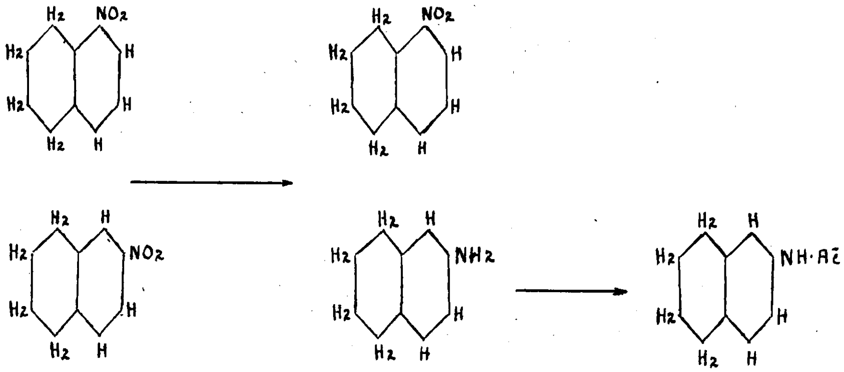
Tetrahydronaphthalene was first nitrated(Schroeter, Ann., 1922,<u>426</u>,43) to yield a mixture of 1- and 2-nitrotetrahydronaphthalenes



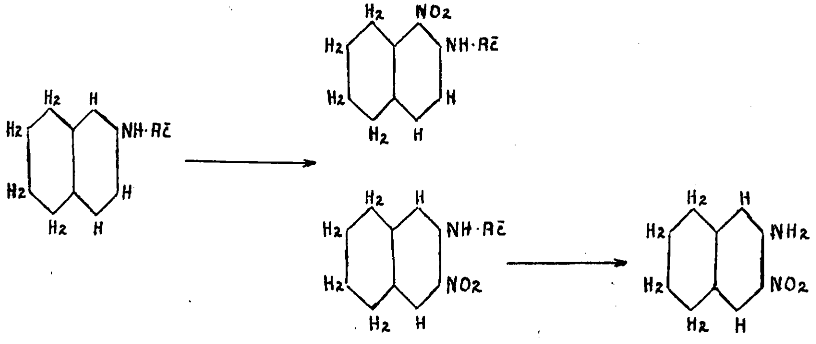
and the mixture selectively reduced with sodium hydrogen sulphide according to the method of Veselý and Chudožilov(Rec.Trav.Chim.,1925,<u>44</u>,352). The 2-nitrotetrahydronaphthalene is reduced to 2-aminotetrahydronaphthalene while the

1-nitro-isomer remains unaffected. Schroeter(loc.cit.) by reduction of the mixed nitro-compounds with hydrogen under pressure and in presence of nickel as catalyst performed the same selective reduction.

The base, which is readily separated from the unchanged nitrotetrahydronaphthalenes, gives on acetylation 2-acetyl-:aminotetrahydronaphthalene(Schroeter, loc.cit.; Veselý and Chudožilov, loc.cit.).

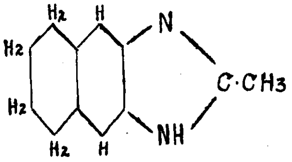


The 2-acetylaminotetrahydronaphthalene was next nitrated in glacial acetic acid solution when a mixture of 1-nitro-2-acetylaminotetrahydronaphthalene and 3-nitro-2-acetyl-:aminotetrahydronaphthalene is formed(Schroeter, loc.cit.). The latter, which is easily obtained pure by fractional recrystallisation of the mixture from alcohol, forms on hydrolysis 3-nitro-2-aminotetrahydronaphthalene.

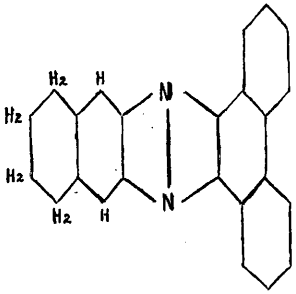


The constitution of 3-nitro-2-aminotetrahydronaphthalene has been established by Schroeter. The diamine, formed on reduction, was shown to be an orthodiamine by the formation of the anhydro-base (A) with glacial acetic acid and also of 2:3-tetrahydronaphthalenephenanthrazine (B) with phenanthraquinone.

(A)

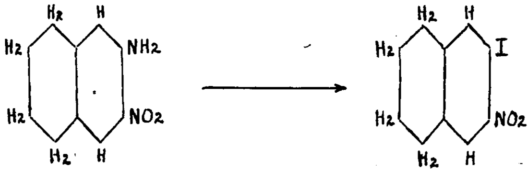


(B)

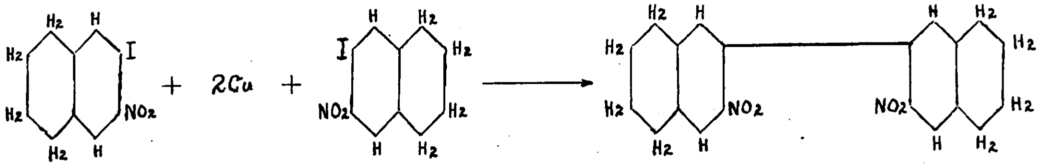


Further, the amino-groups must be in the 2- and 3-positions since the above diamine proved different from the only other possible orthodiamine, 1:2-diaminotetrahydronaphthalene, the reduction product of 1:2-diaminonaphthalene using sodium and alcohol(Bamberger, Ber.,1889,<u>22</u>,1377).

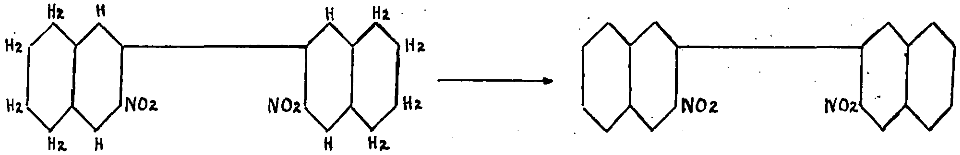
By replacement of the amino-group in 3-nitro-2-aminotetrahydronaphthalene with iodine 3-nitro-2-iodotetrahydronaphthalene was obtained.



The iodo-compound proved readily capable of condensation by fusion with copper powder to yield 3:3'-dinitro-2:2'-ditetrahydrodinaphthyl.



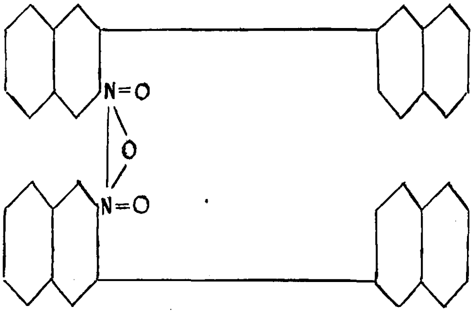
3:3'-Dinitro-2:2'-dinaphthyl was finally obtained by oxidation of the 3:3'-dinitro-2:2'-ditetrahydrodinaphthyl with bromine.

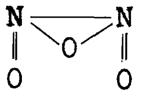


The oxidation by bromine of 3-nitro-2-iodotetrahydronaphthalene was observed but, while 3-nitro-2-iodonaphthalene was formed, the yield, due to excessive decomposition, was extremely poor and in consequence the condensation of 3-nitro-2-iodonaphthalene to 3:3'-dinitro-2:2'-dinaphthyl could not be investigated.

By reduction of 3:3'-dinitro-2:2'-dinaphthyl in acid solution 3:3'-diamino-2:2'-dinaphthyl was not obtained but a compound of empirical formula $C_{40}H_{26}N_2O_3$(found C = 82.5, 83.3, 83.1, H = 4.6, 4.6, 4.5, N = 4.9, 4.8, O(by difference) = 7.7; required C = 82.5, H = 4.5, N = 4.8, O = 8.2%). Recrystallised from benzene it formed greenish yellow plates, m.p. about 350° but first beginning to decompose at 320°; the yellow colour was not removed by treatment with animal charcoal. It dissolved in cold concentrated sulphuric acid to give a red solution which turned apple green on addition of a drop of concentrated nitric acid, a colour reaction which is suggestive of a compound containing an azoxy-grouping. It had no reaction with nitrous acid and, therefore, cannot be a primary or secondary amine.

In view of its properties the following formula derived by linking together two molecules of the dinitro-compound, is suggested as its constitution.



This involves two of the nitro-groups, one from each molecule of the dinitrodinaphthyl, condensing, by loss of one oxygen, to give the group  $\underset{O}{\underset{\|}{N}}\overset{\quad}{—}\!\!\!\underset{O}{\diagdown\!\diagup}\!\!\!—\underset{O}{\underset{\|}{N}}$ and the remaining two nitro-groups being eliminated by complete reduction to ammonia. The mode of formation of such a compound as suggested cannot be explained at the moment but the compound is being further investigated.

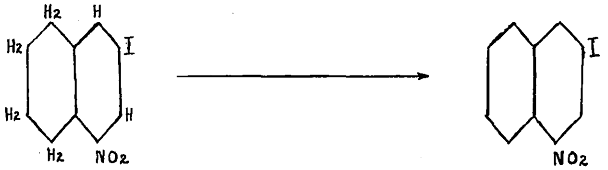
The reduction of 3:3'-dinitro-2:2'-dinaphthyl in alkaline solution, using excess sodium sulphide, was attempted but no pure compound could be isolated.

4:4'-DIAMINO-2:2'-DINAPHTHYL.

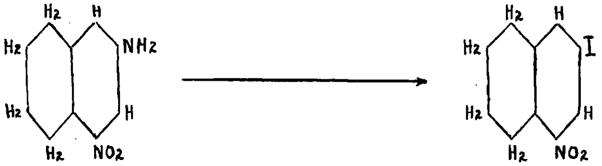
Attempts to prepare this base failed since 4:4'-dinitro-2:2'-dinaphthyl could not be synthesised although several methods were investigated.

4-Nitro-2-iodonaphthalene was obtained by two methods but in both cases only in quantity insufficient to condense it to 4:4'-dinitro-2:2'-dinaphthyl.

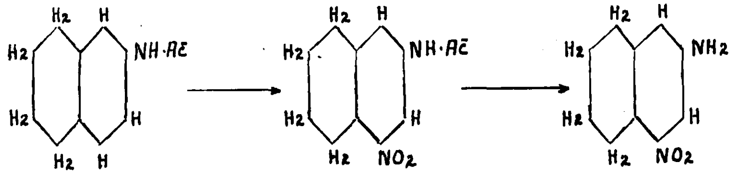
The constitution of 4-nitro-2-iodonaphthalene was established by its formation on oxidation, with bromine, of 4-nitro-2-iodotetrahydronaphthalene,



the 4-nitro-2-iodotetrahydronaphthalene, itself, being obtained by replacement with iodine of the amino-group in 4-nitro-2-aminotetrahydronaphthalene.



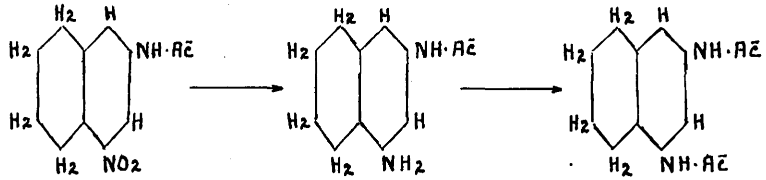
The 4-nitro-2-aminotetrahydronaphthalene was prepared by the hydrolysis of 4-nitro-2-acetylaminotetrahydronaphthalene obtained according to the method of Schroeter(Ann.,1922, 426,43) by the nitration in sulphuric acid solution of 2-acetylaminotetrahydronaphthalene. The nitration yields a mixture of the 1-, 3- and 4-nitro-isomers with predomination of the 4-nitro-compound which is readily obtained pure by fractional recrystallisation of the mixture from alcohol.



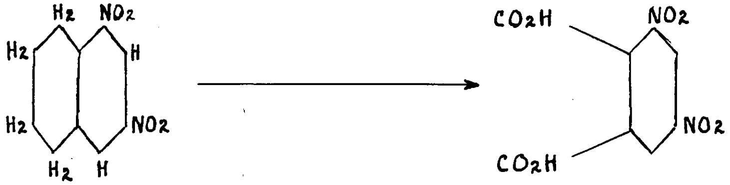
Schroeter has proved the structure of the 4-nitro-2-amino-:tetrahydronaphthalene in several ways chief among which are:-

(1). On removal of the amino-group 1-nitrotetrahydronaph-:thalene was obtained.

(2). By catalytic reduction of the nitroacetylamine and acetylation of the monacetyldiamine so formed 2:4(1:3)-diacetyldiaminotetrahydronaphthalene resulted.

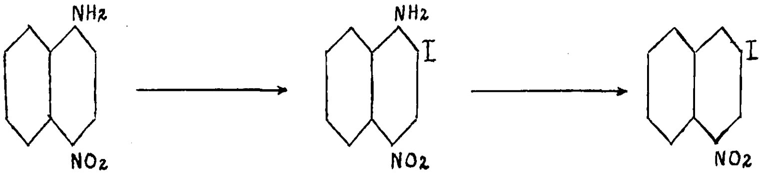


The same 1:3(2:4)-diacetyldiaminotetrahydronaphthalene was formed by the acetylation of the reduction product, 1:3(2:4)-diaminotetrahydronaphthalene, of 1:3(2:4)-dinitrotetrahydronaphthalene, the constitution of which(see p. 37) was established by formation on oxidation of 3:5-dinitrophthalic acid.



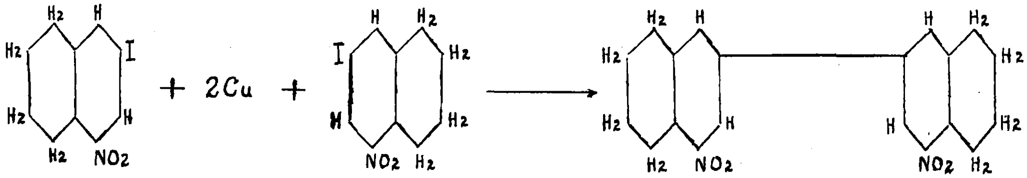
Due to the excessive decomposition which took place in the oxidation of 4-nitro-2-iodotetrahydronaphthalene to 4-nitro-2-iodonaphthalene the yield of the nitroiodonaphthalene was extremely poor.

By the action of iodine monochloride on 4-nitro-1-aminonaphthalene, a nitroiodoaminonaphthalene was readily obtained which on removal of the amino-group, by reduction of the diazonium compound with alcohol, gave 4-nitro-2-iodonaphthalene. Hence, it follows that the nitroiodoamine is 4-nitro-2-iodo-1-aminonaphthalene.



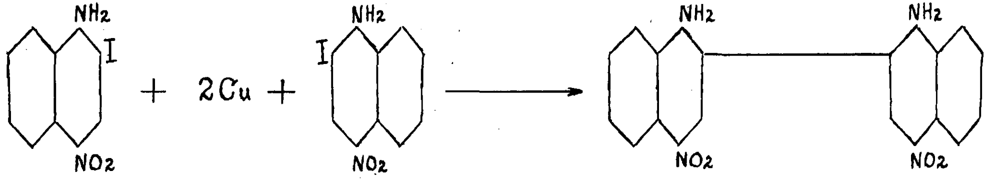
The yield of 4-nitro-2-iodonaphthalene by this method was again exceedingly poor.

An attempt to prepare 4:4'-dinitro-2:2'-ditetrahydrodinaphthyl, by condensation of 4-nitro-2-iodotetrahydronaphthalene by fusion with copper powder, failed, the high temperature necessary for the reaction to proceed causing complete decomposition.



The oxidation of 4:4'-dinitro-2:2'-ditetrahydrodinaphthyl to 4:4'-dinitro-2:2'-dinaphthyl, therefore, could not be studied.

A similar attempt to condense 4-nitro-2-iodo-1-aminonaphthalene to 4:4'-dinitro-1:1'-diamino-2:2'-dinaphthyl resulted in failure.

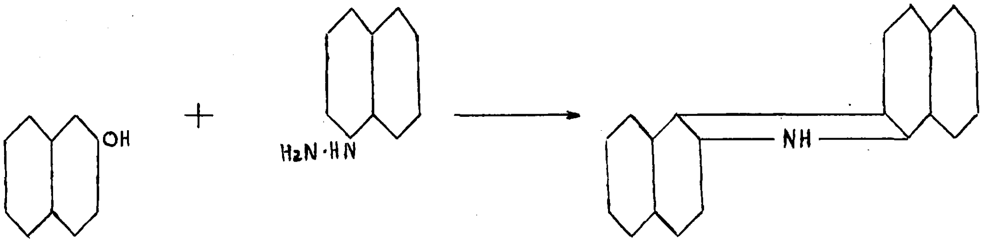


By fusion with copper powder the reaction proceeded so vigorously as to be uncontrollable, while refluxing in nitrobenzene solution with copper powder caused no reaction at all.

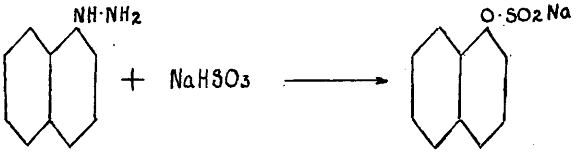
The possibility of preparing 4:4'-dinitro-2:2'-ditetrahydrodinaphthyl by nitration of 2:2'-ditetrahydrodinaphthyl was considered but the idea was discarded since it would be practically impossible, considering the number of possible positions that the nitro-groups might enter, to establish definitely the constitution of the dinitro-compound.

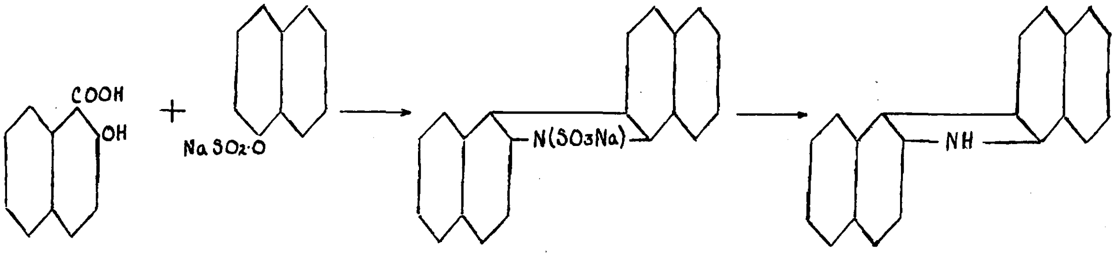
1:2'-IMINE-2:1'-DINAPHTHYL.

Japp and Maitland(J.C.S.,1903,83,274) by condensation of 2-naphthol and 1-naphthylhydrazine isolated 1:2'-imine-2:1'-dinaphthyl.



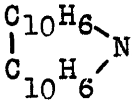
Bucherer and Schmidt(J.pr.Chem.,1909,79,369) by inter:action between 2-hydroxynaphthoic acid and sodium hydrogen sulphite in presence of 1-naphthylhydrazine obtained 1:2'-dinaphthyl-2:1'-carbazole sulphonic acid which on heating with hydrochloric acid or sodium hydroxide yielded 1:2'-imine-2:1'-dinaphthyl.





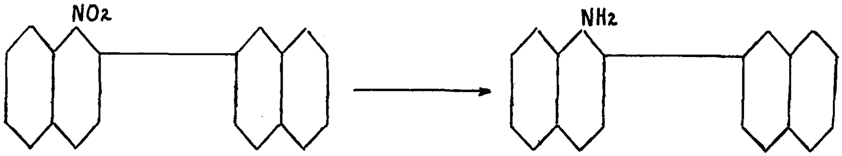
The base corresponding to this imine appears to be unknown.

β.DINAPHTHYLCARBAZOLE.

Ris(Ber.,1887,19,2240) by heating an intimate mixture of thio-β-dinaphthyleneimine and copper powder prepared a compound which he describes as β.dinaphthylcarbazole and gives the formula  $\begin{matrix} C_{10}H_6 & \diagdown & \\ | & & NH. \\ C_{10}H_6 & \diagup & \end{matrix}$ He advanced no constitution for the imine. From benzene if formed almost colourless needles, m.p. 170°.

1-AMINO-2:2'-DINAPHTHYL.

This base was obtained by reduction of 1-nitro-2:2'-di:naphthyl obtained by the mononitration of 2:2'-dinaphthyl(see p. 49).



It formed silvery plates of m.p. 220°.

NOTES on the PREPARATION of SYMMETRICAL DINAPHTHYL DERIVATIVES by CONDENSATION of the CORRESPONDING HALOGENDINAPHTHYL DERIVATIVE.

