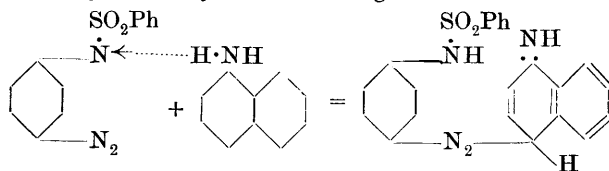


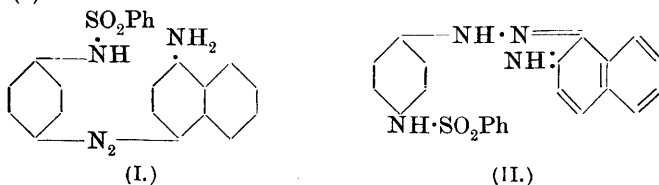
CXLIIV.—*The Interactions of Aromatic Amines and para-Diazoimides.*

By GILBERT T. MORGAN and FRANCES M. G. MICKLETHWAIT.

IN this communication the authors call attention to a direct method of producing certain aminoazo-compounds, which, although not generally applicable to all aromatic bases,* is, nevertheless, of some interest, as it consists of a simple additive process occurring between the more reactive amines and the para-diazoimides (Trans., 1905, 87, 82, 1302). This interaction does not take place with aniline and its homologues and alkyl derivatives, but proceeds quantitatively with the naphthylamines and the more active meta-diamines, such as 2:4-tolylenediamine (Trans., 1905, 87, 1305). The formation of an aminoazo-compound also occurs, although less readily, with the monoalkylnaphthylamines, but this reaction does not take place with the dialkylnaphthylamines. It is therefore very probable that the first step in this additive process consists in the migration of an aminic hydrogen from the base to the diazoimide with the assumption of a quinonoid configuration by the interacting amine:



The resulting compound may subsequently revert to the benzenoid form (I):

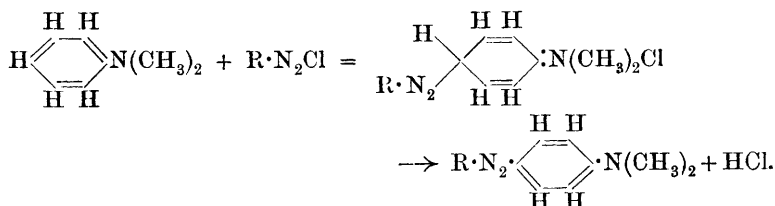


The reaction with β -naphthylamine occurs in a similar manner, only in this case it is the orthoquinonoid configuration (II) which is assumed.

If this explanation of the reaction is correct, it is obvious that the change will occur only when the aminic nitrogen is associated with, at least, one hydrogen atom, and this deduction accords with the fact that no combination takes place between the diazoimides and the dialkyl-

* Meldola and Eynon have summarised the methods generally available for the production of aminoazo-compounds (Trans., 1905, 87, 1), and it will be seen on reference to this résumé that the changes involved are usually substitutive and not merely additive.

naphthylamines. In several instances where the interaction could not be effected in this way, it was, nevertheless, brought about by coupling the base, generally a tertiary amine, with the corresponding diazonium salt, $C_6H_5 \cdot SO_2 \cdot NH \cdot C_6H_4 \cdot N_2Cl$, in aqueous solution, provided that sodium acetate or an alkali, or even excess of the base, was added to eliminate the hydrochloric acid set free in the following reaction :



I. Benzenesulphonyl-*p*-phenylenediazoimide and Benzenoid Amines.

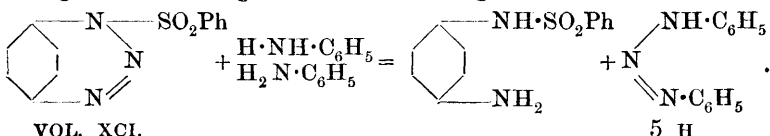
1. *Aniline*.—Benzenesulphonyl-*p*-phenylenediazoimide and excess of aniline did not interact when warmed at 40—50° for twelve hours, and the former compound crystallised unchanged on cooling the solution. At higher temperatures, the diazoimide decomposed, giving rise to tarry products.

Equal parts by weight of the diazoimide and aniline hydrochloride (3.5 grams of each) were heated in excess of aniline for seven hours at 45°, a small quantity of nitrogen was evolved and the solution darkened. Treatment of the product with dilute hydrochloric acid led to the formation of a dark blue, sparingly soluble hydrochloride, which, after crystallisation from dilute alcoholic hydrochloric acid, separated in steel-blue crystals and was identified as aminoazobenzene hydrochloride :

Cl = 14.87 and 15.09 ; theory requires Cl = 15.01 per cent. This product weighed 1.5 grams and gave, on treatment with ammonia, aminoazobenzene melting at 122°.