Ullmann prepared diphenyl, as well as its differently substituted symmetrical derivatives, by fusion of the corresponding halogenbenzene with copper powder(Ber.,1901,34, 2174; Ann.,1904,332,38). The reaction is

$$R.Hal + 2Cu + Hal.R = R.R + 2Cu.Hal$$

Ullmann found that this condensation runs very smoothly and used it in the preparation of many diphenyl derivatives, namely methyl-, nitro-, halogen-, sulpho-, amino-, oxy-, carboxy-, aldehydo-, keto-, quinoline- and azo-derivatives. The method not only made possible the preparation of numerous symmetrical diphenyl derivatives otherwise inaccessible but has this considerable advantage over the classical method of Fittig for the preparation of simple hydrocarbons i.e. symmetrical alkyl diphenyls, that it gives better results. Ullmann states in the introduction to his paper(Ann.,1904, 332,39), that the effect of copper on aromatic derivatives of iodine always runs smoothly without formation of any by-products. Concerning the conditions of the reaction Ullmann states:-

(1). Iodo-derivatives react with copper the most easily, less easily the bromo- and least easily the chloro-derivatives.

(2). The closer the acid group in the benzene nucleus is to the halogen the more smoothly the reaction runsparticularly nitro-groups because these cause greater reactivity of halogen.

(3). The finer the copper and the more intimately it be mixed then the more easily the reaction proceeds.

Chudožilov(Chem.Listy, 1925,19,187) has applied Ullmann's method for the preparation of numerous symmetrical dinitrodinaphthyls employing for the condensation the corresponding iodonitronaphthalene. His results show that, only when the nitro-groups are ortho to the halogen does the reaction proceed at all well. Thus 1:2- and 2:1-iodonitronaphthalenes react readily whereas employing 3- and 4-iodo-1-nitronaphthalenes condensation only takes place over 200° and is accompanied by much decomposition. In cases where the halogen and nitro-groups were in different nuclei e.g. in 2-iodo-5-nitronaphthalene and 2-iodo-8-nitronaphthalene, nothing definite was isolated from the reaction mixture.

Attempts to condense polynitro-derivatives, so successful in the benzene series, resulted in failure in all cases excepting in the condensation of 1-chloro-2:4-dinitronaphthalene but even in this case the yield was negligible.

The cause of the failure of the reaction with the halogen and nitro-groups in different nuclei and almost all the polynitro-derivatives was due to the fact that the reaction only proceeded at such high temperatures that the nitrodinaphthyls formed were decomposed.

Whereas 3-nitro-1-iodonaphthalene condenses to give a small yield of the dinitrodinaphthyl we have shown that the reaction completely fails when 3-nitro-1-bromonaphthalene is employed.

It is interesting to note that the ease of condensation of the ortho and meta nitroiodo-compounds in the tetrahydronaphthalene series is even more marked as while 2:1- and 3:2-iodonitrotetrahydronaphthalenes readily condensed the reaction failed when 1:3- and 2:4-iodonitrotetrahydronaphthalenes were employed.

No condensation of the nitrohalogen-naphthalenes could be effected by sodium; not even in the case of 1-nitro-2-iodonaphthalene and 2-nitro-1-iodonaphthalene, the reaction with which proceeded so readily by fusion with copper powder.

Further, under no conditions could 1-bromo-2-acetylnaphthylamine or 4-bromo-1-acetylnaphthylamine or the free bases be made to condense. Similarly, the reaction failed with 4-nitro-2-iodo-1-aminonaphthalene and 4-iodo-2-nitro-1-aminonaphthalene.

As a comparison with the benzene series, the action of sodium amalgam on o- and p-chloronitrobenzenes was noted. In the case of the o-compound a trace of 2:2'-dinitrodiphenyl was formed but the main reaction with both compounds was one of hydrolysis, the corresponding nitrophenol being formed.

In the preparation of 1:1'- and 2:2'-dinaphthyls fusion of the iodonaphthalene with copper powder gives good results. Schoepfle(J.Amer.C.S.,1923,<u>45</u>,1566) was only able to condense 1-bromonaphthalene at a high temperature and the yield obtained was barely 50% as compared with 74% when the iodo-compound is used(Ullmann, loc.cit.). The condensation of 2-chloronaphthalene by sodium gives 12-15% 2:2'-dinaphthyl (Chattaway and Lewis, J.C.S.,1894,65,879) as against 67% by fusion of the iodo-compound with copper(Ullmann, loc.cit.).

From the above results it is concluded that Ullmann's statement, as detailed at the beginning of this note, for the preparation of symmetrical diphenyls also holds good in both the naphthalene and tetrahydronaphthalene series.

EXPERIMENTAL.

The PREPARATION of 1:1'-AZOXY-, 1:1'-AZO- and 1:1'-HYDRAZO-:NAPHTHALENES.

1:1'-AZOXYNAPHTHALENE.

The method of Cumming and Steel(J.C.S.,1923,123,2464) is as follows:-

20g. 1-nitronaphthalene, 175c.cs. 90% alcohol, 50c.cs. water and 40g. ammonium chloride are heated together on a water bath at 70°, the nitronaphthalene going completely into solution but some ammonium chloride remaining undissolved. 28g. zinc dust are then added at such a rate as to maintain the temperature at 70-75°; above 75° some tarring takes place and below 70° nitronaphthalene is precipitated. The solution which gradually changes from yellow to red is filtered hot; the residue extracted with 90% alcohol and the combined extract and filtrate cooled. The yellow crystalline precipitate is removed and the filtrate concentrated under reduced pressure, a further deposit being obtained. When kept for more than 12 hours or if heated, the filtrate becomes dark in colour and decomposition takes place. The crystalline product is extracted with warm water to remove ammonium chloride and then several times with alcohol. White slightly efflorescent needles of a zinc compound remain which are insoluble in water but dissolve readily in dilute hydrochloric acid. Corresponding formula $5Zn(OH)_2.2NH_4Cl$.

The product obtained from the alcoholic extracts is recrystallised from alcohol and the yellow crystals deposited on cooling melt at 127° and give the properties of 1:1'-azoxynaphthalene.

<u>Influence of the Quantity of Zinc Added.</u>

Reductions were carried out as above employing 5g. nitronaphthalene, 44c.cs. 90% alcohol, 12.5c.cs. water and 10g. ammonium chloride but varying the quantity of zinc dust. The yields are noted below:-

(a). Using 5g. zinc dust: 1.00g.(23.7% of theory) 1:1'-azoxynaphthalene.
(b). .. 7g. .. .. : 1.35g.(32.0% .. ..) ..
(c). .. 8g. .. .. : 1.30g.(30.8% .. ..) ..

In the case of the 32% yield 59% 1-naphthylamine as estimated by N/2 $NaNO_2$, was formed.

A similar reduction carried out with a brisk current of carbon dioxide passing through the reaction mixture yielded 0.15g.(2.2% of theory) of azoxynaphthalene and 96.6% of theory of naphthylamine; further only a little double zinc salt was formed.

Carbon dioxide replaced by sulphur dioxide yielded only naphthylamine(99.8% of theory), no azoxynaphthalene or double zinc salt being formed.

Effect of Altering the Neutral Salt.

5g. nitronaphthalene were reduced, using 7g. zinc dust, by the standard method employing sodium chloride, magnesium chloride or calcium chloride in place of ammonium chloride. Little colour change was observed except in the case of calcium chloride when the reduction was most vigorous yielding a black product. Zinc chloride in presence of ammonium chloride had a similar action to calcium chloride. In no case was azoxynaphthalene or the double zinc salt formed but chiefly naphthylamine which was estimated in the usual way by means of standard nitrite. The results are tabulated below:-

Salt	% of 1-Naphthylamine.
Sodium chloride	53.7
Magnesium chloride	64.2
Calcium chloride	98.1
Zinc chloride and ammonium chloride	75.9

Effect of Altering Temperature and Solvent.

5g. nitronaphthalene were reduced as before, the temperature being maintained at 65-68°. The reduction proceeded slowly as was indicated by the rate of change of colour.

Azoxynaphthalene formed........ 0.3g. or 4.4% of theory.
Naphthylamine(estimated).............. 44.7% of theory.

A reduction at 65-66° in which ethyl alcohol was replaced by methyl alcohol again proceeded slowly.

Azoxynaphthalene formed........ 0.2g. or 2.9% of theory.

Naphthylamine(estimated).............. 40.0% of theory.

Modification of the Reduction by Adding the Water to a Mixture of the Nitro-compound in Absolute Alcohol, Ammonium Chloride and Zinc Dust.

5g. nitronaphthalene were dissolved in 45c.cs. absolute alcohol and 10g. ammonium chloride and 7g. zinc dust added. The temperature was raised to 70°, no reaction taking place. 12.5g. water were then slowly added(2-3 drops at a time) during 30 minutes when the solution had attained the usual bright red colour. On working up as before, 1.31g. azoxynaphthalene or 31% of theory were obtained.

Modification of the Reduction for the Preparation of Large Quantities of 1:1'-Azoxynaphthalene.

80g.(largest practical laboratory scale) nitronaphthalene were reduced in the same manner as in reduction (b), p. 68, the requisite quantities of ammonium chloride, water, alcohol and zinc dust being employed but the mother liquor, obtained on removal of the crystalline deposit, instead of being concentrated under reduced pressure allowed to stand 72 hours in absence of light. The copious crystalline deposit was removed, washed with water and recrystallised from alcohol with addition of animal charcoal. Yield = 18g. or 26% of theory.

Due to the large amount of inorganic matter present and its tendency to crystallise out, the concentration under reduced pressure of large quantities of solution proved impracticable. In the above modification a little tar is produced but is easily removed by means of animal charcoal.

Reaction between Zinc and Ammonium Chloride.

(1). 0.5g. ammonium chloride in aqueous solution and 0.32g. zinc dust(theoretical quantity + 5% excess as required by the equation,

$$2NH_4Cl + Zn = ZnCl_2 + 2NH_3 + H_2)$$

were refluxed for 3 hours in a Kjeldahl apparatus and the ammonia given off estimated in the usual way.

Ammonium chloride decomposed.......... 4.4 per cent.

(2). 2g. ammonium chloride in aqueous solution and 4.6g. zinc dust were refluxed for 11 hours and the ammonia estimated.

Ammonium chloride decomposed......... 22.5 per cent.

(3). An experiment was carried out under conditions similar to those obtaining during the reduction of 1-nitronaphthalene.

44c.cs. 90% alcohol, 12.5c.cs. water and 10g. ammonium chloride were heated to 70-75°. 6.5g. zinc dust were added and the whole refluxed for 4.5 hours.

Ammonium chloride decomposed.......... 4.38 per cent.

(4). The percentage ammonium chloride decomposed during the reduction of 1-nitronaphthalene was obtained as follows:-

5g. 1-nitronaphthalene were dissolved in 45c.cs. absolute alcohol and 10g. ammonium chloride and 7g. zinc dust added. The whole was maintained at 70-75^{0} on a water bath and 12.5 c.cs. water added gradually during 30 minutes.

Ammonium chloride decomposed.......... 2.68 per cent.

(5). Ammonium chloride and excess zinc dust were heated together in the dry state in a test tube. Ammonia fumes were copiously evolved but little ammonium chloride was volatilised. A fused mass of zinc chloride finally remained in which the excess zinc melted to a silvery ball. Hydrogen was shown to be evolved by the fact that the gases collected over acidified water exploded on ignition.

1:1'-AZONAPHTHALENE.

Neutral Reduction of 1:1'-Azoxynaphthalene.

1g. 1:1'-azoxynaphthalene, dissolved in a mixture of 66c.cs. 90% alcohol and 3c.cs. water containing 3g. ammonium chloride, was reduced at 70-75° employing 0.3g. zinc dust(5% excess of theory to yield 1:1'-azonaphthalene). The pale red solution was filtered hot and the filtrate cooled when a white crystalline deposit was thrown down which, on extraction with alcohol, yielded a few white crystals, m.p. 274°, corresponding to 1:1'-hydrazonaphthalene. The mother liquor, on concentration under reduced pressure, yielded azoxynaphthalene but no azonaphthalene.

Preparation of 1:1'-Azonaphthalene.

(1). By the method of Nietzki and Goll(Ber.,1885,18,297; 3252). The following modification was found to give the best results:-

9g. 4-amino-1:1'-azonaphthalene were dissolved in 900c.cs. absolute alcohol and 26c.cs. concentrated sulphuric acid slowly added when the solution turned a deep purple. Excess amyl nitrite was then added gradually and the whole refluxed until the solution had attained a deep reddish-yellow. Addition of water precipitated a brownish mass which was removed and recrystallised several times from glacial acetic acid with addition of animal charcoal. Orange red needles, m.p. 188°, of 1:1'-azonaphthalene were obtained. A further yield was obtained by addition of water to the glacial acetic acid filtrates and recrystallising the precipitate from a little more glacial acetic acid. The total yield was 3g.

(2). By the method of Hantzsch and Schmiedel(Ber.,1897, 30,82).

1g. pure 1-naphthylamine is suspended in 40c.cs. water and 2g. concentrated hydrochloric acid and diazotised in the cold with 0.6g. sodium nitrite. The solution is filtered and the dark red diazonium solution cooled and treated with an equally cold alkaline solution of potassium sulphite. Without evolution of gas, an intensively dark orange coloured precipitate is formed. This is immediately filtered off and well washed with ice-cold water. By repeated washing its orange colour is converted due to decomposition into brownish-red.

The 1-naphthalene syndiazonium sulphonate so formed is allowed to stand for a day at the ordinary temperature when the decomposition to the azonaphthalene becomes complete. The dried residue is extracted with chloroform, the extract concentrated and the crystalline mass so obtained recrystallised from glacial acetic acid.

Using 20g. 1-naphthylamine 2.5g. 1:1'-azonaphthalene were obtained as orange red needles, m.p. 188°.

Nietzki and Goll give m.p. 190°, Hantzsch and Schmiedel 188-189°, Cumming and Steel(J.C.S.,1923,123,2464) 186° for

1:1'-azonaphthalene while we determined it to be 188°. The variation may be explained by the fact that the azonaphthalene begins to sublime about 170°.

Reactions between 1:1'-Azoxynaphthalene and Benzyl Alcohol, Benzaldehyde and a Mixture of Benzaldehyde and Quinoline.

The azoxynaphthalene employed was the yellow symmetrical variety, m.p. 127°.

(1). 1:1'-Azoxynaphthalene and Benzyl Alcohol.

A solution of 5g. azoxynaphthalene in 70c.cs. benzyl alcohol was employed and the following results noted:-

(a). On maintaining for several hours at 100° no colour change took place.

(b). At 140° the colour slowly deepened until after 6 hours heating it had attained an intense red.

(c). At 170° the colour change was complete in 4 hours.

The red solution on concentration under reduced pressure, a stream of carbon dioxide not air, which would oxidise any azonaphthalene that might be present, being employed to give even boiling, yielded a deep red solid mass which, on slow recrystallisation from alcohol, formed bright scarlet crystals, m.p. 127°, and giving the properties of unsymmetrical 1:1'-azoxynaphthalene. Concentration of the red solution under ordinary pressure or steam distillation to remove benzyl alcohol caused tarring. In no case was azonaphthalene obtained.

1-Nitronaphthalene under similar conditions had no reaction.

(2). 1:1'-Azoxynaphthalene and Benzaldehyde.

1.5g. azoxynaphthalene were refluxed with 40c.cs. benzaldehyde for 1½ hours, the colour rapidly changing to a deep red. On concentration under reduced pressure and slow recrystallisation of the product obtained from alcohol unsymmetrical azoxynaphthalene was again obtained but no azonaphthalene.

1-Nitronaphthalene had no reaction with benzaldehyde even on refluxing for several days.

(3). 1:1'-Azoxynaphthalene and Benzaldehyde and Quinoline.

2g. azoxynaphthalene were heated at 170° with 60c.cs. benzaldehyde and 30c.cs. quinoline for 12 hours. On concentration, under reduced pressure, to small bulk the product obtained was removed, washed with ether, in which it was practically insoluble, to remove benzaldehyde and quinoline and recrystallised twice from benzene. It consisted of brownish green prismatic needles, m.p. 230°, and gave the reactions of 2-hydroxy-1:1'-azonaphthalene(found N = 9.35, 9.30; required N = 9.39%). A mixed m.p. with 2-hydroxy-1:1'-azonaphthalene, m.p. 230°, obtained by coupling diazotised 1-naphthylamine to 2-naphthol, showed no depression. The product of Cumming and Steel, obtained by continued exposure of 1:1'-azoxynaphthalene to light, gave m.p. 230° after one recrystallisation from benzene and proved identical with the 2-hydroxy-1:1'-azonaphthalene obtained above.

The filtrate, obtained on removal of the hydroxyazonaphthalene, after extracting with dilute hydrochloric acid to remove quinoline and with sodium carbonate to remove benzoic acid yielded a sticky mass which could not be made to give crystals. However, from appearance and previous experience it probably consisted of unsymmetrical 1:1'-azoxynaphthalene.

The yield of 2-hydroxy-1:1'-azonaphthalene was 33%.

The above experiment repeated in absence of light yielded as before 2-hydroxy-1:1'-azonaphthalene in similar yield.

The hydroxyazonaphthalene is insoluble in dilute sodium hydroxide and but slightly soluble in alcohol. It gives a blue solution with concentrated sulphuric acid which goes red on dilution.

(4). 1:1'-Azoxynaphthalene and Quinoline.

2g. azoxynaphthalene on heating with 20c.cs. quinoline at 170° for 12 hours and subsequent treatment as before yielded both unsymmetrical azoxynaphthalene and hydroxyazonaphthalene.

Action of Light on Unsymmetrical 1:1'-Azoxynaphthalene.

The azoxy-compound was dissolved in boiling alcohol and exposed to ultra-violet light for 20 hours. The solution on standing 24 hours deposited greenish coloured crystals which, recrystallised from benzene, gave 2-hydroxy-1:1'-azonaphthalene, m.p. 230°. Continued exposure of the hydroxyazo-compound to light caused no further change.

THE REDUCTION TO THE HYDRAZO-STAGE OF SYMMETRICAL AND UNSYMMETRICAL 1:1'-AZOXYNAPHTHALENES AND OF 1:1'-AZONAPHTHALENE IN NEUTRAL, ALKALINE AND ACID SOLUTIONS.

In Neutral Solution.

(1). Symmetrical 1:1'-Azoxynaphthalene.

(a). Isolation of unsymmetrical 1:1'-hydrazonaphthalene and naphthidine.

3g. azoxynaphthalene, 200c.cs. alcohol, 2c.cs. water and 9g. ammonium chloride were heated on a water bath to 70° and zinc dust added until the solution was rendered colourless, about 4.5g. being necessary. After rapid filtration the solution, which had slightly reddened, was decolourised by addition of a little more zinc dust and evaporated nearly to dryness under reduced pressure. The solid matter which separated was removed, quickly dried and extracted with petroleum ether. The white crystalline mass so obtained, gave after five fractional recrystallisations from the same solvent, unsymmetrical 1:1'-hydrazonaphthalene, m.p. 153° with decomposition, turning red(found N = 9.92, 9.90; required N = 9.86%) and naphthidine. The latter recrystallised from alcohol formed colourless plates, m.p. 202°; a mixed m.p. with the naphthidine obtained by the method of Cumming and Steel(reduction of 1:1'-azoxynaphthalene by stannous chloride in hydrochloric acid solution) gave 202°. The yields of the pure compounds were extremely poor.

Filtration of the reduction mixture, after being rendered colourless, into water containing ammonium sulphide yielded a badly discoloured mass from which nothing definite could be isolated.

Unsymmetrical 1:1'-hydrazonaphthalene is insoluble in water, sparingly soluble in alcohol and petroleum ether but readily soluble in benzene. In the solid state it is only slightly soluble in hot or cold dilute or concentrated hydrochloric acid, completely insoluble in hot or cold oxalic acid but readily soluble in cold dilute hydrochloric acid when in a fine state obtained by first dissolving it in alcohol and then precipitating by water. This solution had no reaction with nitrous acid. Treatment of a dilute hydrochloric acid suspension of the compound with a drop of bleaching powder solution gives a bluish violet colour and on standing a greenish yellow solid is precipitated; addition of excess bleaching powder solution discharges the colour. On exposure to air the compound turns pale yellow while an alcoholic solution reddens somewhat when a current of air is passed through.

Similarly to the symmetrical compound a hot alcoholic solution of unsymmetrical 1:1'-hydrazonaphthalene was converted, by addition of dilute hydrochloric acid, into the base dinaphthyline, m.p. 281°. In the case of the unsymmetrical variety sulphurous acid was sufficient to cause the conversion.

(b). Isolation of the double zinc salt $9Zn(OH)_2.4NH_4Cl.6H_2O$.

The previous experiment was repeated but the filtrate, obtained after filtration of the reduction mixture, cooled when a white crystalline mass was precipitated. This was removed and washed with water to remove free ammonium chloride and finally the organic matter present extracted from the residue by washing several times with an alcohol-water mixture(200c.cs. alcohol and 9c.cs. water) at 70-75°. White needles of a double zinc salt remained; 90% boiling alcohol decomposed the salt leaving a residue of zinc oxide and so a more dilute alcohol and a lower temperature were employed. The salt corresponded to the formula $9Zn(OH)_2.4NH_4Cl.6H_2O$(found Zn = 48.67, Cl = 11.64, NH_4 = 5.90; required Zn = 48.38, Cl = 11.86, NH_4 = 5.92%).

(2). Unsymmetrical 1:1'-Azoxynaphthalene; isolation of naphthidine and probably unsymmetrical 1:1'-hydrazonaphthalene and dinaphthyleneimine.

1g. unsymmetrical 1:1'-azoxynaphthalene dissolved in a mixture of 150c.cs. alcohol and 10c.cs. water containing 6g. ammonium chloride was reduced at 70-75° using zinc dust, the addition of the zinc dust being continued until the solution was rendered colourless. After rapid filtration and decolourisation of the filtrate by addition of a little more zinc dust the alcohol was nearly all removed under reduced pressure. The solid matter which had separated was removed, dried and extracted with benzene. On concentration of the benzene solution to about 20c.cs. and cooling, naphthidine crystallised out. Recrystallised several times from alcohol it finally melted at 202°. By further concentration of the benzene filtrate from the naphthidine, two sets of crystals were obtained. The first recrystallised as often as possible from benzene melted at 180-185° but first turning yellow at 140-150°; this yellowing is characteristic of unsymmetrical 1:1'-hydrazonaphthalene and this fraction, therefore, probably contained a trace. The second crop recrystallised as often as possible from benzene gave m.p. 212-215°. This gave a colour test for dinaphthyleneimine, m.p. 221°, as it dissolved in concentrated sulphuric acid to give a red solution which turned green on addition of a drop of dilute nitric acid.

(3). 1:1'-Azonaphthalene; isolation of dinaphthyline.

1g. azonaphthalene was dissolved in 325c.cs. 90% alcohol and 12c.cs. water followed by 15g. ammonium chloride added. The reduction was carried out at 70-75°, zinc dust being added until the solution became colourless. On filtration into water containing ammonium sulphide, to prevent oxidation, a yellowish precipitate was thrown down. This extracted with absolute alcohol and the crystals so obtained recrystallised several times from the same solvent yielded a few needles of dinaphthyline, m.p. 281°. The deep red colour of the mother liquors indicated that hydrazonaphthalene had been present although none was isolated, complete oxidation having taken place in the process of working up.

In Alkaline Solution.

(1). Symmetrical 1:1'-Azoxynaphthalene.

(a). Isolation of unsymmetrical 1:1'-hydrazonaphthalene.

4g. azoxynaphthalene dissolved in 300c.cs. 90% alcohol containing 8g. sodium hydroxide were heated to the boil and zinc dust added until the solution was rendered nearly colourless. Without filtering, the most of the alcohol was removed under reduced pressure. During concentration the reduction was completed, the solution going completely colourless. When nearly to dryness the contents of the flask were removed, quickly dried and extracted with benzene. The benzene solution was concentrated and cooled when a copious yield of a yellowish product was obtained. This recrystallised twice from benzene formed colourless plates, m.p. 153° with decomposition, turning red, of unsymmetrical 1:1'-hydrazonaphthalene. The yield obtained was 1.3g. or 34% of theory.

Under similar conditions azoxybenzene yielded the usual hydrazobenzene, m.p. 131°.

(b). Isolation of the base dinaphthyline.

4g. azoxynaphthalene dissolved in 300c.cs. 90% alcohol containing a solution of 30g. sodium hydroxide were reduced at the boil, zinc dust being added until the solution was completely colourless. The whole was then refluxed for ½ hour when the solution was concentrated under ordinary pressure and rapidly filtered. The solid residue was dried, extracted with benzene and the crystals so obtained recrystallised 3 times from benzene when colourless plates, m.p. 281°, of dinaphthyline were obtained; the base recrystallised from alcohol gives colourless needles of the same melting point. A mixed m.p. with the dinaphthyline, m.p. 281°, obtained by the acid conversion of unsymmetrical 1:1'-hydrazonaphthalene gave no depression.

The yield obtained was 0.9g.

(2). Unsymmetrical 1:1'-Azoxynaphthalene; isolation of unsymmetrical 1:1'-hydrazonaphthalene.

1g. unsymmetrical azoxynaphthalene was dissolved in 100 c.cs. 90% alcohol containing 3g. sodium hydroxide. The solution was reduced at the boil with zinc dust, the colour being rapidly discharged. Without filtering, the colourless solution was concentrated under reduced pressure and the solid matter which separated quickly removed, dried and extracted with benzene. The benzene extract, on concentration, gave unsymmetrical 1:1'-hydrazonaphthalene which, recrystallised from benzene, formed colourless plates, m.p. 153° with decomposition, turning red.

(3). 1:1'-Azonaphthalene; isolation of unsymmetrical 1:1'-hydrazonaphthalene.

1g. azonaphthalene was suspended in 150c.cs. 90% alcohol containing 4.5g. sodium hydroxide and, using zinc dust, the whole reduced at the boil until colourless when all had passed into solution. The reduction mixture was quickly filtered into water containing a little ammonium sulphide and the slightly yellow precipitate removed and rapidly dried. This on extraction and recrystallisation of the product obtained from benzene yielded unsymmetrical 1:1'-hydrazonaphthalene, m.p. 153° with decomposition, turning red. The mother liquors, which were of a deep red, gave, on concentration under reduced pressure, azonaphthalene and so it is concluded that some symmetrical hydrazonaphthalene must have been present but had been oxidised back to azonaphthalene.

Concentration, under reduced pressure, of the reduction mixture, after being rendered colourless, gave rise to a mixture of compounds consisting of unsymmetrical 1:1'-hydrazonaphthalene, m.p. 153° with decomposition, turning red, and probably dinaphthyline although no definite m.p. was obtained for the latter compound.

In Acid Solution.

(1). Symmetrical 1:1'-Azoxynaphthalene.

(a). Reduction with stannous chloride: isolation of naphthidine.

The method of Cumming and Steel(J.C.S.,1923,123,2464) was employed.

The azoxynaphthalene is dissolved in glacial acetic acid and a solution of stannous chloride in hydrochloric acid added until the yellow colour is discharged. Concentrated hydrochloric acid is then added and the hydrochloride of the base filtered off. The hydrochloride is recrystallised several times from dilute hydrochloric acid and the free base finally liberated by addition of ammonia solution. The naphthidine repeatedly recrystallised from alcohol gave m.p. 202° and not 198° as given by Cumming and Steel.

(b). Reduction with zinc and hydrochloric acid; isolation of dinaphthyleneimine.

2g. azoxynaphthalene were dissolved in 300c.cs. 90% alcohol and the solution cooled to 40° when it was treated with dilute hydrochloric acid. Zinc dust was added until the solution was rendered colourless when, after rapid filtration, it was concentrated, under reduced pressure, to small bulk. The solid which had separated was removed, dried and extracted with petroleum ether. Colourless leaflets were obtained and these recrystallised from petroleum ether gave dinaphthyleneimine, m.p. 221°.

The reduction carried out employing acetic acid in place of hydrochloric acid gave the same compound.

In one reduction, by keeping the temperature as low as possible- below 30°- dinaphthyleneimine was not obtained but the parent base dinaphthyline along with a little naphthidine.

(2). Unsymmetrical 1:1'-Azoxynaphthalene; isolation of naphthidine.

Unsymmetrical azoxynaphthalene in glacial acetic acid solution was reduced with a hydrochloric acid solution of stannous chloride, the procedure being similar to the stannous chloride reduction of the symmetrical compound. Naphthidine, m.p. 202°, was obtained. It was noted that the rate of discharge of colour on addition of the zinc dust was much slower in the case of the unsymmetrical azoxynaphthalene than the symmetrical variety.

(3). 1:1'-Azonaphthalene; isolation of naphthidine.

The method of Nietzki and Goll(Ber.,1885,18,3252) was employed.

The azonaphthalene is dissolved in glacial acetic acid and reduced with stannous chloride solution in hydrochloric acid. The procedure is similar to the stannous chloride reduction of the azoxynaphthalenes. Naphthidine, m.p. 202°, was obtained.

The reduction proceeds much more smoothly than with the azoxynaphthalenes and gives a nearly theoretical yield.

A summary of all the above results is contained on the appended table.

SUMMARY OF RESULTS.

Reducing medium.	1:1'-Azoxynaphthalene		1:1'-Azonaphthalene
	Symmetrical	Unsymmetrical	
Acid. Alc. HCl over 40°	Dinaphthyleneimine m.p. 221°		
Alc. HCl under 40°	Dinaphthyline m.p. 281° and Naphthidine m.p. 202°		
$SnCl_2$ in HCl	Naphthidine m.p. 202°	Naphthidine m.p. 202°	Naphthidine m.p. 202°
Neutral.	Unsym. Hydrazonaphthalene m.p. 153° and Naphthidine m.p. 202°	Naphthidine m.p. 202° and unsym. Hydrazonaphthalene and Dinaphthyleneimine *	Dinaphthyline m.p. 281°
To Azo-stage	Sym. Hydrazonaphthalene m.p. 274° and unchanged azoxynaphthalene		
Alkaline. Alc. NaOH (3%)	Unsym. Hydrazonaphthalene m.p. 153°.	Unsym. Hydrazonaphthalene m.p. 153°	Unsym. Hydrazonaphthalene m.p. 153°
Alc. NaOH (10%)	Dinaphthyline m.p. 281°		

* The quantity available was insufficient to give definite melting points but evidence of their presence was established by other means (see p.80).

PREPARATION of 2:2'-DIAMINO-1:1'-DINAPHTHYL by REDUCTION of 2:2'-AZONAPHTHALENE.

2:2'-Azonaphthalene.

The method of Hantzsch and Schmiedel(Ber.,1897,30,82) is as follows:-

1g. pure 2-naphthylamine is suspended in 40g. water and 2g. concentrated hydrochloric acid and diazotised in the cold with 0.6g. sodium nitrite. The solution is filtered and the bright red diazonium solution well cooled and treated with an equally cold alkaline solution of potassium sulphite. 2-Naphthalene-syndiazonium sulphonate is immediately precipitated as a beautiful and clean reddish orange salt. The sulphonate rapidly decomposes even if immediately removed and washed. The solution is filtered, well washed and the residual reddish brown mass extracted with hot chloroform. The extract, on concentration and cooling, gives 2:2'-azonaphthalene as dark red prisms.

From 20g. 2-naphthylamine and treated as above 10g. 2:2'-azonaphthalene were obtained. The m.p. recorded was 208°; Hantzsch and Schmiedel give 204°: Meisenheimer and Witte 208°.

2:2'-Diamino-1:1'-Dinaphthyl.

The method of Meisenheimer and Witte(loc.cit.) is as follows:-

3g. 2:2'-azonaphthalene dissolved in 250c.cs. glacial acetic acid are reduced at the boil with 2g. zinc dust. The solution, which rapidly becomes colourless, is filtered and the filtrate diluted with 4 times its volume of water. After ½ hour the precipitate is removed and recrystallised from alcohol when the difficultly soluble 2:2'-diamino-1:1'-di:naphthyl, m.p. 191°, is obtained.

By reduction of 10g. 2:2'-azonaphthalene 2.5g. 2:2'-di:amino-1:1'-dinaphthyl, m.p. 191°, were obtained as slightly discoloured needles.

It was noted that the alcoholic filtrate from the recrys:tallisation of the base, on concentration, did not give a further crop of the base but of the imine 2:2'-imine-1:1'-dinaphthyl, m.p. 158°(Meisenheimer and Witte 157°). The imine must have been formed from the base, by loss of ammonia, while in acid solution during the reduction process(vide dinaphthyline).

CONSTITUTION and SYNTHESIS of the NAPHTHIDINE BASES.

NAPHTHIDINE: 4:4'-DIAMINO-1:1'-DINAPHTHYL.

Attempted Preparation of 4:4'-Diacetyldiamino-1:1'-Dinaphthyl by Condensation of 4-Bromo-1-Acetylnaphthylamine.

(1). Using Copper-bronze Powder.

1g. 4-bromo-1-acetylnaphthylamine was maintained at 200°(10° above its m.p.) and 1g. copper-bronze powder gradually added. No rise in temperature or change in appearance of the copper was observed. Even at 200° a strong smell of acetic acid was noted while on raising the temperature to 230° visible decomposition set in, the liquid turning a deep red. On cooling, an oily mass was obtained which could not be made to yield crystals.

(2). Employing Sodium.

The reaction was carried out, using 2.46g.(1/100 mol) 4-bromo-1-acetylnaphthylamine and 0.25g.(excess) sodium, in various solvents with a view to obtaining a gradual rise in temperature. The results are noted below:-

(a). Suspending the bromo-compound in 200c.cs. anhydrous ether and refluxing for 16 hours no change in the sodium was observed and on removal of the ether the bromoacetylnaphthyl-

:amine was recovered unchanged.

(b). Using 200c.cs. dry benzene and refluxing for 14 hours the result was similar.

(c). Using 200c.cs. dry toluene and refluxing for 10 hours similar results were again obtained.

(d). Using 200c.cs. dry xylene and refluxing for 10 hours a darkening of the solution was observed. The sodium, however, remained unchanged, the darkening being due to decomposition of the bromo-compound. No condensation product was isolated.

(e). Using 200c.cs. dry dimethylaniline and refluxing for 10 hours decomposition rapidly set in. As before the sodium remained unchanged and no condensation product was isolated.

(3). Fusion with Sodium Amalgam.

An amalgam containing 2½% sodium was maintained at 200-210° and 2g. bromoacetylnaphthylamine gradually added, the whole being continuously stirred. A dirty green colour developed and on completion of the addition the mass had become sticky. On addition of each batch of the bromo-compound a strong smell of naphthylamine was observed.

On cooling, the mass became solid apart from much free mercury, the presence of which showed that some reaction had taken place. The filtrate, obtained by extraction of the solid mass with benzene, gave after decolourisation with animal charcoal and concentration to about 40c.cs. a deposit of unchanged 4-bromo-1-acetylnaphthylamine, m.p. 190°. On removal of the bromo-compound and further concentration of the benzene solution a second crop of crystals was obtained. These recrystallised several times from benzene gave m.p. 159^{o} and showed the properties of 1-acetylnaphthylamine, m.p. 159^{o}; a mixed m.p. with 1-acetylnaphthylamine gave no depression. No condensation product was obtained.

(4). Employing Aluminium Chloride.

4g. bromoacetylnaphthylamine were dissolved in 75c.cs. anhydrous acetone and 2.4g. 1-naphthylamine added. To the solution 2g. anhydrous aluminium chloride, followed by 25 c.cs. carbon disulphide, were gradually added. At the end of half an hour, the whole having been maintained at gentle reflux, the aluminium chloride remained unchanged and, on removal of the solvents, the bromoacetylnaphthylamine was recovered.

Similar results were obtained when 4g. aluminium chloride (a large excess) were employed and refluxing continued for 6 hours.

Attempted Preparation of 4:4'-Diamino-1:1'-Dinaphthyl by Condensation of 4-Bromo-1-Naphthylamine.

2.22g.(1/100 mol) 4-bromo-1-naphthylamine, as in the case of the acetyl-compound, were refluxed for varying periods of time in different solvents and in presence of 0.25g. sodium. Again no condensation occurred. The free base is much less stable than the acetyl-compound as the solutions at the end of the time of refluxing had turned a dirty red colour.

Preparation of 4:4'-Dinitro-1:1'-Dinaphthyl.

(1). By Condensation of 4-Nitro-1-Iodonaphthalene.

4-Nitro-1-Aminonaphthalene.

The nitration was carried out in accordance with the directions of Lellmann and Remy(Ber.,1886,19,796) and the separation of the isomers formed, by the method of Morgan and Micklethwait(J.C.S.,1905,87,928).

100g. 1-acetylnaphthylamine are dissolved in 600c.cs. glacial acetic acid and during stirring a mixture of 45g. nitric acid(sp.gr. 1.54) and 40g. glacial acetic acid is added drop by drop to the cold solution, the temperature not being allowed to exceed 35°. On standing 24 hours a crystalline deposit consisting of equal parts of the 4- and 2-nitro-derivatives separates out. This is removed, washed and dissolved in the minimum quantity of hot alcohol and treated with half the necessary amount of potassium hydroxide solution required to hydrolyse the total acetyl-compounds present. On maintaining for 20 minutes at the boil the hydrolysis of the 4-nitro-1-acetylnaphthylamine is complete while the 2-nitro-1-acetylnaphthylamine remains unaffected. The crystals obtained on allowing the solution to stand 24 hours are dissolved in just sufficient boiling ethyl acetate and the solution rapidly cooled when the 2-nitro-1-acetylnaphthyl:amine is completely precipitated. The filtrate is evaporated to dryness and the residue recrystallised from alcohol. 20g. 4-nitro-1-naphthylamine were obtained as orange needles of m.p. 191-192°(Morgan and Micklethwait, 191-192°).

The 2-nitro-1-acetylnaphthylamine is recrystallised from alcohol. 17g. were obtained as pale yellow needles of m.p. 201°(Morgan and Micklethwait, 199-200°).

4-Nitro-1-Iodonaphthalene.

The method of Meldola(J.C.S.,1885,47,519) was utilised as follows:-

14g. 4-nitro-1-naphthylamine were dissolved in a slight excess of glacial acetic acid and the solution rapidly cool:ed, the precipitation of the nitro-compound being completed by addition of about 200c.cs. dilute sulphuric acid. 5.5g. sodium nitrite dissolved in 50c.cs. water were then slowly added. The solution after stirring 5-10 minutes was filtered to remove the small quantity of undiazotised base and the filtrate gradually added to a solution of 20g. potassium iodide in 200c.cs. water. The crude iodo-compound so formed was dissolved in alcohol, the solution refluxed with animal charcoal and filtered into dilute sodium hydroxide to remove all free iodine. The precipitate was well washed and recrys:tallised from alcohol when 9.5g. 4-nitro-1-iodonaphthalene were obtained as pale yellow needles, m.p. 123°(Meldola, 123°).

The use of concentrated sulphuric acid, as recommended by Meldola, as solvent for the base and diazotising by addition of solid sodium nitrite does not give too good results causing even more tarring than the method above described. Meldola mentions no yield.

4:4'-Dinitro-1:1'-Dinaphthyl.

(1). By Condensation of 4-Nitro-1-Iodonaphthalene.

(a). Using copper powder.

Schoepfle(J.Amer.C.S.,1923,45,1566) by fusion of the nitroiodonaphthalene with copper powder for 4 hours at 220-230° obtained a yield of 52% of theory of 4:4'-dinitro-1:1'-dinaphthyl. By a similar fusion but maintaining the temperature for 80 minutes at 260° Chudožilov(Chem.Listy, 1925, 19,187) obtained a greatly diminished yield.

It has been found that, on refluxing the nitroiodo-compound in nitrobenzene solution for 6 hours with copper powder, no condensation took place.

(b). Attempted condensation with sodium.

0.3g. iodo-compound was refluxed for 16 hours, both in ether and toluene solutions, with 0.25g. sodium. The addition of dry ethyl acetate failed to aid the reaction, the sodium remaining unchanged and the iodo-compound being completely recovered.

(2). By Attempted Decomposition of 4-Nitronaphthalene-1-Diazonium Sulphate with Copper Powder.

The 4-nitro-1-aminonaphthalene was dissolved in alcohol and the alcoholic solution gradually added, with stirring, to a sulphuric acid solution of nitrous acid. The diazonium solution was then rendered nearly neutral to Congo Red by addition of sodium carbonate when it was treated with excess freshly prepared copper powder. A strong smell of acetaldehyde was noted on addition of the copper to the diazonium solution. The vigorous reaction which took place was complete after stirring for ¼ hour. On addition of water to the filtrate from the reaction mixture a yellowish precipitate was obtained which, recrystallised from alcohol, gave m.p. 61° and showed the properties of 1-nitronaphthalene.

Replacement of acetone as solvent gave rise to an extremely vigorous reaction and only tars were isolated.

(3). By Dinitration of 1:1'-Dinaphthyl.

1:1'-Dinaphthyl.

The preparation of 1:1'-dinaphthyl and its subsequent nitration were carried out according to the method of Schoepfle (loc.cit.).

200g. 1-bromonaphthalene, 75g. copper powder and 5g. iodine are heated for 4-5 hours at 280-285°. The cooled reaction mixture is extracted with benzene and the extract, after removal of the benzene, fractionally distilled at a pressure of 13m.m. The fraction distilling between 220-265° is retained and recrystallised from glacial acetic acid when 1:1'-dinaphthyl, m.p. 157°, is obtained. By redistillation of the fractions boiling below 220° and above 265° respectively the total yield of dinaphthyl amounts to 50g. The boiling point of the pure compound at 15m.m. pressure was found to be 247°; Schoepfle gives 240° at 13m.m. pressure.

4:4'-Dinitro-1:1'-Dinaphthyl.