The filtrate from this hydrochloride, when treated with sodium acetate, furnished a pale yellow base, which, after crystallisation from dilute alcohol, was identified as benzenesulphonyl-*p*-phenylenediamine (m. p. 168—170°), the yield of which was 3.3 grams, this being more than 90 per cent. of the calculated amount.

This result shows that the reaction under investigation is an interesting case of the migration of diazo-nitrogen :



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In the presence of aniline hydrochloride, the diazoaminobenzene thus produced is chiefly converted into the isomeric aminoazobenzene, whilst a small proportion undergoes a destructive change, evolving nitrogen and giving rise to tarry products.

2. *Methylaniline*.—The diazoimide and redistilled methylaniline did not interact when warmed together for eighteen hours at 45–50°.

The azo-derivative was obtained by dissolving the diazoimide in dilute hydrochloric acid and mixing this solution with methylaniline dissolved in alcohol. A faint red coloration was produced and the addition of sodium acetate induced the gradual deposition of a viscid, orange precipitate. This product when crystallised from alcohol separated in large, yellowish-brown, prismatic crystals and melted at 143°:

0.2482 gave 29.2 c.c. nitrogen at 20° and 762.5 mm. $N = 13.50$.

$C_{19}H_{18}O_2N_4S \cdot C_2H_5 \cdot OH$ requires $N = 13.59$ per cent.

Another specimen of this compound, after three crystallisations from benzene, separated in ochreous crystals melting at 170°:

0.1420 gave 18.6 c.c. nitrogen at 21° and 761 mm. $N = 14.95$.

$C_{19}H_{18}O_2N_4S$ requires $N = 15.31$ per cent.

3. *Dimethylaniline*.—Negative results only were obtained on heating benzenesulphonyl-*p*-phenylenediazoimide with dry dimethylaniline, either alone or in the presence of dimethylaniline hydrochloride. In the former experiment, 90 per cent. of the diazoimide was recovered unchanged, whilst in the latter, nitrogen was evolved and tarry products only were formed.

Benzenesulphonyl-p-aminobenzeneazodimethylaniline,

$C_6H_5 \cdot SO_2 \cdot NH \cdot C_6H_4 \cdot N_2 \cdot C_6H_4 \cdot N(CH_3)_2$

was produced when benzenesulphonyl-*p*-aminobenzenediazonium chloride, produced either by direct diazotisation or by dissolving the diazoimide in cold hydrochloric acid, was allowed to react with dimethylaniline dissolved in alcohol. Only a faint coloration developed at first, showing that the tendency for the azo-condensation is very slight. The interaction was, however, promoted by adding sodium acetate in insufficient amount to precipitate the diazoimide. The aminoazo-derivative separated in the form of its purple hydrochloride and was set free and crystallised from benzene, when it separated partly in sheaf-like clusters of yellow needles and partly as orange prisms, both forms melting at 182–183°:

0.0596 gave 7.5 c.c. nitrogen at 19° and 762 mm. $N = 14.51$.

$C_{20}H_{20}O_2N_4S$ requires $N = 14.73$ per cent.

The two preceding aminoazo-compounds developed brownish-orange colorations with concentrated sulphuric acid.

II. Benzenesulphonyl-p-phenylenediazoimide and Naphthalenoid Amines.

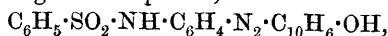
1. *α-Naphthylamine*.—The interaction of benzenesulphonyl-p-phenylenediazoimide and *α*-naphthylamine occurred even on triturating these substances together at the ordinary temperature, the solid mixture immediately developing a red colour. The formation of aminoazo-compound was completed by gently warming the mixture, and the excess of *α*-naphthylamine employed was removed by treatment with dilute hydrochloric acid. The residue, which consisted of the dark purple hydrochloride of the aminoazo-base, was treated with ammonia, and the liberated amine crystallised repeatedly from alcohol, when brownish-orange needles were obtained, melting at 172°; an intense crimson coloration was developed on treating the compound with concentrated sulphuric acid:

0.2542 gave 20.3 c.c. nitrogen at 18° and 763 mm. $N = 13.83$.

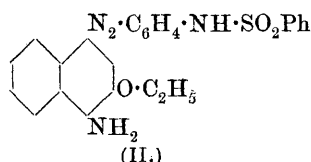
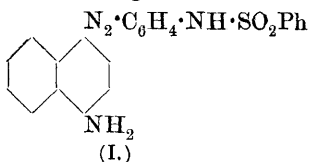
$C_{22}H_{18}O_2N_4S$ requires $N = 13.93$ per cent.