10g. dinaphthyl suspended in 100c.cs. glacial acetic acid are nitrated at 100° employing 20g. nitric acid(sp.gr. 1.42). In 2 hours the nitration is complete. The yield of the dinitrodinaphthyl amounts to 8g. It was found best to recrystallise the dinitro-compound from nitrobenzene, not benzene as employed by Schoepfle, when it formed beautiful light yellow prisms, m.p. 246°(Schoepfle 246°).

The Reduction of 4:4'-Dinitro-1:1'-Dinaphthyl.

4-Amino-4'-Nitro-1:1'-Dinaphthyl.

2g. dinitro-compound were suspended in 100c.cs. alcohol and a mixture of 12c.cs. ammonia solution(sp.gr. 0.88) and 4c.cs. water added. The cold solution was saturated with hydrogen sulphide and then refluxed for 15 minutes. On cooling a further 12c.cs. ammonia solution(sp.gr. 0.88) were added, the solution again saturated with hydrogen sulphide and refluxed for a further 15 minutes. 3g. sodium sulphide,

$Na_2S.9H_2O$, dissolved in 10c.cs. water were now added and refluxing continued for approximately 10 minutes when all the dinitro-compound had disappeared. The dark brownish red solution was maintained at the boil and water gradually added until no more nitroamine separated; care must be taken not to add too much water as sulphur will be precipitated as well. The solution was filtered hot and the residue recrystallised twice from 80% alcohol when 0.9g. 4-amino-4'-nitro-1:1'-dinaphthyl, m.p. 195-196°, were obtained as yellowish brown spangles(found, by micro-analysis, N = 8.61; required N = 8.92%).

Ammonium hydrogen sulphide itself is not powerful enough to reduce the dinitrodinaphthyl to the nitroamine while sodium sulphide or sodium hydrogen sulphide alone act too vigorously. By employing a mixture of the two sulphides as described the reduction proceeds smoothly. By reduction of dinitro-compound in larger quantities than 2g. the proportion of the diamine formed is considerably increased with consequent loss in yield of the required nitroamine.

The base is insoluble in dilute or concentrated hydrochloric acid. The hydrochloride was obtained as colourless crystals by addition of concentrated hydrochloric acid to an alcoholic solution of the base. The hydrochloride on diazotisation forms a pale yellow diazonium compound which coupled with 2-naphthol gives a bright red insoluble dyestuff.

The acetyl-derivative was readily obtained by treatment of a boiling glacial acetic acid solution of the base for a few minutes with excess acetic anhydride. Recrystallised from alcohol the 4-acetylamino-4'-nitro-1:1'-dinaphthyl formed pale yellow irregular plates, m.p. 243-244^{O}(found N = 7.76; required N = 7.87).

4:4'-Diamino-1:1'-Dinaphthyl.

5g. 4:4'-dinitro-1:1'-dinaphthyl were suspended in 100 c.cs. glacial acetic acid, 10c.cs. concentrated hydrochloric acid added and the whole maintained at gentle boil under a reflux. Zinc dust was added, a little at a time, until a clear solution was obtained. The reduction was complete in about an hour. On filtration and cooling of the filtrate, the insoluble hydrochloride of the base separated out. This was recrystallised several times from boiling water and the free base finally liberated by addition of ammonia solution to a solution of the hydrochloride. Recrystallised from alcohol 3.5g. 4:4'-diamino-1:1'-dinaphthyl(naphthidine) were obtain:ed as silvery plates, m.p. 202^{O}.

An interesting reduction was carried out as follows:-

1g. dinitro-compound and zinc dust were added alternately, in small quantities at a time, to a melt of about 20g. salicylic acid. On completion of the reduction, when the whole had gone a dirty brown colour, the melt was poured into water and excess sodium hydroxide added to remove the salicylic acid. The residue was dissolved in alcohol and re:precipitated by sodium hydroxide to remove the last traces of salicylic acid. On removal of the precipitate and recrystallising several times from alcohol with addition of decolourising carbon, silvery plates of 4:4'-diamino-1:1'-dinaphthyl, m.p. 198.5-199°, were obtained; the yield was insufficient for a further recrystallisation.

Using either zinc dust or iron filings no reduction of the dinitro-compound, when suspended in boiling dilute hydrochloric acid, took place. Even in a fine state of division, obtained by first dissolving the dinitrodinaphthyl in aniline and then adding a large excess of boiling dilute hydrochloric acid, the reduction failed.

<u>By the Method of Clemo, Cockburn and Spence</u>(J.C.S.,1931, 1271).

1g. 4:4'-dinitro-1:1'-dinaphthyl is dissolved in 100c.cs. boiling glacial acetic acid and 5g. zinc dust added. 5c.cs. hydrochloric acid are added drop by drop and after 10 minutes the solution is diluted with an equal volume of water and filtered. The amine is precipitated by addition of solid potassium hydroxide, sufficient to keep the zinc in solution, collected, extracted with a little dilute hydrochloric acid to remove zinc, again heated with sodium hydroxide solution, collected, dried and distilled at 1m.m. The product crystallises from alcohol in small fan-shaped plates, m.p. 191° "alone or mixed with an authentic naphthidine".

The product obtained by us by this method gave m.p. 195-196° after one recrystallisation from alcohol and 196-197°

after a further recrystallisation with addition of animal charcoal; the yield was insufficient for further recrystallisation.

Reduction of 4-Acetylamino-4'-Nitro-1:1'-Dinaphthyl.

4-Acetylamino-4'-Amino-1:1'-Dinaphthyl.

The nitroacetyl-compound was dissolved in excess glacial acetic acid, the solution saturated with water and zinc dust added at 30° until the solution was rendered colourless. The product obtained by addition of water to the filtrate was recrystallised as often as possible from dilute alcohol when it finally melted at about 225°.

Reduction with stannous chloride at 40°, the nitroacetyl-compound being again in glacial acetic acid solution, gave rise to the same product, m.p. 220-225°.

The difficulty of preparing the nitroacetyl-compound has prevented further study of the reduction.

3:3'-DIAMINO-1:1'-DINAPHTHYL.

Attempted Preparation of 3:3'-Dinitro-4:4'-Diamino-1:1'-Di:naphthyl.

(1). By Condensation of 3-Nitro-4-Amino-1-Bromonaphthalene.

3-Nitro-4-Amino-1-Bromonaphthalene.

3-Nitro-4-amino-1-bromonaphthalene was prepared by the method of Liebermann and Scheidung(Ber.,1875,8,1108) as follows:-

55g. 4-acetylamino-1-bromonaphthalene are dissolved in 400 c.cs. glacial acetic acid and the solution cooled as far as possible in order just not to allow compound to crystallise out. A mixture of 15g. nitric acid(sp.gr. 1.54) and 5c.cs. water is slowly added, the temperature of the solution being allowed to rise to 70-80° at which it is maintained for ½ hour. The nitro-compound gradually separates as fine silky needles. These are removed, washed with water and recrystallised from acetone. 46g. 3-nitro-4-acetylamino-1-bromonaphthalene were thus obtained. The acetyl-compound is hydrolysed by dissolving it in concentrated sulphuric acid and gradually diluting with water, the heat of dilution being sufficient to cause the hydrolysis. Excess water is then added, the precipitate removed, washed, dried and recrystallised from benzene. 34g. 3-nitro-4-amino-1-bromonaphthalene, m.p. 201°(

Liebermann and Scheidung, 200°), were obtained.

Attempted Condensation.

1g. 3-nitro-4-amino-1-bromonaphthalene and 1g. copper powder were fused together but no reaction appeared to take place other than decomposition as was indicated by the gradual darkening of the melt as the temperature was raised. No condensation product was isolated.

(2). By Condensation of 3-Nitro-4-Amino-1-Iodonaphthalene.

3-Nitro-4-Amino-1-Iodonaphthalene.

2g. 3(2)-nitro-4(1)-aminonaphthalene(for preparation see p. 93) were dissolved in 75c.cs. glacial acetic acid and the solution cooled to room temperature when 1.8g. iodine monochloride dissolved in 20c.cs. glacial acetic acid were added. After standing 18 hours, the crystals which had separated were removed, washed with a little glacial acetic acid and finally with water. On recrystallisation from alcohol 1.95g. bright orange coloured needles of 3-nitro-4-amino-1-iodonaphthalene, m.p. 192-193°, were obtained(found I = 40.60; required I = 40.45%).

Attempted Condensation.

1g. 3-nitro-4-amino-1-iodonaphthalene and 1g. copper powder were fused. A reaction apparently took place at 215-220° and on maintaining at this temperature for 20 minutes the mass hardened. However, on extraction with alcohol and decolour-

:isation of the dark extract with animal charcoal only a few crystals of indefinite melting point were obtained on concentration of the solution.

Attempted Preparation of 3:3'-Dinitro-1:1'-Ditetrahydrodinaphthyl.

3-Nitro-1-Aminotetrahydronaphthalene.

The method of Schroeter(Ann.,1922,426,43) was utilised, 1:3-dinitrotetrahydronaphthalene(for preparation see p. 106) being reduced by stannous chloride similarly to the reduction of 1:3-dinitronaphthalene to 3-nitro-1-aminonaphthalene(see p. 109).

11g. 1:3-dinitrotetrahydronaphthalene reduced with 37.5g. stannous chloride gave 4g. 3-nitro-1-aminotetrahydronaphthalene hydrochloride. The reduction was carried out at 35-40°.

3-Nitro-1-Iodotetrahydronaphthalene.

Employing 3-nitro-1-aminotetrahydronaphthalene hydrochloride the iodo-compound was prepared similarly to the preparation of 3-nitro-1-iodonaphthalene from 3-nitro-1-aminonaphthalene hydrochloride(see p. 111). 3.5g. 3-nitro-1-aminotetrahydronaphthalene hydrochloride yielded 1.5g. 3-nitro-1-iodotetrahydronaphthalene which, recrystallised from alcohol, formed colourless needles, m.p. 118-118.5°(found I = 41.96; required I = 41.91%).

Attempted Condensation.

1g. 3-nitro-1-iodotetrahydronaphthalene and 1g. copper powder were fused together a reaction taking place about 260° when the mixture slowly hardened. Serious decomposition had, however, set in and on working up no condensation product was isolated.

Preparation of 3:3'-Dinitro-1:1'-Dinaphthyl.

(1). By Attempted Condensation of 3-Nitro-1-Bromonaphthalene.

3-Nitro-1-Bromonaphthalene.

34g. 3-nitro-4-amino-1-bromonaphthalene were dissolved in 400c.cs. concentrated sulphuric acid, the solution diluted with a few c.cs. water and diazotisation carried out employing 9g. solid sodium nitrite. The diazonium solution was slowly added to 800c.cs. 90% alcohol and when all reaction had ceased the solution was diluted with water, the precipitate removed and recrystallised from alcohol with addition of animal charcoal. 11g. 3-nitro-1-bromonaphthalene were obtained as brownish yellow needles, m.p. 132-133°(Liebermann and Scheidung, loc.cit., 131-132°).

The above method is that devised by Meldola(J.C.S.,1885, 47,497) for the removal of an amino-group and it was found in the case of several compounds(details given later) to yield better results than diazotisation in absolute alcohol and subsequent boiling of the diazonium solution. The method avoids excessive tarring and, moreover, 90% alcohol proves quite efficient.

Attempted Condensation.

(a). Fusion with copper powder.

4g. bromo-compound and 4g. copper powder were fused together. A reaction took place about 300° but was accompanied by much decomposition and on working up only a charred mass was obtained from which no crystals could be isolated.

(b). Refluxing in nitrobenzene solution with copper powder.

1g. bromo-compound was dissolved in 20c.cs. nitrobenzene and 1g. copper powder added. No reaction had taken place at the end of 6 hours refluxing.

(c). Refluxing in solution with sodium.

1g. bromo-compound was refluxed in both ether and toluene solutions, with addition of dry ethyl acetate, with 1g. sodium but no reaction had taken place after 16 hours heating.

(2). By Condensation of 3-Nitro-1-Iodonaphthalene.

1:3-Dinitrotetrahydronaphthalene.

Technical tetrahydronaphthalene was employed, the fraction, b.p. 208-212°, being used. The nitration was carried out in accordance with the directions of Schroeter(loc.cit.).

To a mixture of 170g. nitric acid(sp.gr. 1.49) and 420g. sulphuric acid(96%) cooled to 0° is added 132g. tetrahydro-

:naphthalene at such a rate that, during strong agitation and external cooling, the temperature at the end of the nitration does not exceed 35-40°. It was found advantageous to raise the temperature after the addition of the acid to 50° and to allow the mixture to cool gradually, the stirring being maintained until the mass solidified. The yellow product is removed, washed with water, recrystallised from glacial acetic acid and finally from an alcohol-glacial acetic acid mixture (7:3). This product, yield 80g., consists of about an equal mixture of the 1:2- and 1:3-dinitro-isomers.

100g. mixed isomers are dissolved by heating in about 350 c.cs. concentrated sulphuric acid and the solution cooled when the 1:2-dinitro-isomer, m.p. 102-103°, completely crystallises out. The filtrate, containing the 1:3-isomer, is precipitated with water and the precipitate obtained recrystallised from glacial acetic acid. 35g. 1:3-dinitrotetrahydronaphthalene were obtained as small prisms, m.p. 95°(Schroeter, 95°).

1:3-Dinitronaphthalene.

(a). By oxidation of 1:3-dinitrotetrahydronaphthalene.

The method of Veselý and Dvořák(Bull.Soc.chim.,1923,33, 326) was used.

20g. dinitro-compound are mixed with 30g. bromine and maintained under a reflux on an oil bath at 100° until all reaction has ceased as is indicated by the disappearance of fumes of hydrogen bromide and bromine. The product at this stage of the oxidation consists of a dibromodinitroditetrahydronaphthalene of unknown constitution. By slowly raising the temperature to 180° decomposition of this product takes place, the bromine oxidising the remaining hydrogens with formation of the required dinitronaphthalene. At the end of about 2 hours the oxidation is complete. The cold mass on recrystallisation from glacial acetic acid with addition of animal charcoal yielded 11.5g. 1:3-dinitronaphthalene, m.p. 144-145°(Veselý and Dvořák, 144-145°).

(b). By removal of the amino-group in 1:3-dinitro-4-aminonaphthalene.

1:3-Dinitro-4-Aminonaphthalene.

The method of Morgan and Evans(J.C.S.,1919,115,1126), as follows, was employed:-

50g. 1-acetylnaphthylamine are dissolved in 100c.cs. glacial acetic acid and nitrated with 26c.cs. nitric acid(sp.gr. 1.52) dissolved in 26c.cs. glacial acetic acid. During the addition of the acid the temperature is kept below 70° and subsequently raised to 96° until the dinitro-compound begins to appear. The mixture is then cooled and the solid removed and recrystallised from glacial acetic acid. 30g. 1(4):3(2)-dinitro-4(1)-acetylaminonaphthalene, m.p. 247°, were obtained. The acetyl-compound is added to a cold mixture of 45c.cs. water and 300c.cs. concentrated sulphuric acid and the whole heated at 60-70° for a few minutes, allowed to cool for 15 minutes and finally poured into water when the 1:3-dinitro-4-amino-

:naphthalene is precipitated. Recrystallised from alcohol 20 g., m.p. 237°, were obtained(Morgan and Evans, 237°).

1:3-Dinitronaphthalene.

20g. 1:3-dinitro-4-aminonaphthalene were dissolved in 300 c.cs. concentrated sulphuric acid, the solution diluted with a few c.cs. water and diazotised employing 6g. solid sodium nitrite. The diazonium solution was slowly added to 700c.cs. 90% alcohol and when all reaction had ceased the solution was diluted and the precipitate removed. Recrystallised from alcohol, with addition of animal charcoal, 3g. 1:3-dinitronaphthalene were obtained as brownish yellow needles, m.p. 143-144°. The loss in yield was entirely due to tarring. The above method was found to give better results than diazotisation and subsequent boiling of the diazonium solution in absolute alcohol.

3-Nitro-1-Aminonaphthalene.

The method of Veselý and Dvořák(loc.cit.) was utilised; the authors give no details.

20g. 1:3-dinitronaphthalene were dissolved by heating in 250c.cs. glacial acetic acid, the solution being maintained at 50-60° during the reduction. The stannous chloride which was slowly added through a tap funnel was prepared by dissolving 68.2g. stannous chloride in 100c.cs. alcohol and then adding 62c.cs. concentrated hydrochloric acid. On completion of the addition, the reduction mixture was concentrated under reduced pressure to about 100c.cs. By addition of water to the concentrated solution unchanged dinitro-compound was pre:cipitated and after removal the filtrate was rendered alkaline. The alkaline solution was extracted with ether, the ethereal solution dried and the hydrochloride of the base precipitated by passing through a stream of hydrochloric acid gas. The hydrochloride was recrystallised from dilute hydro:chloric acid when 8g. 3-nitro-1-aminonaphthalene hydro:chloride were obtained.

The use of stannous chloride was found to be preferable to ammonium hydrogen sulphide as the latter tended to cause tarring.

3-Nitro-1-Iodonaphthalene.

(1). Attempted replacement of bromine by iodine in 3-nitro-1-bromonaphthalene(for preparation see p.105).

(a). 2g. bromo-compound were dissolved in 150c.cs. alcohol and 2g.(excess) sodium iodide added. After refluxing for 2½ hours the bromo-compound was recovered unchanged.

(b). 1g. bromo-compound was fused for 1 hour at 145° with 2g. sodium iodide but no reaction took place.

(2). Removal of the amino-group in 3-nitro-4-amino-1-iodo:naphthalene(for preparation see p.103).

1g. iodo-compound was dissolved in 150c.cs. absolute alcohol and 4c.cs. concentrated sulphuric acid added, the acid having been previously diluted with about 25c.cs. absolute alcohol. 1g. amyl nitrite in absolute alcohol solution was then added and the whole brought to the boil and maintained so for 10 minutes. On addition of water a yellowish precipitate was thrown down which, recrystallised from alcohol with addition of animal charcoal, gave orange yellow needles of 3-nitro-1-iodonaphthalene, m.p. 147°(Chudožilov, see below, 142-143°). The yield obtained was 0.2g.

Diazotisation in concentrated sulphuric acid solution and reduction of the diazonium compound with 90% alcohol gave a tarry product from which no crystals could be obtained. Moreover, during the reduction a strong smell of iodine was noted indicating serious decomposition.

(3). Replacement of the amino-group in 3-nitro-1-aminonaphthalene by iodine.

The method of Chudožilov(Chem.Listy, 1925,<u>19</u>,187) was employed. Chudožilov gives no conditions but the following were found to give a satisfactory result.

8g. 3-nitro-1-aminonaphthalene hydrochloride were dissolved by heating in 200c.cs. N/2 hydrochloric acid and the solution rapidly cooled when the hydrochloride crystallised out in a fine condition. Diazotisation was carried out employing a solution of 2.1g. sodium nitrite in 50c.cs. water. The diazonium solution was slowly added with stirring to a solution of 10g. potassium iodide in 200c.cs. water. The crude iodo-compound so formed was dissolved in alcohol, the alcoholic solution refluxed with animal charcoal and filtered into dilute sodium hydroxide solution to remove the last traces of free iodine. Recrystallised from alcohol 4g. 3-nitro-1-iodonaphthalene were obtained as brownish yellow needles, m.p. 147°.; Chudožilov gives 142-143°.

3:3'-Dinitro-1:1'-Dinaphthyl.

The method of Chudožilov(loc.cit.) was employed.

4g. 3-nitro-1-iodonaphthalene and 3g. copper powder are fused together. The reaction begins about 200° and after slowly raising the temperature to 240° is complete. It was observed that some iodo-compound was lost due to sublimation and that a large amount of charring took place. The cold reaction mixture is powdered and extracted with benzene, the dark coloured extract being clarified as far as possible by animal charcoal. On addition of petroleum ether to the benzene solution 0.8g. crude dinitrodinaphthyl was precipitated. This was removed and recrystallised twice from glacial acetic acid, not a mixture of benzene and petroleum ether as used by Chudožilov, when 0.4g. 3:3'-dinitro-1:1'-dinaphthyl was obtained as golden yellow plates, m.p. 281°.

Chudožilov obtained a somewhat higher yield but describes his product as greenish coloured crystals, m.p. 262-264°.

Reduction of 3:3'-Dinitro-1:1'-Dinaphthyl.

3:3'-Diamino-1:1'-Dinaphthyl.

0.4g. 3:3'-dinitro-1:1'-dinaphthyl was dissolved in 50c.cs.

glacial acetic acid and the solution reduced at the boil with zinc dust until colourless. After filtration, the filtrate was rendered alkaline and extracted with ether. The ether was removed and the residue repeatedly recrystallised from benzene when 3:3'-diamino-1:1'-dinaphthyl was finally obtained as colourless plates, m.p. 270°.