Benzenesulphonyl-p-aminobenzene-4-azo-α-naphthylamine (formula I) was also readily obtained by coupling *α*-naphthylamine with benzenesulphonyl-p-aminobenzenediazonium chloride in dilute alcoholic solution, when it separated in the form of its purple hydrochloride. The base, when prepared by this method, melted at 172° and gave nitrogen = 13.56 per cent.

This compound contains the groups NH_2 and $NH \cdot SO_2 \cdot C_6H_5$ separated by the residue $-C_6H_4 \cdot N_2 \cdot C_{10}H_6-$, and an attempt was made to prepare the cyclic diazoimide, $C_6H_5 \cdot SO_2 \cdot N \cdot C_6H_4 \cdot N_2 \cdot C_{10}H_6 \cdot N$, corresponding with the quinone, $O \cdot C_6H_4 \cdot N_2 \cdot C_{10}H_6 \cdot O$, but diazotisation of the base in glacial acetic acid with amyl nitrite or hydrochloric acid and sodium nitrite was accompanied by an elimination of nitrogen, and the corresponding azo-*α*-naphthol,



was produced. This compound gave a dark brown, sparingly soluble sodium derivative, which developed a bluish-purple coloration with concentrated sulphuric acid.



2. *β-Ethoxy-α-naphthylamine*.—This base reacted with the para-diazoimide quite as readily as *α*-naphthylamine itself, the substances combining even when intimately mixed in cold pyridine solution.

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The azo-compound was also readily obtained when the base and the corresponding diazonium chloride were coupled in aqueous solutions.

Benzenesulphonyl-p-aminobenzene-4-azo-2-ethoxy- α -naphthylamine (formula II) crystallised from benzene in red, acicular prisms with a green reflex; it melted at 176° and yielded a hydrochloride which separated from its deep purple solution in green crystals melting at $203-204^{\circ}$. The free azo-base furnished the following analytical result:

0.2378 gave 27.1 c.c. nitrogen at 22° and 758 mm. $N = 12.87$.

$C_{24}H_{22}O_3N_4S$ requires $N = 12.55$ per cent.

3. *Ethyl- α -naphthylamine*.—This base was prepared by adding slowly 85 grams of ethyl bromide, dissolved in 80 c.c. of alcohol, to a boiling solution of 100 grams of α -naphthylamine in 240 c.c. of the same solvent. A crystalline precipitate of ethyl- α -naphthylamine hydrobromide was slowly produced, and this salt when treated with either potassium hydroxide or potassium carbonate yielded ethyl- α -naphthylamine, an oily base which was extracted with ether and subsequently dried and fractionated. This amine boiled at $325-330^{\circ}/776$ mm., and when rectified under diminished pressure it boiled at $191^{\circ}/16$ mm., and was then obtained colourless, although on exposure to the atmosphere it darkened and became dichroic, being brown by transmitted and violet by reflected light.

The ease with which this base can be obtained from its hydrobromide by the action of alkali hydroxides does not bear out the statement that this salt on treatment with potassium hydroxide yields α -naphthylamine and not ethyl- α -naphthylamine (Limpricht, *Annalen*, 1856, 99, 117; Schiff, *ibid.*, 1857, 101, 90). When treated with sodium nitrite and hydrochloric acid, this base gives rise to nitroso-ethyl- α -naphthylamine (compare Koch, *Annalen*, 1888, 243, 310).

Ethyl- α -naphthylamine was also prepared by ethylating benzenesulphonyl- α -naphthylamine and then hydrolysing the benzenesulphonyl-ethyl- α -naphthylamine with alcoholic hydrochloric acid in sealed tubes at 135° . The foregoing method is, however, much more convenient, and yields ethyl- α -naphthylamine containing only a trace of unaltered α -naphthylamine.

Benzenesulphonyl-ethyl- α -naphthylamine, $C_6H_5 \cdot SO_2 \cdot N(C_2H_5) \cdot C_{10}H_7$, crystallised from alcohol in colourless prisms which acquired a mauve tint; it melted at $112-113^{\circ}$:

0.5852 gave 0.4442 $BaSO_4$. $S = 10.42$.

$C_{18}H_{17}O_2NS$ requires $S = 10.28$ per cent.

Ethyl- α -naphthylamine and benzenesulphonyl-*p*-phenylenediazoimide interacted when warmed together in pyridine for five hours at 50° , although the combination did not occur so readily when the reagents

were mixed in the absence of this medium. The aminoazo-compound when crystallised from alcohol separated in dark red, prismatic crystals and melted at 177—179°.