The base forms an extremely soluble hydrochloride which is readily diazotised. The results of various couplings are noted on p. 150.

2:2'-DIAMINO-1:1'-DINAPHTHYL.

Attempted Preparation of 2:2'-Diacetyldiamino-1:1'-Dinaphthyl by Condensation of 1-Bromo-2-Acetylnaphthylamine.

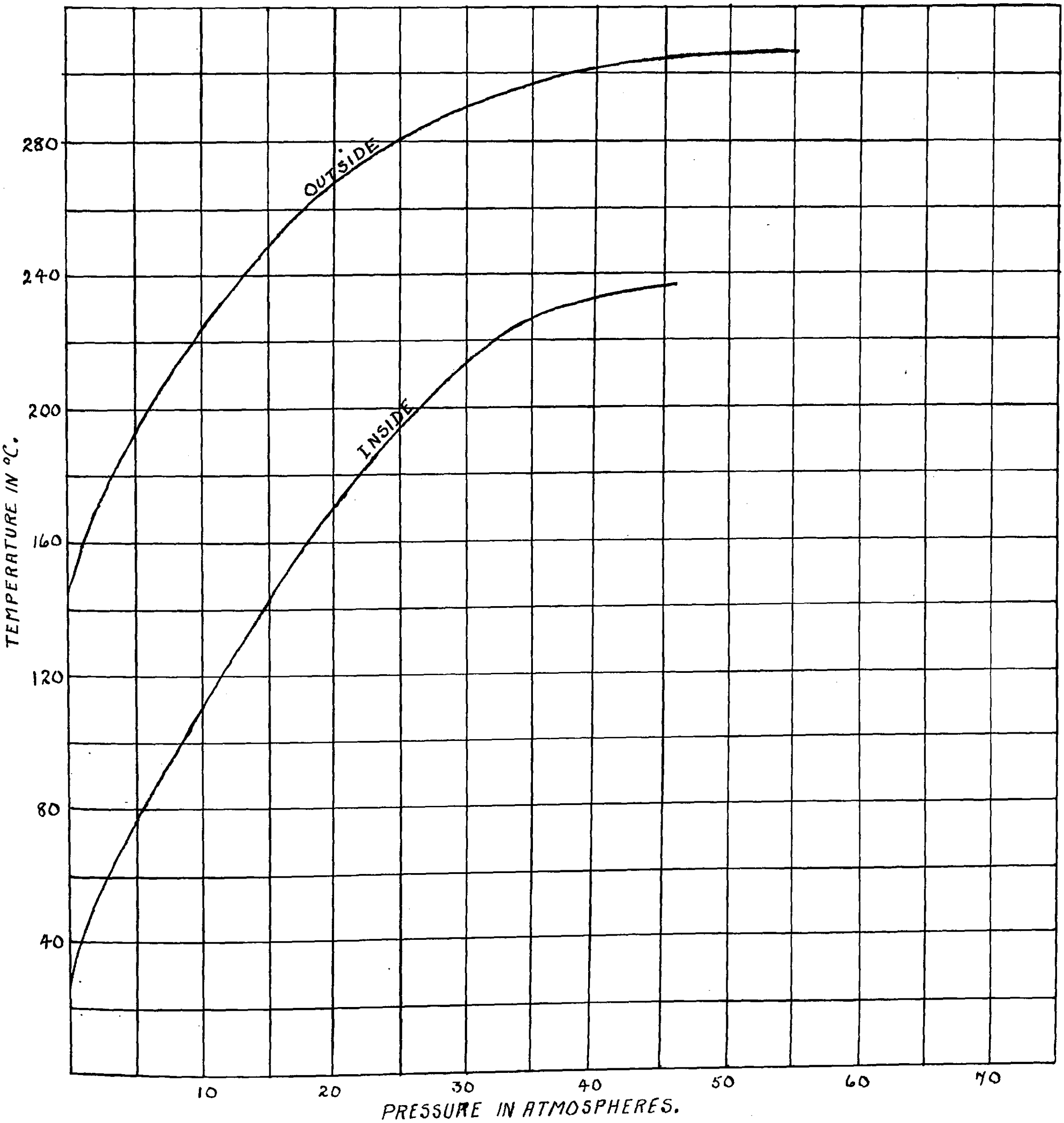
The experiments(see p. 90) carried out with 4-bromo-1-acetylnaphthylamine were repeated, the 4-bromo-1-acetylnaphthylamine being replaced by 1-bromo-2-acetylnaphthylamine. In all cases the results were similar, no condensation products being isolated.

In the fusion with sodium amalgam the temperature was maintained at 140-150°(1-bromo-2-acetylnaphthylamine melts at 132°). In this case, 2-acetylnaphthylamine was obtained as well as unchanged 1-bromo-2-acetylnaphthylamine.

Attempted Amidation of 2:2'-Dinaphthol.

7.5g. 2:2'-dinaphthol, 53g. ammonium hydrogen sulphite and 35c.cs. ammonia solution(sp.gr. 0.88) were heated in an autoclave for 30 hours at 230-236°. The product so obtained consisted of a charred mass from which no basic compound was isolated. A little 2:2'-dinaphthol was recovered. The pressure and both inside and outside temperatures of the autoclave were noted every 2 hours. The curve obtained by plotting temperature against pressure was smooth. A typical curve for a day's heating(approximately 11 hours) is to be seen below.

The amidation employing ammonium carbonate and calcium chloride, to remove water, was no more successful.



Preparation of 2:2'-Dinitro-1:1'-Dinaphthyl.

2-Nitro-1-Aminonaphthalene.

2-Nitro-1-acetylaminonaphthalene(for preparation see p. 93) was hydrolysed(Morgan and Micklethwait, loc.cit.) by dissolving the acetyl-compound in concentrated sulphuric acid and gradually diluting the solution with water, the heat of dilution being sufficient to cause the hydrolysis. The base is recrystallised from alcohol. From 17g. acetyl-compound, 13g. 2-nitro-1-aminonaphthalene were obtained as brownish yellow needles, m.p. 144°(Morgan and Micklethwait, 144°).

2-Nitro-1-Iodonaphthalene.

The method of Meldola(loc.cit.) was utilised, the amino-group in 2-nitro-1-aminonaphthalene being replaced by iodine. The conditions are similar to the preparation of 4-nitro-1-iodonaphthalene from 4-nitro-1-aminonaphthalene(see p. 94). 9g. iodo-compound were obtained from 13g. nitroaminonaphthalene. It formed pale yellow plates, m.p. 108°(Meldola, 108.5°).

2:2'-Dinitro-1:1'-Dinaphthyl.

(a). By fusion of the iodo-compound with copper powder.

The procedure of Chudožilov(loc.cit.) in which he heated together an intimate mixture of the iodo-compound and copper powder does not give too reliable results as the reaction sometimes proceeds with violence causing charring. The following modification was adopted.

10g. iodo-compound were maintained at 120-130° and 10g. copper powder gradually added, in small quantities at a time, over a period of 1 hour. The now hard mass was cooled, crushed, extracted with benzene and the extract decolourised with animal charcoal. On removal of the benzene the residue was recrystallised from alcohol when 4g. 2:2'-dinitro-1:1'-dinaphthyl were obtained as light yellow needles, m.p. 187°(Chudožilov describes his product as greenish needles, m.p. 179-180°).

(b). By refluxing the iodo-compound in nitrobenzene solution with copper powder.

2g. iodonitronaphthalene were dissolved in 30c.cs. nitrobenzene, 2g. copper powder added and the solution refluxed for 5 hours. The nitrobenzene was nearly all removed under reduced pressure, the remainder by steam distillation. The residue recrystallised from alcohol, with addition of animal charcoal, formed 0.1g. 2:2'-dinitro-1:1'-dinaphthyl, m.p. 187°.

On keeping, the distillate from the steam distillation deposited crystals. These recrystallised from petroleum ether gave m.p. 79° and showed the properties of 2-nitronaphthalene. The poor yield of the condensed product is, therefore, largely due to decomposition of the iodonitro-compound to produce nitronaphthalene.

(c). By refluxing the iodo-compound in solution with sodium.

0.3g. iodonitronaphthalene was refluxed in both ether and toluene solutions, containing ethyl acetate, with 0.25g. sodium. No reaction took place, the sodium and the iodonitrocompound being recovered unchanged.

The Reduction of 2:2'-Dinitro-1:1'-Dinaphthyl.

2-Amino-2'-Nitro-1:1'-Dinaphthyl.

1.5g. dinitro-compound were suspended in 75c.cs. alcohol and 5g. sodium sulphide, $Na_2S.9H_2O$, in 10c.cs. water added. The solution was refluxed until all had passed into solution when the colour of the liquid was a brownish yellow. To the boiling solution water was added to precipitate the nitroamine and the solution filtered hot. The residue recrystallised from alcohol gave 0.5g. 2-amino-2'-nitro-1:1'-dinaphthyl as lemon yellow prisms, m.p. 251°(found, by microanalysis, N = 9.31; required N = 8.92%).

The dinitro-compound is unaffected by ammonium hydrogen sulphide.

The nitroamine proved incapable of acetylation by all ordinary means. The addition of a drop of concentrated sulphuric acid to a solution of the base in acetic anhydride only caused decomposition. Further, the base could not be diazotised.

2:2'-Diamino-1:1'-Dinaphthyl.

1g. dinitro-compound was dissolved in 40c.cs. glacial acetic acid and reduced(2-3 minutes) at the boil with 5g.

zinc dust. The solution was filtered hot and precipitated by water. The yellowish precipitate was removed, washed with water and extracted with a little dilute hydrochloric acid. The extract was rendered alkaline, the base filtered off and recrystallised several times from alcohol when it formed colourless plates, m.p. 191°. A mixed m.p. with 2:2'-di:amino-1:1'-dinaphthyl, m.p. 191°, obtained by conversion of 2:2'-hydrazonaphthalene gave no depression. The yield obtain:ed was 0.1g.

2:2'-Imine-1:1'-Dinaphthyl.

The above reduction was repeated but the reduction mixture maintained at the boil for ½ hour when the solution was filtered, cooled and precipitated by water. The precipitate was removed, washed with water and recrystallised from alcohol when the imine was obtained as colourless prisms, m.p. 158°. Meisenheimer and Witte(Ber.,1903,36,4153) give m.p. 157°.

DINAPHTHYLINE: 1:1'-DIAMINO-2:2'-DINAPHTHYL.

Preparation of 1:1'-Dinitro-2:2'-Dinaphthyl.

(1). By Condensation of 1-Nitro-2-Iodonaphthalene.

1-Nitro-2-Aminonaphthalene.

(a). Employing the method of Veselý and Jakeš(Bull.Soc. chim.,1923,33,942).

90g. 2-acetylnaphthylamine are dissolved in 150c.cs. glacial acetic acid and the solution quickly cooled to 25° when the acetyl-compound separates in a fine state. 60g. nitric acid(sp.gr. 1.40) are then added drop by drop, the temperature not being allowed to exceed 30°. At the end of the nitration the whole is heated, if necessary, until a clear solution is obtained. After standing 2½ hours the crystals which have separated are removed, washed with 50% acetic acid and finally with ether. On recrystallisation from alcohol 40g. 1-nitro-2-acetylaminonaphthalene were obtained as pale yellow needles, m.p. 125°(Veselý and Jakeš, 126°).

The glacial acetic acid filtrate obtained on removal of the 1-nitro-2-acetylaminonaphthalene and also the alcoholic filtrates from the recrystallisation of the nitro-compound contain a mixture of the 2:6-, 2:8- and 2:1-isomers. The separation of the 2:1-isomer, of which the proportion is small, is not easy and the mixture was, therefore, discarded.

The acetyl-compound was hydrolysed by dissolving it in 100 c.cs. alcohol, adding 12g. potassium hydroxide in 15c.cs. water and maintaining at the boil for 10 minutes. On cooling, 27g. 1-nitro-2-aminonaphthalene crystallised out as orange red needles, m.p. 127°(Veselý and Jakeš, 126-127°).

(b). Employing the method of Veselý and Dvořák(Bull.Soc. chim.,1923,33,326).

1:2-Dinitronaphthalene.

1:2-Dinitrotetrahydronaphthalene(for preparation see p. 106) is oxidised by bromine, the procedure being similar to the oxidation of 1:3-dinitrotetrahydronaphthalene to 1:3-dinitronaphthalene(see p.106). 10g. dinitrotetrahydronaphthalene gave 5g. dinitronaphthalene which, recrystallised from alcohol, formed long brownish yellow needles, m.p. 160°(Veselý and Dvořák, 158°).

1-Nitro-2-Aminonaphthalene.

1:2-dinitronaphthalene is reduced with stannous chloride, the conditions being similar to the reduction of 1:3-dinitronaphthalene to 3-nitro-1-aminonaphthalene(see p.109). Since the base does not form a hydrochloride the ether in the ethereal extract, obtained in the extraction of the concentrated reduction mixture with ether, was removed and the residue recrystallised from alcohol. A large amount of tarring takes place in the reduction and in consequence the yield of

1g. nitroamino-compound from 5g. dinitronaphthalene was poor.

1-Nitro-2-Iodonaphthalene.

The method of Meldola(loc.cit.) was employed, 1-nitro-2-aminonaphthalene being diazotised and the diazonium solution decomposed by potassium iodide. The conditions are similar to the preparation of 4-nitro-1-iodonaphthalene from 4-nitro-1-aminonaphthalene(see p. 94). From 24g. 1-nitro-2-aminonaphthalene 20g. 1-nitro-2-iodonaphthalene were obtained as brownish yellow needles, m.p. 89°(Meldola, 88.5°).

1:1'-Dinitro-2:2'-Dinaphthyl.

(a). Action of sodium on 1-nitro-2-iodonaphthalene.

0.3g. iodo-compound was refluxed in both ether and toluene solutions for 16 hours with 0.25g. sodium. The addition of dry ethyl acetate failed to aid the reaction, the sodium remaining unchanged and the iodo-compound being recovered.

(b). Fusion of the iodo-compound with copper powder.

The method of Chudožilov(loc.cit.) was utilised as follows:-

10g. 1-nitro-2-iodonaphthalene were fused and maintained at 120-125° when 8g. copper powder were gradually added over 1 hour. The now hard mass was cooled, crushed and extracted with nitrobenzene. On decolourisation of the nitrobenzene solution with animal charcoal and cooling, the crystals so obtained were removed and washed with benzene. The product recrystallised from nitrobenzene gave 3g. 1:1'-dinitro-2:2'-

dinaphthyl as pale yellow plates, m.p. 284° with decomposition(Chudožilov, 264-265°; Veselý(Ber.,1905,38,136), 276° with decomposition).

As in the condensation of 2-nitro-1-iodonaphthalene the fusion of the iodo-compound with copper powder tends to be violent if the total quantity of copper powder be added at once.

In the extraction of the dinitro-compound, Chudožilov employed benzene but since it is but very slightly soluble in benzene as indeed in most common solvents other than nitro:benzene and aniline the procedure was found extremely tedious. At the end of 3 days extraction in a Soxhlet apparatus much dinitro-compound remained unextracted.

(2). By Oxidation of 1:1'-Dinitro-2:2'-Ditetrahydrodinaphthyl.

1-Nitro-2-Aminotetrahydronaphthalene.

The method of Schroeter(Ann.,1922,426,43) was utilised, 1:2-dinitrotetrahydronaphthalene being reduced by stannous chloride. The procedure was similar to the preparation of 3-nitro-1-aminotetrahydronaphthalene from 1:3-dinitrotetra:hydronaphthalene(see p. 104). From 11g. 1:2-dinitro-com:pound 3g. 1-nitro-2-aminotetrahydronaphthalene were obtained as red needles, m.p. 96°, from alcohol(Schroeter, 96°).

1-Nitro-2-Iodotetrahydronaphthalene.

3g. 1-nitro-2-aminotetrahydronaphthalene were dissolved in

20c.cs. glacial acetic acid and 40c.cs. N/2 sulphuric acid added. Diazotisation was carried out employing 1.2g. sodium nitrite in 30c.cs. water. The diazonium solution was gradually added with stirring to a solution of 5g. potassium iodide in 50c.cs. water. The crude brown iodo-compound recrystallised twice from alcohol formed orange red needles, m.p. 84°, of 1-nitro-2-iodotetrahydronaphthalene(found I = 41.70; required I = 41.91%). The yield obtained was 1.7g.

1:1'-Dinitro-2:2'-Ditetrahydrodinaphthyl.

1.7g. 1-nitro-2-iodotetrahydronaphthalene were fused with 1.5g. copper powder. The reaction began about 135° and was complete when the temperature had been raised to 190°. The fused mass was cooled, crushed and extracted with benzene with addition of animal charcoal. On removal of the benzene, the residue was recrystallised from glacial acetic acid when 0.2g. 1:1'-dinitro-2:2'-ditetrahydrodinaphthyl was obtained as irregular prisms, m.p. 187-188°(found N = 8.00; required N = 7.95%).

1:1'-Dinitro-2:2'-Dinaphthyl.

The oxidation was carried out similarly to the oxidation of 1:3-dinitrotetrahydronaphthalene to 1:3-dinitronaphthalene(see p. 107).

0.2g. 1:1'-dinitro-2:2'-ditetrahydrodinaphthyl was oxidised with 0.4g. bromine and the product obtained recrystallised from benzene when a few needles, m.p. 240-245°(1:1'-dinitro-

2:2'-dinaphthyl melts at 284°) were obtained. The yield was insufficient for a further recrystallisation.

(3). By Nitration of 2:2'-Dinaphthyl.

2-Iodonaphthalene.

28.6g. 2-naphthylamine(1 mol) were dissolved in glacial acetic acid and excess dilute sulphuric acid run in when the sulphate was precipitated in a fine state. The acid employed contained 200c.cs. concentrated sulphuric acid diluted with about twice its volume of water. After cooling to 10°, the base was diazotised using 13.8g.(1 mol) sodium nitrite dissolved in 200c.cs. water. The diazonium solution was then slowly added, with stirring, to a solution of 50g. potassium iodide in 100c.cs. water. At the end of 2 hours the black oily scum was removed and extracted with alcohol, the tarry residue being discarded. The extract was refluxed for half an hour with animal charcoal and filtered into dilute sodium hydroxide solution to remove free iodine. The precipitate recrystallised from alcohol gave 10g. 2-iodonaphthalene as beautiful white crystals, m.p. 54°(Jacobson, Ber.,1881,14, 804, gives 54.5°).

2:2'-Dinaphthyl.

The condensation of 2-iodonaphthalene was carried out by the method of Ullmann(Ann.,1904,332,38).

7.5g. 2-iodonaphthalene and 5g. copper powder are gradually heated to 260° and maintained at this temperature for a few minutes. On cooling and extracting with benzene 2.5g. 2:2'-dinaphthyl were obtained as colourless leaflets, m.p. 187°(Ullmann, 187°).

1-Nitro-2:2'-Dinaphthyl.

2g. 2:2'-dinaphthyl were suspended in 40c.cs. glacial acetic acid and 0.8c.cs. nitric acid(sp.gr. 1.42) added. The whole was maintained for 1½ hours on a water bath at 100° when the dinaphthyl had disappeared, its place being taken by a light yellow compound. After cooling, the nitro-compound was filtered off, washed free of acid and recrystallised from glacial acetic acid when 2g. 1-nitro-2:2'-dinaphthyl were obtained as beautiful light yellow needles, m.p. 179°(found N = 4.83, 4.64; required N = 4.67%).

1:1'-Dinitro-2:2'-Dinaphthyl and Isomers.

5g. 1-nitro-2:2'-dinaphthyl were dissolved by heating in 45c.cs. glacial acetic acid and the solution maintained at 100° on a water bath. Acid of sp.gr. 1.42 failed to cause nitration, 10c.cs. nitric acid(sp.gr. 1.50) having to be added. At the end of 1 hour most of the dinitro-compounds had separated, the remainder crystallising out on cooling. Recrystallised from glacial acetic acid 3g. dinitro-2:2'-dinaphthyl isomers, m.p. 198-208°, were obtained(found N = 8.05, 8.10; required N = 8.08%). The same mixture resulted on treatment of 2:2'-dinaphthyl, suspended in glacial acetic acid, with excess fuming nitric acid at 100°.

The acid filtrate, obtained on removal of the dinitro-material, gave, on addition of water, an oily mass from which nothing could be obtained. A similar oil resulted when attempts were made to nitrate the mononitrodinaphthyl in concentrated sulphuric acid solution.

No separation of the dinitro-isomers could be effected by fractional recrystallisation e.g. after 5 recrystallisations from glacial acetic acid the product gave m.p. 210-220°.

The Reduction of the Dinitration Product of 2:2'-Dinaphthyl.

1:1'-Imine-2:2'-Dinaphthyl and 1:?'-Diamino-2:2'-Dinaphthyl-Isomers.

1g. mixed dinitrodinaphthyl isomers was dissolved in the minimum quantity of glacial acetic acid and 5c.cs. concentrated hydrochloric acid added. Reduction was carried out at the boil using zinc dust. On completion of the reduction, the acid solution of the bases was maintained at gentle reflux for 6 hours during which time a white compound gradually separated. This on removal and recrystallisation from glacial acetic acid formed colourless leaflets, m.p. 221°, of 1:1'-imine-2:2'-dinaphthyl(dinaphthylcarbazole; dinaphthylene-imine). A mixed m.p. with dinaphthylcarbazole, m.p. 221°, obtained from dinaphthyline showed no depression.

The filtrate, obtained on removal of the imine, on neutralisation with sodium hydroxide yielded a precipitate which still contained more than one diaminodinaphthyl as on extraction and recrystallisation from alcohol colourless crystals, m.p. 200-220°, were obtained. No separation of the isomers by fractional recrystallisation has been effected.

The Reduction of 1:1'-Dinitro-2:2'-Dinaphthyl.

1-Amino-1'-Nitro-2:2'-Dinaphthyl.

2g. 1:1'-dinitro-2:2'-dinaphthyl were suspended in 150 c.cs. alcohol and 9g. sodium sulphide, $Na_2S.9H_2O$, added. The solution was refluxed for ¾ hour when a clear solution was obtained. Water was added to the hot solution when the nitroamine was precipitated. Recrystallised from alcohol with addition of animal charcoal it formed lemon yellow woolly needles, m.p. 264°(found, by micro-analysis, N = 9.46; required N = 8.92%).

The base proved incapable of acetylation even on treatment with acetic anhydride in presence of a drop of concentrated sulphuric acid. Further, attempts to diazotise the base failed.

Preparation of 2:2'-Dinaphthyl from Dinaphthyline.

2g. dinaphthyline were dissolved in absolute alcohol, 5 c.cs. concentrated sulphuric acid added to the cold solution and the base diazotised by addition of 1.8g. amyl nitrite in 20c.cs. absolute alcohol. The diazonium solution was refluxed for one hour and the dinaphthyl formed isolated by concentration of the alcoholic solution. Recrystallised from benzene it gave m.p. 187° and proved to be 2:2'-dinaphthyl, m.p. 187°.

3:3'-DIAMINO-2:2'-DINAPHTHYL.

Preparation of 3:3'-Dinitro-2:2'-Dinaphthyl.

1- and 2-Nitrotetrahydronaphthalenes.

The conditions of Schroeter(Ann.,1922,426,43) for the mononitration of tetrahydronaphthalene do not give the yield (80%) claimed, the product formed consisting of about an equal mixture of mononitro-compounds and unchanged tetrahydro:naphthalene. Moreover, Schroeter's statement that tetrahydro:naphthalene boils over 175° at 13m.m. pressure is incorrect, the b.p. at 16m.m. pressure being found to be 95-97°.

The following modification gave a 70% yield:-

132g. pure tetrahydronaphthalene, b.p. 206-208°, were maintained under strong agitation and external cooling at 15-20° and a mixture of 100g. nitric acid(sp.gr. 1.405) and 260g. sulphuric acid(sp.gr. 1.84) gradually added over about one hour. The mixture was allowed to stir a further half hour at 20° and then poured into ice-water. The brownish coloured emulsion was extracted with carbon tetrachloride, the whole filtered if necessary to cause the separation of the layers and the carbon tetrachloride extract removed and dried. On removal of the carbon tetrachloride, the residue was fractionally distilled at 26m.m. pressure, the mononitro:tetrahydronaphthalenes distilling over at 172-185°. By re:distillation of the fractions boiling below 172° and above

185° respectively the total yield of the mixed 1- and 2-nitrotetrahydronaphthalenes was 125g.

Using redistilled commercial tetrahydronaphthalene 132g. of the fraction of b.p. 208-212° gave 88g. mixed 1- and 2-nitrotetrahydronaphthalenes.

2-Acetylaminotetrahydronaphthalene.

The method of Veselý and Chudožilov(Rec.Trav.Chim.,1925, **44**,352) was utilised.

125g. mixed 1- and 2-nitrotetrahydronaphthalenes are dissolved in 450c.cs. alcohol and, to the boiling solution, 42g. sodium hydrogen sulphide(prepared by saturating with hydrogen sulphide a solution of 90g. sodium sulphide, $Na_2S.9H_2O$, in 100c.cs. water) are gradually added. At the end of 1½ hours refluxing is stopped and the alcohol removed under reduced pressure. The above authors separated the 2-aminotetrahydronaphthalene from unchanged nitro-compounds by steam distilling the extract obtained on extracting with dilute hydrochloric acid, the residue from the removal of the alcohol. The free base was finally obtained pure by rendering the solution of the hydrochloride alkaline and again steam distilling. This long process was simplified by extracting the residue from the removal of the alcohol with ether and precipitating the hydrochloride of the base by passing a stream of hydrochloric acid gas through the dry ethereal solution. The 2-aminotetrahydronaphthalene hydrochloride on recrystallisation from dilute hydrochloric acid formed beautiful colourless plates.

The hydrochloride is suspended in water and sodium acetate solution followed by excess acetic anhydride added. The acetyl-compound which is formed almost immediately is filtered off and recrystallised from 70% alcohol. 45g. 2-acetylaminotetrahydronaphthalene, m.p. 87-90°, were obtained. Further recrystallisation did not raise the melting point showing the 1-acetylaminotetrahydronaphthalene to be contaminated with a little of the 2-isomer which cannot be removed by fractional recrystallisation(Schroeter, loc.cit.).

Schroeter and Veselý and Chudožilov give m.p. 107° for pure 2-acetylaminotetrahydronaphthalene.

3-Nitro-2-Aminotetrahydronaphthalene.

The method of Schroeter(loc.cit.) was employed.

75g. 2-acetylaminotetrahydronaphthalene are dissolved in 300c.cs. glacial acetic acid and a mixture of 35c.cs. nitric acid(sp.gr. 1.40) and 25c.cs. sulphuric acid(sp.gr. 1.84) gradually added, the temperature not being allowed to exceed 45°. At the end of half an hour the solution is poured into ice-water and the yellow precipitate removed and recrystallised from 300c.cs. alcohol. The crystals so obtained gave on a further recrystallisation from alcohol 29g. 3-nitro-2-acetylaminotetrahydronaphthalene as pale yellow needles, m.p. 136°(Schroeter, 134-135°).

The acetyl-compound is hydrolysed by dissolving it in 130 c.cs. alcohol, adding 32c.cs. concentrated sulphuric acid and maintaining the solution at the boil for 10 minutes. The free base is precipitated by water and recrystallised from alcohol. It formed red needles, m.p. 126-127°(Schroeter, 125-126°).

3-Nitro-2-Iodotetrahydronaphthalene.

23.5g. 3-nitro-2-aminotetrahydronaphthalene were dissolved in 200c.cs. 50% sulphuric acid and the cold solution diazo:tised employing a solution of 9g. sodium nitrite in 150c.cs. water. The diazonium solution was then added, during stirring, to a solution containing excess potassium iodide. The mixture was allowed to stand several hours, the dark mass removed and extracted with alcohol, the insoluble residue of tar being discarded. The alcoholic solution was decolourised by animal charcoal and filtered into dilute sodium hydroxide solution to remove the last traces of free iodine. The precipitate re:crystallised several times from alcohol gave 17g. 3-nitro-2-iodotetrahydronaphthalene as long orange yellow prisms, m.p. 76-76.5°(found I = 41.94; required I = 41.91%).

3-Nitro-2-Iodonaphthalene.

1g. 3-nitro-2-iodotetrahydronaphthalene and 1g. bromine were maintained at 100° until all reaction had ceased, no more hydrogen bromide or bromine being evolved. On raising the temperature to 130-135° the second stage in the oxidation commenced, hydrogen bromide being again evolved, and the re:action was complete on maintaining the temperature of the mass at 160° for one hour. However, at the higher temperatures serious decomposition set in as was shown by the formation of a considerable quantity of iodine vapour. The cold reaction product gave, after 3 recrystallisations from alcohol with addition of animal charcoal, about 0.05g. 3-nitro-2-iodonaphthalene as greenish yellow prisms, m.p. 89-89.5°(found I = 42.26; required I = 42.47%).

3:3'-Dinitro-2:2'-Ditetrahydrodinaphthyl.

16g. 3-nitro-2-iodotetrahydronaphthalene were maintained at 110-120° and 16g. copper powder gradually added. The temperature was then raised to 140° when the mass hardened at the end of half an hour. The reaction product was cooled, crushed, extracted with benzene and the extract decolourised with animal charcoal. The benzene was removed and the residue recrystallised twice from glacial acetic acid when 7g. 3:3'-dinitro-2:2'-ditetrahydrodinaphthyl were obtained as yellow silky needles, m.p. 201°(found N = 8.10; required N = 7.95%).

3:3'-Dinitro-2:2'-Dinaphthyl.

6g. 3:3'-dinitro-2:2'-ditetrahydrodinaphthyl and 11g. bromine were maintained at 100° until no more fumes of hydrogen bromide or bromine were evolved. The oxidation was completed by gradually raising the temperature to 180° and maintaining so until all reaction was finished. In the latter half of the oxidation excessive charring and decomposition was noted, the mass turning black. The dark product was extracted with glacial acetic acid, the extract decolourised with animal charcoal and the solution cooled. The crystals so formed gave after several recrystallisations from glacial acetic acid 0.5g. 3:3'-dinitro-2:2'-dinaphthyl as golden yellow needles, m.p. 257-258^{0}(found N = 8.00; required N = 8.14%).

The Reduction of 3:3'-Dinitro-2:2'-Dinaphthyl.

The dinitro-compound was dissolved in glacial acetic acid, a few c.cs. concentrated hydrochloric acid added and the reduction carried out at the boil employing zinc dust. The yellow solution passed through a reddish brown stage and finally became yellow again. As the reduction proceeded a yellowish compound gradually separated from solution, a further crop of the same compound being obtained by cooling the solution on completion of the reduction. The filtrate from the yellow product was rendered alkaline with sodium hydroxide, extracted with ether and the ether removed from the extract. Only a minute quantity of a dark brown residue remained.

The yellow product recrystallised from benzene with addition of animal charcoal gave greenish yellow plates, m.p. about 350^{0} but first beginning to decompose at 320^{0}. The compound corresponded to the formula $C_{40}H_{26}N_{2}O_{3}$(found C = 82.5, 83.3, 83.1, H = 4.6, 4.5, 4.6, N = 4.9, 4.8; required C = 82.5, H = 4.5, N = 4.8%).

Treatment of the dinitrodinaphthyl with excess sodium sulphide in boiling alcoholic solution gave rise to a yellow product which, recrystallised as often as possible from benzene, melted at 310-330° but had no definite crystalline form under the microscope.

The compound $C_{40}H_{26}N_2O_3$ is nearly insoluble in alcohol and glacial acetic acid; sparingly soluble in acetone; fairly soluble in hot benzene but practically insoluble in the cold. It is soluble in cold concentrated sulphuric acid to give a red solution which turns apple green on addition of a drop of concentrated nitric acid. Hot concentrated sulphuric acid or cold concentrated nitric acid alone causes charring.

The compound had no reaction with nitrous acid.

4:4'-DIAMINO-2:2'-DINAPHTHYL.

Attempted Preparation of 4:4'-Dinitro-1:1'-Diamino-2:2'-Dinaphthyl.

4-Nitro-2-Iodo-1-Aminonaphthalene.

2g. 4-nitro-1-aminonaphthalene(for preparation see p. 93) were dissolved in 60c.cs. glacial acetic acid and the solution cooled as far as possible without the nitroamine separating out. 1.8g. iodine monochloride in 10c.cs. glacial acetic acid were then added and the solution allowed to stand 18 hours. The crystals which had separated were removed, washed with a little glacial acetic acid and then with water. The product recrystallised from alcohol or glacial acetic acid with addition of animal charcoal, gave 2.1g. 4-nitro-2-iodo-1-aminonaphthalene as yellowish brown prisms, m.p. 234°(found I = 39.61; required I = 40.45%).

Attempted Condensation.

(1). By fusion with copper powder.

2g. iodo-compound were maintained at 235-240° and 2g. copper powder gradually added. On addition of each batch of copper a violent reaction took place, much heat being evolved and excessive charring taking place. The cold reaction mixture was extracted with benzene, the benzene solution decolourised with animal charcoal and the benzene removed. Only a trace of a dark coloured residue remained.

(2). By refluxing in nitrobenzene solution with copper powder.

1g. iodo-compound was dissolved in 20c.cs. nitrobenzene, 1g. copper powder added and the solution refluxed for 1 hour. The copper powder which appeared unchanged was removed by filtration and the solution steam distilled to remove the nitrobenzene. The solid residue recrystallised from alcohol gave unchanged 4-nitro-2-iodo-1-aminonaphthalene, m.p. 234°.

Attempted Preparation of 4:4'-Dinitro-2:2'-Ditetrahydrodi:naphthyl.

4-Nitro-2-Acetylaminotetrahydronaphthalene.

The method of Schroeter(Ann.,1922,426,43) was employed but the nitration carried out at 15-20° and not below 0°.

19g. 2-acetylaminotetrahydronaphthalene(for preparation see p. 131) are dissolved in 200c.cs. concentrated sulphuric acid and, under powerful agitation and external cooling, a mixture of 8.2g. 82% nitric acid and 8.2g. sulphuric acid(sp.gr. 1.84) gradually added. The nitration was carried out at 15-20°. On completion of the addition of the acid the mixture is allowed to stir a few minutes and then poured into ice-water. The yellow product is removed, washed with water, then with cold alcohol and finally recrystallised from alcohol. 7g. 4-nitro-2-acetylaminotetrahydronaphthalene were obtained as nearly colourless needles, m.p. 193.5-194°(Schroeter, 194°.

4-Nitro-2-Iodotetrahydronaphthalene.

20g. 4-nitro-2-acetylaminotetrahydronaphthalene were hydrolysed by refluxing for 2 hours with 200c.cs. 25% sulphuric acid. The now clear solution was cooled when the sulphate of the base crystallised out in a fine state. 250 c.cs. 50% sulphuric acid were now added and the base diazotised by addition of a solution of 6g. sodium nitrite in 100 c.cs. water. The diazonium solution was poured into a solution of 50g. potassium iodide in 250c.cs. water and the mixture allowed to stand 2 hours when the black tarry scum was removed. This was extracted with alcohol, the tarry residue discarded and the extract boiled with animal charcoal when it was filtered into dilute sodium hydroxide solution to remove the last traces of free iodine. The oily precipitate was removed, washed with water, then with a little cold alcohol and finally fractionally distilled under a vacuum. The fraction, b.p. 175-195°/8m.m. solidified on cooling to a yellowish crystalline mass. This recrystallised from alcohol gave 7g. 4-nitro-2-iodotetrahydronaphthalene as pale yellow needles, m.p. 64-64.5°(found I = 41.85; required I = 41.91%).

Attempted Condensation.

4g. 4-nitro-2-iodotetrahydronaphthalene and 4g. copper powder were fused together. The copper became slightly discoloured at 215-220° and on raising the temperature to 250° and maintaining so for 1 hour the mass became sticky but did not harden; a considerable amount of decomposition took place as was shown by the gradual darkening of the mass. The reaction mixture was cooled, extracted with benzene, the dark coloured benzene extract decolourised with animal charcoal and the benzene removed. A small residue consisting of a reddish oil which would not solidify remained. This was redissolved in about 5c.cs. benzene and petroleum ether added when a small brownish yellow precipitate was thrown down. The quantity was, however, too small to recrystallise.

Preparation of 4-Nitro-2-Iodonaphthalene.

(1). By Oxidation of 4-Nitro-2-Iodotetrahydronaphthalene.

1g. 4-nitro-2-iodotetrahydronaphthalene and 1.2g. bromine were maintained at 100° until all reaction had ceased, no more hydrogen bromide or bromine being evolved. The temperature was then gradually raised to 160° and maintained so for 1 hour when the oxidation was complete. At higher temperatures decomposition was excessive, as was shown by evolution of iodine vapours, while even at 160° a considerable amount of decomposition took place. The cold mass was extracted with alcohol, the extract decolourised with animal charcoal and concentrated to about 10c.cs. On cooling, a gummy solid separated followed by crystals. The latter were mechanically removed and recrystallised from alcohol when a small quantity of 4-nitro-2-iodonaphthalene was obtained as pale yellow needles, m.p. 108°(found I = 41.51; required I = 42.47%).

(2). Removal of the Amino-group in 4-Nitro-2-Iodo-1-Aminonaph:thalene.

1g. 4-nitro-2-iodo-1-aminonaphthalene was dissolved in 150c.cs. absolute alcohol, 4c.cs. concentrated sulphuric acid diluted with 50c.cs. absolute alcohol and 1g. amyl nitrite(excess) in alcoholic solution added. Reduction of the diazonium compound was complete on maintaining the solution at the boil for 10 minutes. Water was then added when a dark red product was precipitated. This was dissolved in alcohol, the solution boil with animal charcoal and the filtrate concentrated to about 10c.cs. On cooling, 0.05g. 4-nitro-2-iodonaphthalene was obtained as pale yellow needles, m.p. 108°. A mixed m.p. with 4-nitro-2-iodonaphthalene obtained by oxidation of 4-nitro-2-iodotetrahydronaphthalene gave no depression.

Diazotisation of the 4-nitro-2-iodo-1-aminonaphthalene in concentrated sulphuric acid solution and subsequent treatment with 90% alcohol gave rise to nothing but tars.

1-AMINO-2:2'-DINAPHTHYL.

1g. 1-nitro-2:2'-dinaphthyl(for preparation see p. 126) was dissolved in 20c.cs. glacial acetic acid and 2c.cs. concentrated hydrochloric acid added. Reduction was carried out at the boil using zinc dust. On completion of the reduction, the solution was filtered and the filtrate cooled when the hydrochloride of the base separated as lustrous plates. The hydrochloride was recrystallised from alcohol and the free base liberated by addition of ammonia solution. Recrystallised from alcohol, 0.8g. 1-amino-2:2'-dinaphthyl was obtained as silvery plates, m.p. 220°.

PROPERTIES and DERIVATIVES of the NAPHTHIDINE BASES and IMINES.

4:4'-Diamino-1:1'-Dinaphthyl(Naphthidine).

The base formed silvery plates, m.p. 202°, from alcohol. It is fairly soluble in most common organic solvents but completely insoluble in water.

The hydrochloride and sulphate(Nietski and Goll, Ber., 1885,18,3252) both consist of lustrous plates. The hydrochloride is soluble in hot water but practically insoluble in the cold; a water solution, on treatment with oxidising agents, gives a carmine colour(Cumming and Steel, J.C.S., 1923,123,2464).

Acetyl-derivative.

Acetylation of the base readily took place by boiling for a few minutes with acetic anhydride. The acetyl-derivative, so formed, gave colourless microscopic needles, m.p. 363-364°, from nitrobenzene. It was practically insoluble in low boiling solvents but readily soluble in hot nitrobenzene.

Benzoyl-derivative.

Benzoylation of the base was easily effected by the Schotten-Baumann method. The product formed colourless plates, m.p. 318.5-319.5°, from nitrobenzene. It was practically insoluble in low boiling solvents.

Picrate.

The picrate formed brownish yellow needles, m.p. 146-147°, from benzene.

3:3'-Diamino-1:1'-Dinaphthyl.

The base formed colourless plates, m.p. 270°, from benzene. It was readily soluble in alcohol and hot benzene but sparingly soluble in cold benzene.

Both the hydrochloride and sulphate proved exceedingly soluble in water and in consequence neither have been isolated.

The small quantity of the base available prevented the preparation of any derivatives.

2:2'-Diamino-1:1'-Dinaphthyl.

The base formed silvery plates, m.p. 191°, from alcohol. It is fairly soluble in hot alcohol but sparingly soluble in the cold; practically insoluble in hot or cold petroleum ether; fairly soluble in cold benzene.

Both the hydrochloride and sulphate are very soluble in water. The former has, however, been obtained by Meisenheimer and Witte(Ber.,1903,36,4153) by treatment of the base with concentrated hydrochloric acid; it formed long colourless needles.

2:2'-Imine-1:1'-Dinaphthyl.

Prolonged refluxing of the base in glacial acetic acid solution partially converts it into the imine. The latter is easily separated from unchanged base by fractional recrystallisation from alcohol. The properties and derivatives of the imine are described later.

Acetyl-derivative.

The base was very readily acetylated, the reaction with acetic anhydride taking place in the cold. The acetyl-derivative formed colourless cubes, m.p. 241°, from alcohol.

Benzoyl-derivative.

The base was readily benzoylated by the Schotten-Baumann method. The product gave colourless prisms, m.p. 232-233°, from nitrobenzene. It was practically insoluble in low boiling solvents.

Picrate.

The picrate formed light brownish yellow plates, m.p. 185°, from benzene.

1:1'-Diamino-2:2'-Dinaphthyl(Dinaphthyline).

The base formed colourless plates, m.p. 281°, from benzene. It is sparingly soluble in alcohol; slightly soluble in cold benzene but fairly soluble in the heat; insoluble in water.

Both the hydrochloride and sulphate are exceedingly soluble in water and neither have been isolated.

1:1'-Imine-2:2'-Dinaphthyl.

The base is completely converted into the imine by refluxing in acid solution for a short period. The properties and derivatives of the imine are given later.

Acetyl-derivative.

The base, on treatment with excess acetic anhydride for

24 hours in the cold, gave an acetyl-derivative which, recrystallised from alcohol, formed colourless irregular plates, m.p. 230-231°.

Considering the ease with which the base, on treatment with hot acid, gives the imine, it is remarkable that an acetyl-derivative should be formed at all.

Benzoyl-derivative.

Benzoylation of the base readily took place by the Schotten-Baumann method. The derivative formed colourless irregular plates, m.p. 278-279°, from nitrobenzene; a mixed m.p. with dinaphthyline, m.p. 281°, gave 240-245°.

Picrate.

Since dinaphthyline is decomposed by picric acid, giving the imine, the picrate could not be obtained pure. The product from benzene gave m.p. 170-180°.

1-Amino-2:2'-Dinaphthyl.

The base formed colourless plates, m.p. 220°, from alcohol. It is fairly soluble in most organic solvents but insoluble in water.

The hydrochloride and sulphate both form lustrous plates.

Acetyl-derivative.

The base was readily acetylated by maintaining for 2-3 minutes at the boil with acetic anhydride. The acetyl-derivative formed colourless plates, m.p. 229-230°, from alcohol.

1:1'-Imine-2:2'-Dinaphthyl(Dinaphthyleneimine; Dinaphthyl-:carbazole).

The imine gave colourless leaflets, m.p. 221°, from glacial acetic acid. It is readily soluble in hot glacial acetic acid but sparingly soluble in the cold; fairly soluble in alcohol and benzene; slightly soluble in petroleum ether.

Acetyl-derivative.

The acetyl-derivative was obtained by Nietzki and Goll(loc.cit.) by treatment of the imine with acetic anhydride at 220°. It formed colourless plates, m.p. over 300°.

Benzoyl-derivative.

The benzoyl-derivative was isolated by Cumming and Steel(loc.cit.) as colourless plates, m.p. 119°.

Picrate.

The picrate was obtained by Nietzki and Goll(loc.cit.) as red needles, m.p. 226°, from either alcohol or benzene.

Nitroso-derivative.

The nitroso-derivative was obtained, by treatment of a glacial acetic acid solution of the imine with excess sodium nitrite, as fine yellow plates, m.p. over 300°(Nietzki and Goll, loc.cit.).

2:2'-Imine-1:1'-Dinaphthyl.

The imine gave colourless prisms, m.p. 158°, from alcohol. It is very soluble in most organic solvents other than petroleum ether.

Acetyl-derivative.

The imine was not acetylated after 4 hours refluxing with acetic anhydride. The addition of a drop of concentrated sulphuric acid failed to aid the reaction.

Benzoyl-derivative.

Repeated attempts to benzoylate the imine by the Schotten-Baumann method always resulted in the formation of gums which could not be made to yield crystals.

Picrate.

The picrate was obtained by Meisenheimer and Witte(loc. cit.) as black needles, m.p. 217°, from benzene.

Nitroso-derivative.

Treatment of the imine in glacial acetic acid solution with excess solid sodium nitrite gave the nitroso-derivative which gradually separated from solution. Recrystallised from carbon tetrachloride it formed reddish yellow needles, m.p. 154°, with decomposition.

Dyestuffs Derived from the Naphthidine Bases.

Solutions of the hydrochlorides of the bases were diazotised and coupled to various compounds. The colours of the solutions obtained are given on the table on p. 150.

TABLE OF DERIVATIVES OF THE NAPHTHIDINE BASES AND IMINES.

	Hydro-:chloride	Sulphate	Acetyl-derivative	Benzoyl-derivative	Picrate	Nitroso-derivative
4:4'-Diamino-1:1'-dinaphthyl (Naphthidine)	Colourless spangles; insol. in the cold	Colourless spangles; insol.	Colourless needles, m.p. 363-364°	Colourless plates, m.p. 318.5-319.5°	Brownish yellow needles, m.p. 146-147°	
3:3'-Diamino-1:1'-dinaphthyl	Exceeding-:ly soluble	Exceeding-:ly soluble				
2:2'-Diamino-1:1'-dinaphthyl	Colourless plates; readily soluble	Exceeding-:ly soluble	Colourless cubes, m.p. 241°	Colourless prisms, m.p. 232-233°	Brownish yellow plates m.p. 185°	
1:1'-Diamino-2:2'-dinaphthyl (Dinaphthyline)	Exceeding-:ly soluble	Exceeding-ly soluble	Colourless irregular plates, m.p. 230-231°	Colourless irregular plates, m.p. 278-279°	Not obtained pure, m.p. 170-180°	
1-Amino-2:2'-dinaphthyl	Colourless plates; insol. in the cold	Colourless plates; insol. in the cold	Colourless plates, m.p. 229-230°			
2:2'-Imine-1:1'-dinaphthyl			Not obtained	Not obtained	Black needles, m.p. 217°	Reddish yellow needles, m.p. 154°
1:1'-Imine-2:2'-dinaphthyl (Dinaphthylene-:imine; dinaph-:thylcarbazole)			Colourless plates, m.p. over 300°	Colourless plates, m.p. 119°	Red needles, m.p. 226°	Yellow plates, m.p. over 300°

TABLE OF COLOURS OBTAINED BY COUPLING NAPHTHIDINE BASES TO VARIOUS COMPOUNDS

Compound	Base				
	4:4'-Diamino-1:1'-dinaphthyl (Naphthidine)	3:3'-Diamino-1:1'-dinaphthyl	2:2'-Diamino-1:1'-dinaphthyl	1:1'-Diamino-2:2'-dinaphthyl (Dinaphthybine)	1-Amino 2:2'-dinaphthyl
1:4-Naphthol sulphonic acid	brownish red	insol. reddish yellow	poor brownish red	pale brownish red with a blue fluorescence	very faint yellow
Naphthionic acid	yellowish red	orange red	insol. yellowish brown	pale yellowish green	no colour
2-Naphthol	Reddish violet	insol. bright red	insol. bright red	pink	faint red
H-acid	excellent purple	splendid crimson violet	splendid reddish violet	fine red with a blue fluorescence	poor brownish red
G-acid	red	faint yellow	insol. brownish yellow	pale reddish yellow	faint yellow
R-salt	red with a blue fluorescence	poor yellowish red	insol. brownish red	poor red	faint yellow

It should be noted that the above colours all proved stable to acid. In this respect they differ remarkably from several of the corresponding diphenyl derivatives e.g. Congo Red, obtained by coupling benzidine to naphthionic acid, turns blue on treatment with acid.

Absorption Spectrum of the Naphthidine Bases and Imines.

The absorption spectrum of the bases and imines was photographed by means of a Hilger Spectrograph, using an iron arc as the source of light. Solutions of the compounds in spectroscopically pure alcohol were made up to a concentration of exactly N/2,000 and the absorption spectrum of various thicknesses of these solutions then photographed. The graphs, obtained by plotting the logarithms of relative thicknesses of the solutions against oscillation frequencies, are shown in figures 2 and 3.

As a matter of interest and to see how it compared with those of the bases, the absorption spectrum of unsymmetrical 1:1'-hydrazonaphthalene was also photographed. The graph is given in figure 1. The quantity of symmetrical 1:1'-hydrazonaphthalene and of 2:2'-hydrazonaphthalene available was insufficient for this purpose.

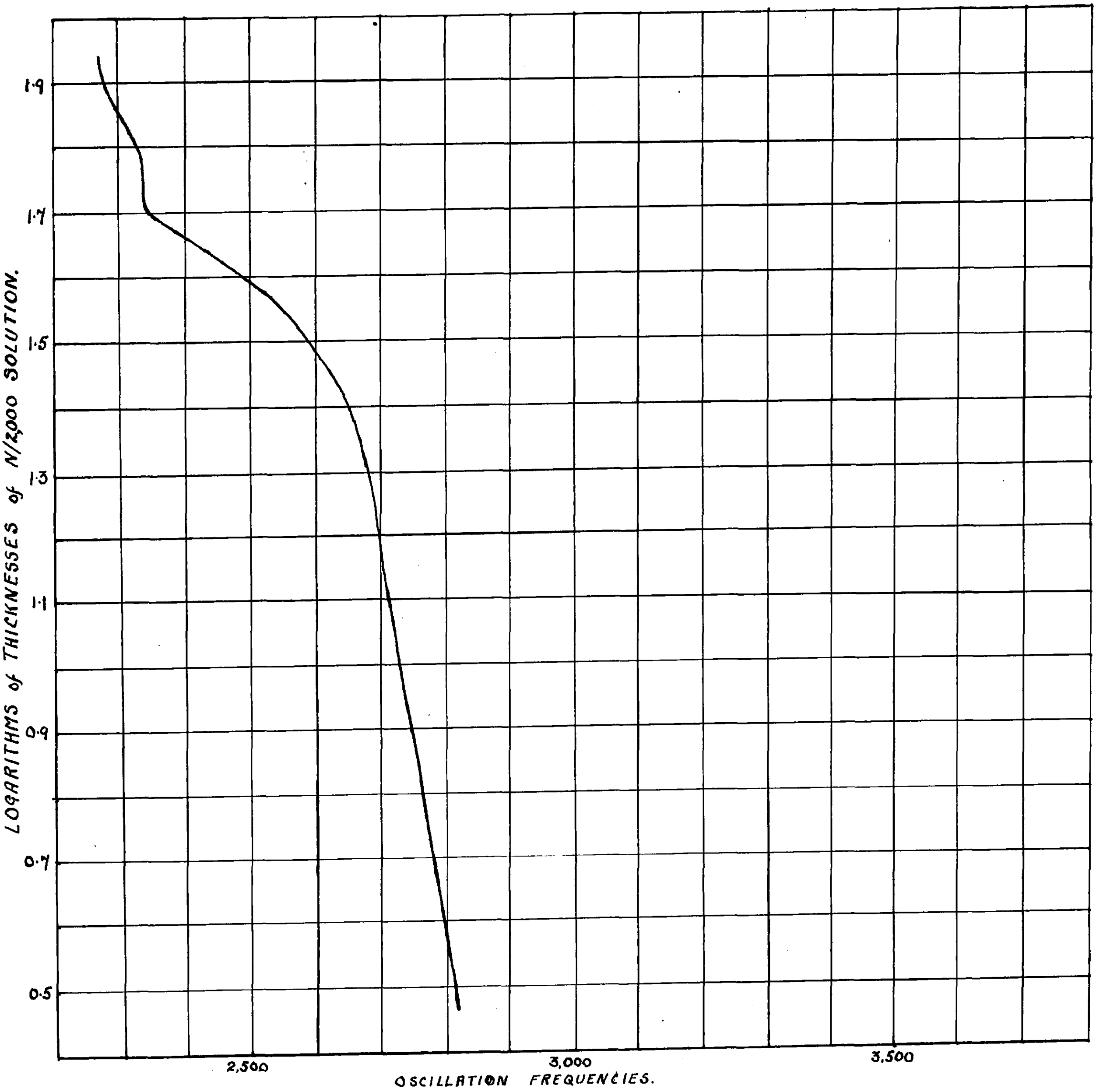
It is worthy of note that, in the light of the iron arc, the naphthidine solution acquired a pale blue fluorescence, the dinaphthyline solution a brilliant bluish green fluorescence, the 2:2'-diamino-1:1'-dinaphthyl solution a purple fluorescence, the 2:2'-imine-1:1'-dinaphthyl solution a violet fluorescence and the dinaphthyleneimine solution a purple fluorescence. No fluorescence was observed with the unsymmetrical 1:1'-hydrazonaphthalene solution.

In the case of the diamino-compounds(Fig. 2) it is to be noted that as the distance from the amino-group to the bond of union increases the absorption passes further towards the region of lower frequency. A small band appears in the 2:2'-diamino- and 4:4'-diamino-1:1'-dinaphthyl curves with head about 2,950 and 3,150 respectively.

In the case of 2:2'-imine-1:1'-dinaphthyl(Fig. 3) the absorption is displaced slightly towards the red. A small band appears with head at about 2,900 corresponding approximately to the band in the diamine from which it is derived. Similarly the absorption of the 1:1'-imine-2:2'-dinaphthyl corresponds approximately with that of the diamine from which it is derived, the absorption being displaced towards the violet end.

The unsymmetrical hydrazo-compound(Fig. 1) offers a contrast to the bases. From frequencies of about 2,850 to 2,700 the absorption is identical with that of the base dinaphthyline(Fig. 2) which it forms by conversion. For frequencies below 2,700, the absorption of the unsymmetrical hydrazo-compound becomes much more complete towards the red.

Fig. 1.



Unsymmetrical 1:1'-Hydrazonaphthalene.

Fig. 2.

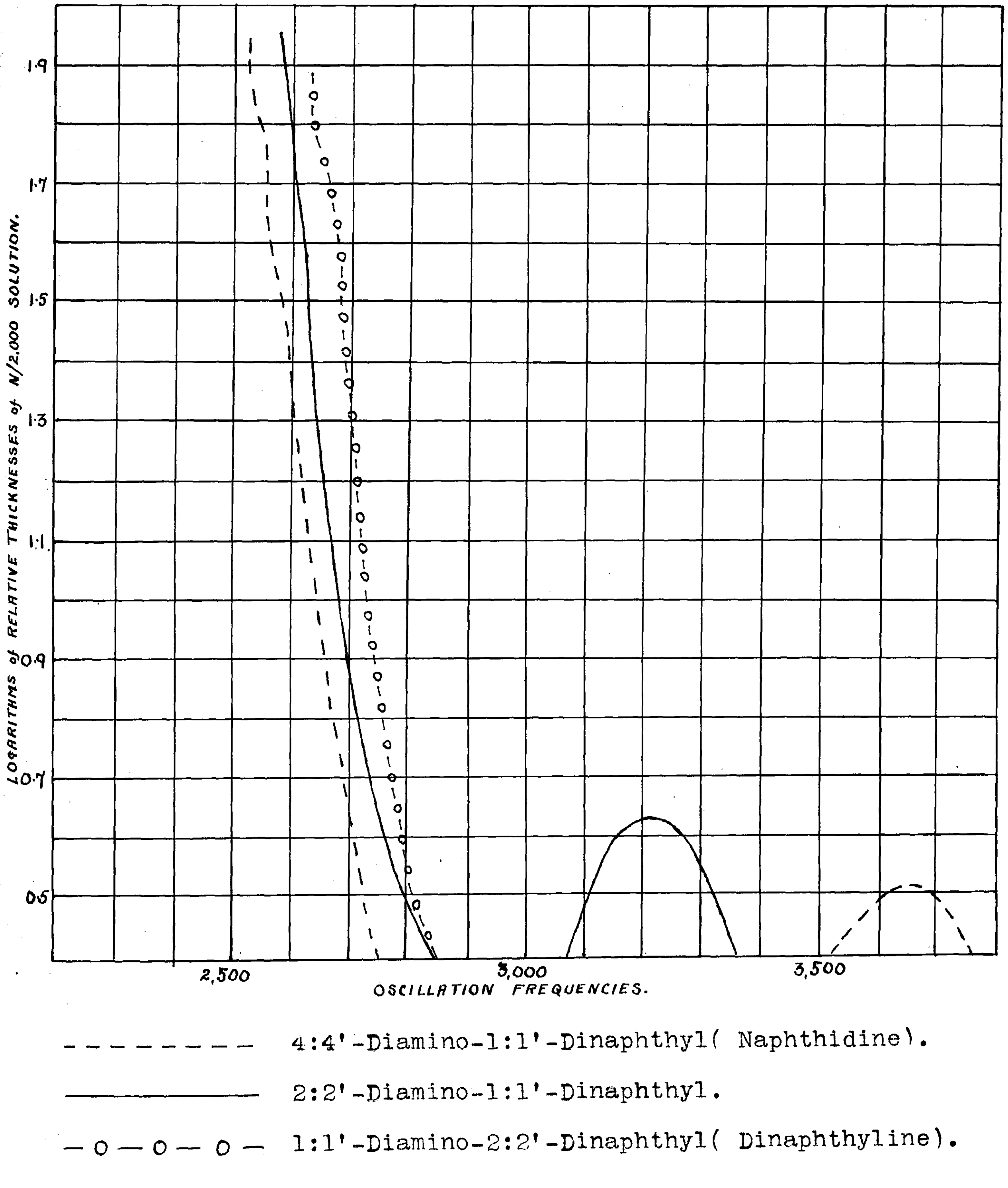
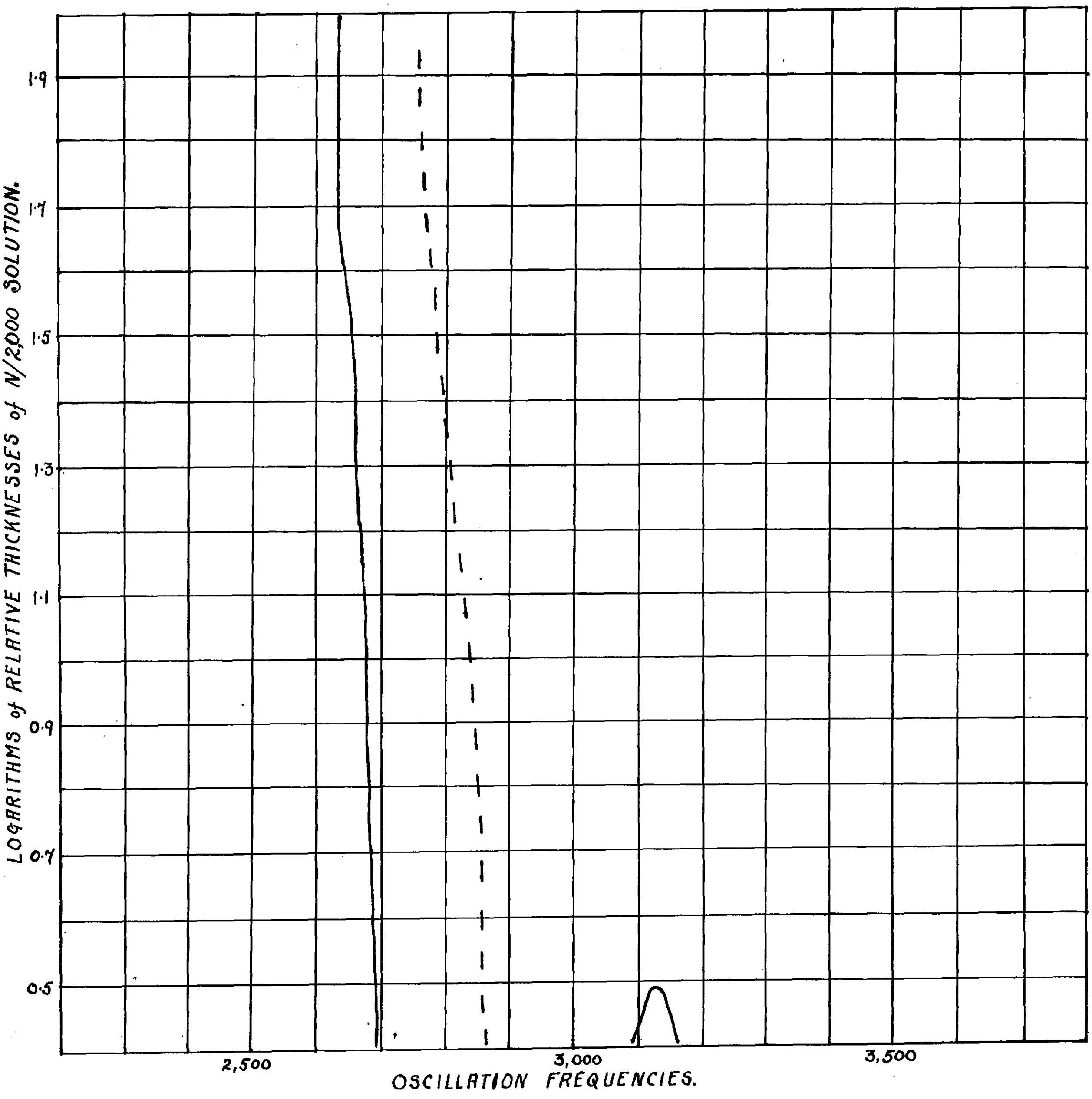

1·9
1·7
1·5
1·3
1·1
0·9
0·7
0·5
LOGARITHMS of RELATIVE THICKNESSES of N/2,000 SOLUTION.
2,500
3,000
3,500
OSCILLATION FREQUENCIES.
4:4'-Diamino-1:1'-Dinaphthyl(Naphthidine).
2:2'-Diamino-1:1'-Dinaphthyl.
1:1'-Diamino-2:2'-Dinaphthyl(Dinaphthyline).

Fig. 3.



——— 2:2'-Imine-1:1'-Dinaphthyl.

– – – –1:1'-Imine-2:2'-Dinaphthyl(Dinaphthyleneimine; Dinaphthylcarbazole).

Action of Sodium Amalgam on the Nitrochlorobenzenes.

(1). O-Chloronitrobenzene.

(a). 4g. compound were gradually added to a 2½% amalgam. At temperatures under 130° no reaction took place while over 130° the reaction was most vigorous, flashes of light and a rapid rise in temperature being observed after each addition. Much decomposition took place. Extraction with benzene yielded a few crystals, m.p. 117-118°, of probably 2:2'-dinitrodiphenyl, m.p. 124°.

(b). 6g. o-chloronitrobenzene were dissolved in 25c.cs. benzene and a large excess of the amalgam added. On heating to the boil, the solution rapidly attained a bright red colour. After refluxing for 12 hours most of the amalgam had disappeared, much free mercury as well as a copious black precipitate being present. The latter was removed, washed well with benzene and extracted with water when a deep red solution was obtained. This solution, after refluxing with animal charcoal and filtering, was acidified and the precipitate so obtained recrystallised from alcohol when o-nitrophenol, m.p. 42-43°, was formed.

No 2:2'-dinitrodiphenyl was obtained.

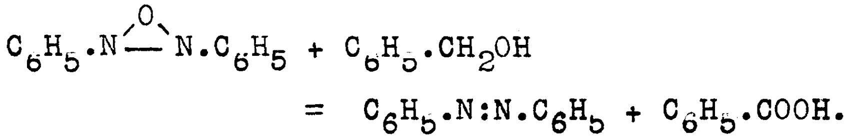
(2). p-Chloronitrobenzene.

The effect of refluxing p-nitrochlorobenzene in benzene solution with sodium amalgam was noted. Employing the same quantities as in the reaction with o-nitrochlorobenzene, a similar black precipitate was obtained after refluxing for 2 hours. This on treatment as above yielded probably p-nitrophenol, m.p. 70-79°. The poor yield prevented further recrystallisation.

THE REACTION BETWEEN BENZYL ALCOHOL, BENZALDEHYDE and QUINOLINE on AZOXY- and AZOBENZENES and AZOXY- and AZOTOLUENES.

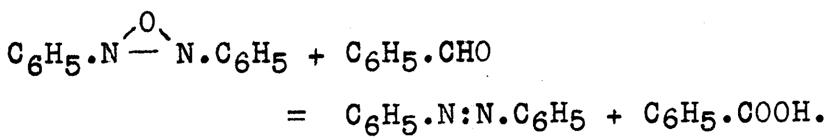
The action of benzyl alcohol, benzaldehyde and quinoline on symmetrical 1:1'-azoxynaphthalene having lead to such remarkable results, it was decided to study the effect of these reagents on azoxybenzene and azoxytoluene in order to determine if the results were common to all azoxy-compounds and, if possible, to advance a satisfactory explanation of the mechanism of the reaction.

However, it was found that on refluxing azoxybenzene with benzyl alcohol no trace of an unsymmetrical azoxybenzene was formed, reduction having taken place with formation of azobenzene, the benzyl alcohol being oxidised to benzaldehyde or benzoic acid.

(a) 

$$C_6H_5.N\overset{O}{—}N.C_6H_5 + C_6H_5.CH_2OH = C_6H_5.N{:}N.C_6H_5 + C_6H_5.COOH.$$

When benzaldehyde was employed the reaction proceeded in a most remarkable manner about 10% of the azoxybenzene being converted into benzanilide while again no trace of an unsymmetrical azoxy-compound was noted. It will be observed that benzaldehyde cannot possibly reduce azoxybenzene to other than azobenzene

(b) 

$$C_6H_5.N\overset{O}{—}N.C_6H_5 + C_6H_5.CHO = C_6H_5.N{:}N.C_6H_5 + C_6H_5.COOH.$$

and, therefore, the production of a monamine is impossible by direct reduction.

Assuming first the preliminary reduction of azoxybenzene to azobenzene the formation of benzanilide is possible by either of the following two methods:-

(1). By partial condensation of the benzaldehyde benzoin could be produced and this would be capable of reducing azobenzene to aniline, the benzoin itself being oxidised to benzil.

$$C_6H_5.CHO + C_6H_5.CHO = C_6H_5.CH(OH).CO.C_6H_5.$$

$$2C_6H_5.CH(OH).CO.C_6H_5 + C_6H_5.N{:}N.C_6H_5$$
$$= 2C_6H_5.CO.CO.C_6H_5 + 2C_6H_5.NH_2.$$

The aniline obtained could react with the benzoic acid produced as in equation (a) and so give rise to benzanilide.

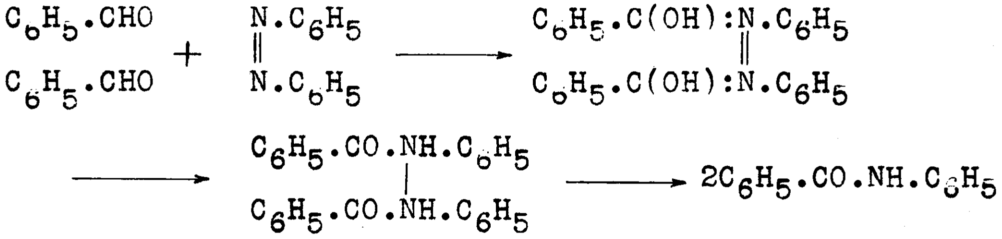
$$C_6H_5.NH_2 + C_6H_5.COOH = C_6H_5.NH.CO.C_6H_5 + H_2O.$$

In support of the above it was found that benzoin readily reduced azobenzene to aniline when the two were either directly fused together or refluxed in benzyl alcohol solution. However, the result of refluxing together aniline, benzoic acid and benzaldehyde caused, contrary to expectations, the formation of benzalaniline, benzanilide not being produced.

$$C_6H_5.NH_2 + C_6H_5.CHO = C_6H_5.N{:}CH.C_6H_5 + H_2O.$$

and, moreover, in an exhaustive examination of the original reaction, viz. the refluxing together of benzaldehyde and azoxybenzene, no trace of benzoin, benzil or an anil of either of these two compounds was isolated.

(2). It is a well known fact that benzaldehyde, apart from forming condensation products, is capable of forming numerous additive products and so the possibility, as shown in the following series of equations, of benzaldehyde and azobenzene giving rise to an unstable intermediate additive product which would break down with formation of benzanilide was investigated.



$$\begin{matrix} \mathrm{C_6H_5.CHO} \\ \mathrm{C_6H_5.CHO} \end{matrix} + \begin{matrix} \mathrm{N.C_6H_5} \\ \| \\ \mathrm{N.C_6H_5} \end{matrix} \longrightarrow \begin{matrix} \mathrm{C_6H_5.C(OH):N.C_6H_5} \\ \| \\ \mathrm{C_6H_5.C(OH):N.C_6H_5} \end{matrix}$$

$$\longrightarrow \begin{matrix} \mathrm{C_6H_5.CO.NH.C_6H_5} \\ | \\ \mathrm{C_6H_5.CO.NH.C_6H_5} \end{matrix} \longrightarrow \mathrm{2C_6H_5.CO.NH.C_6H_5}$$

Confirmation of the formation of such an unstable additive compound was obtained by the reaction between benzaldehyde and azobenzene as when refluxed together a nearly theoretical yield of benzanilide resulted.

From the foregoing it is concluded that the formation of the benzanilide is due neither wholly nor in part to benzoin but to the formation of an unstable intermediate additive compound as formulated above.

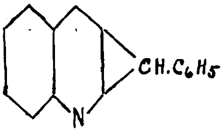
Similarly to the reaction with azoxy- and azobenzenes, benzyl alcohol reduced p-azoxytoluene to p-azotoluene while with benzaldehyde and p-azotoluene benzo-p-toluidide was obtained. In the reaction between benzaldehyde and p-azoxytoluene reduction to p-azotoluene took place.

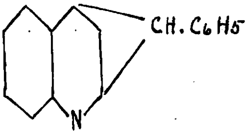
It is interesting to note that benzaldehyde had no reaction with either 1:1'- or 2:2'-azonaphthalenes.

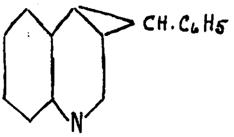
It was observed that the addition of quinoline or pyridine to the reaction between azoxybenzene and benzaldehyde completely inhibited the formation of benzanilide, the azoxybenzene being recovered unchanged. The effect of the addition of quinoline to the reaction between azobenzene and benzaldehyde was, therefore, examined but even in this case benzanilide was not formed, the azobenzene remaining unaffected.

In view of the work of Fry and Bowman(J.Amer.C.S.,1930, 52,1531), the action of quinoline in completely preventing reduction of azoxybenzene to azobenzene is all the more remarkable since these authors found that the addition of quinoline, as well as certain other organic bases, caused reduction by sodium methylate of azoxybenzene to azobenzene, a reduction which does not take place in absence of an organic base.

In the reaction between azobenzene, benzaldehyde and quinoline a few needles, m.p. 99-100°, were obtained by fractional recrystallisation from the unchanged azobenzene. This compound, m.p. 99-100°, proved to be a condensation product of benzaldehyde and quinoline as it resulted in 9% yield when these two reagents alone were refluxed together. The compound contained a basic nitrogen as both the dihydrate and the anhydrous form of the hydrochloride have been prepared. From a determination of its molecular weight and C, H and N content it may be

(1)


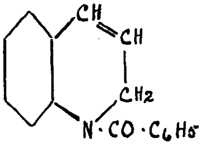
(2)


OR (3)


,

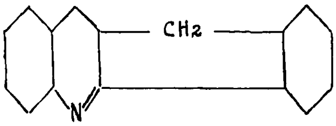
formula (1) being the most probable.

Benrath(Journ.prakt.Chem.,1906,73,383) by exposure of equimolecular quantities of benzaldehyde and quinoline to sunlight isolated a compound to which he ascribed the formula

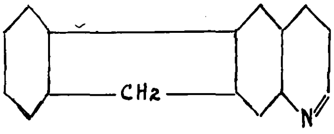


the benzoyl-group being attached to nitrogen as the compound exhibited no basic properties.

Two other isomeric bases are known. Noelting and Blum(Ber.,1901,34,2471) by distillation of quinonylphenylene ketone with a mixture of equal parts zinc dust and zinc oxide obtained quinolylene-phenylenemethane, m.p. 166°.



Diels and Stahlin(Ber.,1902,35,3276) obtained fluorene-quinoline, m.p. 134.5°(corr.), by heating together arsenic acid, concentrated sulphuric acid, 2-aminofluorene and glycerine for 4-5 hours at 140°.



Experimental.

Benzyl Alcohol and Azoxybenzene.

5g. azoxybenzene were vigorously refluxed, in presence of carbon dioxide to prevent oxidation, with 100c.cs. benzyl alcohol for 8 hours. The pale yellow solution slowly turned a bright red. The solution was steam distilled until no more red oily drops passed over. The red oil in the steam distillate was separated from water and repeatedly extracted with hot water, to remove benzyl alcohol, until the residue solidified on cooling. This recrystallised from petroleum ether gave about 0.5g. azobenzene, m.p. 68°, as red plates.

The small residue in the flask from the steam distillation consisted of a dark coloured oil which, after repeated washing with hot water, finally solidified in a freezing mixture. The solid, so obtained, was extracted with petroleum ether and the solution, after drying over calcium chloride, concentrated when a small quantity of a low melting orange red solid separated. It probably consisted of unchanged azoxybenzene.

Benzyl Alcohol and p-Azoxytoluene.

0.4g. p-azoxytoluene and 7c.cs. benzyl alcohol were vigorously refluxed, in presence of carbon dioxide, for 8 hours and the solution steam distilled. The residue in the flask was extracted with petroleum ether, the extract refluxed with animal charcoal and the petroleum ether removed.

The solid obtained gave, after repeated recrystallisation from glacial acetic acid, about 0.1g. p-azotoluene, m.p. 141-142°; a mixed m.p. with p-azotoluene, m.p. 144°, showed no depression. The loss in yield was due to tarring, no other product being isolated.

Benzaldehyde and Azoxybenzene.

10g. azoxybenzene were vigorously refluxed, in presence of carbon dioxide, with 200c.cs. benzaldehyde for 12 hours. The bright red solution was concentrated, under reduced pressure, nearly to dryness and the last traces of benzaldehyde removed by steam distillation. The reddish coloured residue solidified on cooling and this, recrystallised from carbon tetrachloride, gave colourless plates of benzanilide, m.p. 162°; yield 1g. The filtrate from the recrystallisation gave, after evaporation to dryness and recrystallisation of the residue from alcohol, azoxybenzene, m.p. 36°. No benzoin, benzil or an anil of benzoin or benzil was isolated.

The benzanilide was identified as such by the following:-

(a). A mixed m.p. with benzanilide, m.p. 162°, showed no depression.

(b). On hydrolysis with 50% sulphuric acid, benzoic acid, m.p. 122°, was obtained. Aniline was identified in the filtrate from the benzoic acid by (1) giving a purple colour with bleaching powder solution and (2) giving a red dyestuff on coupling with 2-naphthol.

(c). On bromination, the bromo-compound, m.p. 202°, was obtained.

Benzaldehyde and p-Azoxytoluene.

2g. p-azoxytoluene were refluxed as above with 20c.cs. benzaldehyde for 10 hours and the solution steam distilled. The residue was repeatedly recrystallised from glacial acetic acid with addition of animal charcoal when a small quantity of p-azotoluene, m.p. 140-141°, was finally obtained; a mixed m.p. with p-azotoluene, m.p. 144°, gave no depression.

The difficulty of obtaining the p-azotoluene in a pure state showed it to be contaminated with some other product-possibly benzo-p-toluidide although the latter compound was not isolated.

Benzaldehyde and Azobenzene.

5g. azobenzene were vigorously refluxed, in presence of carbon dioxide, with 100c.cs. benzaldehyde for 8 hours. The deep red colour of the solution appeared unaltered at the end of the period of heating. The solution was steam distilled until the residue solidified on cooling. The pale yellow oil which distilled over consisted of unchanged benzaldehyde. The dirty brown residue was recrystallised from carbon tetra:chloride, with addition of animal charcoal, when benzanilide was obtained as colourless plates, m.p. 162°. The yield of the crude benzanilide was almost quantitative and no other product was isolated.

Benzaldehyde and p-Azotoluene.

1g. p-azotoluene and 10c.cs. benzaldehyde were refluxed, in presence of carbon dioxide, for 8 hours. After steam distillation, the residue was extracted with benzene.and the extract refluxed with animal charcoal to remove the large amount of decomposition matter present. The crystals obtained on concentration of the benzene solution, were recrystallised several times from alcohol when benzo-p-toluidide, m.p. 155-156°, was obtained; yield 0.3g. A mixed m.p. with benzo-p-toluidide, m.p. 158°, showed no depression.

Benzaldehyde and 1:1'- and 2:2'-Azonaphthalenes.

1:1'- and 2:2'-azonaphthalenes were refluxed with benzaldehyde but no reaction took place, the azo-compounds being recovered on removal of the benzaldehyde.

Benzaldehyde, Quinoline and Azoxybenzene.

The reaction between azoxybenzene and benzaldehyde was repeated but with addition of 60c.cs. quinoline to the refluxing mixture. Practically no colour change was observed and on working up as above, the only product isolated was unchanged azoxybenzene, m.p. 36°. The substitution of pyridine for quinoline gave identical results.

Benzaldehyde, Quinoline and Azobenzene.

The reaction between benzaldehyde and azobenzene was repeated but with addition of 30c.cs. quinoline. No colour change other than a slight darkening was observed. The solution was steam distilled until no more red oily drops passed over. Unchanged benzaldehyde and quinoline first passed over followed by azobenzene. The latter recrystallised from petroleum ether gave m.p. 68°. The residue from the steam distillation consisted of a brownish oil which, after washing with dilute hydrochloric acid to remove all traces of quinoline and with sodium hydroxide to remove benzoic acid, became nearly solid. This was pressed on porous plate and allowed to stand several days when the mass had become hard. The solid was extracted with petroleum ether and the extract cooled when yellowish crystals separated. These recrystallised twice from alcohol formed nearly colourless needles, m.p. 99-100°, of α,β-benzalquinoline(found C = 88.0, H = 5.7, N = 6.2, M.W. = 218, 232; required C = 88.5, H = 5.1, N = 6.4%, M.W. = 217).

The properties and hydrochlorides of α,β-benzalquinoline are described below.

<u>Benzaldehyde</u> <u>and</u> <u>Quinoline</u>.

53g. quinoline and 100g. benzaldehyde were refluxed for 6 hours in presence of carbon dioxide. Much water was given off at first. Most of the benzaldehyde and quinoline was removed by distillation, the remainder by steam distillation and the residue cooled in a freezing mixture when the mass solidified. This was pressed on porous plate to remove the last traces of liquid and the product recrystallised from acetone, carbon tetrachloride or petroleum ether when α,β-benzalquinoline was obtained as colourless needles, m.p. 99-100°. The yield obtained was 6g.

The anhydrous hydrochloride of the base was obtained by dissolving the base in chloroform and passing a current of dry hydrochloric acid gas through the solution. It formed lemon yellow needles, m.p. 221-221.5°(found N = 5.45; required N = 5.52%). It may be recrystallised from dry acetone.

The dihydrated form of the hydrochloride was obtained by dissolving the base in dilute hydrochloric acid and cooling the solution. The yellow product so obtained gave beautiful yellow needles, m.p. 106-107°, from concentrated hydrochloric acid(found N = 4.81; required N = 4.84%). It is but sparingly soluble in the commoner organic solvents other than alcohol in which it is extremely soluble. It is dissociated in water. Recrystallised from acetone it loses two molecules of water, the anhydrous hydrochloride being formed.

On heating above its melting point, the dihydrated hydrochloride loses water about 120° and solidifies to a lemon yellow mass without decomposition. On further heating it finally melts about 220° giving a dark orange coloured liquid. This product on cooling and dissolving in absolute alcohol gave by slow evaporation of the alcohol by exposure to the air, not the anhydrous hydrochloride but the dihydrated form, water having been extracted from the atmosphere.

The Reducing Action of Benzoin.

Benzoin and Azobenzene.

(1). 5g. azobenzene and 12g.(excess) benzoin were fused together, in presence of carbon dioxide, at 220-225° for 4 hours. About 4c.cs. liquid distilled over. This was identified as aniline by its odour and the formation of its hydrochloride, m.p. 198°; a mixed m.p. with aniline hydrochloride, m.p. 198°, showed no depression. At the end of the 4 hours the temperature was raised to 330° when a yellowish product, which solidified on cooling, distilled over. Recrystallised from alcohol it gave benzil, m.p. 95°.

(2). 5g. azobenzene and 12g. benzoin dissolved in 100c.cs. benzyl alcohol were refluxed, in presence of carbon dioxide, for 2½ hours. The solution was steam distilled until no more oil passed over. From the residue, which solidified to a gum on cooling, by fractional recrystallisation from alcohol, benzil, m.p. 95°, and a small quantity of a gum which could not be made to yield crystals, were obtained.

The steam distillate was acidified and again steam distilled. The residue was extracted with ether, the solution dried over calcium chloride and the ether removed when an oil, b.p. 195-200°, resulted. The presence of aniline was detected by the formation of the characteristic purple colour on addition of bleaching powder solution and further by the formation of a red dyestuff on coupling with 2-naphthol. It proved impossible to separate the aniline from the benzyl alcohol with which it was contaminated.

Benzoin, Azobenzene and Benzoic Acid in Benzyl Alcohol Solution.

The above experiment was repeated but 7g.(excess) benzoic acid were refluxed, in presence of carbon dioxide, for 6 hours. The solution was distilled, under reduced pressure, until no more benzaldehyde passed over. The residue solidified on cooling and after washing with sodium carbonate solution to remove the last traces of benzoic acid, was recrystallised twice from alcohol when colourless needles, m.p. 54°, of benzalaniline were obtained. No benzanilide was isolated.

Aniline, Benzaldehyde and Benzoic Acid.

5g. aniline and 7g.(5% excess) benzoic acid were refluxed for 6 hours with 100c.cs. benzaldehyde; the large excess of benzaldehyde was employed in order that the conditions might be comparable to those in the previous experiments. The solution was steam distilled until no more benzaldehyde passed over when the residue solidified on cooling. This, after washing with sodium carbonate to remove benzoic acid, was recrystallised from alcohol when colourless needles of benzalaniline, m.p. 54°, were obtained. No benzanilide was isolated.

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