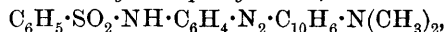
Benzenesulphonyl-p-aminobenzene-4-azoethyl- α -naphthylamine.—Ethyl- α -naphthylamine and benzenesulphonyl-*p*-aminobenzenediazonium chloride interacted very readily in aqueous solution; the hydrochloride of the aminoazo-compound being deposited as a bulky, dark purple precipitate, from which the base was obtained by the action of ammonia.

This preparation, when recrystallised from alcohol, gave transparent, crimson, lath-like crystals, which melted at 179° and did not depress the melting point of the substance prepared from ethyl- α -naphthylamine and the diazoimide:

0.1926 gave 23.3 c.c. nitrogen at 22° and 758 mm. $N = 13.67$.

$C_{24}H_{22}O_2N_4S$ requires $N = 13.04$ per cent.

4. *Dimethyl- α -naphthylamine*.—A sample of this base, prepared by Hantzsch's method (*Ber.*, 1880, 13, 1348; 1888, 21, 3124), was redistilled from acetic anhydride to remove any primary or secondary amine and then, finally, rectified under the ordinary pressure. When the base was heated for several hours with benzenesulphonyl-*p*-phenylenediazoimide at 50°, no combination occurred, and the greater portion of the diazoimide was recovered unchanged. Dimethyl- α -naphthylamine was then coupled with benzenesulphonyl-*p*-aminobenzenediazonium chloride in the manner indicated in the case of dimethylaniline. The dark green hydrochloride of *benzenesulphonyl-p-aminobenzene-4 azodimethyl- α -naphthylamine*,



was deposited very slowly, and the reaction was completed only after several days, sodium acetate being slowly added in small quantities. The free aminoazo-base was crystallised either from glacial acetic acid or from a mixture of benzene and light petroleum (b. p. 80—100°); from the former medium, it separated in dark garnet-red crystals having a green reflex, whilst from the latter it was deposited in red, nodular prisms; both forms melted at 155—156°:

0.1972 gave 23.0 c.c. at 21° and 774 mm. $N = 13.53$.

$C_{24}H_{22}O_2N_4S$ requires $N = 13.04$ per cent.

The two preceding aminoazo-compounds developed a crimson coloration with concentrated sulphuric acid.

5. *β -Naphthylamine*.—The para-diazoimide and β -naphthylamine combined readily when intimately mixed and slightly warmed, the reaction being accelerated by the addition of a small amount of pyridine. The mixture was extracted with dilute hydrochloric acid,

the residual hydrochloride decomposed by ammonia, and the amino-azo-compound then crystallised from alcohol.

Benzenesulphonyl-p-aminobenzeneazo-β-naphthylamine separated in minute, reddish-brown prisms, melted at 211–212°, and developed a deep bluish-purple coloration with concentrated sulphuric acid:

0.1910 gave 23.3 c.c. nitrogen at 20° and 760 mm. $N = 13.95$.

$C_{22}H_{18}O_2N_4S$ requires $N = 13.92$ per cent.

The yield of this base by the foregoing method was practically quantitative.

6. *Ethyl-β-naphthylamine*.—This base and the para-diazoimide did not interact in the cold, but on warming them together with some anhydrous pyridine at 60° for about twelve hours, the colour of the solution deepened and a formation of aminoazo-compound occurred. This substance was, however, contaminated with tarry products and was purified only with great difficulty. After repeated washing with dilute hydrochloric acid and treatment with ammonia, the residue was recrystallised from alcohol until, finally, a small amount of the amino-azo-base was obtained, which melted at 172° and did not depress the melting point of the compound prepared by coupling ethyl-β-naphthylamine and benzenesulphonyl-p-aminobenzenediazonium chloride in dilute alcohol.

Benzenesulphonyl-p-aminobenzeneazoethyl-β-naphthylamine,

$C_6H_5 \cdot SO_2 \cdot NH \cdot C_6H_4 \cdot N_2 \cdot C_{10}H_6 \cdot NH \cdot C_2H_5$,

when prepared by the latter method separated at once as a red precipitate, which, when recrystallised from alcohol, furnished bright scarlet leaflets melting at 176°:

0.1466 gave 17 c.c. nitrogen at 21° and 773 mm. $N = 13.42$.

0.3960 „ 0.2282 $BaSO_4$. $S = 7.91$.

$C_{24}H_{22}O_2N_4S$ requires $N = 13.04$; $S = 7.44$ per cent.

Both preparations gave an intense greenish-blue coloration with concentrated sulphuric acid.

7. *Dimethyl-β-naphthylamine*.—This tertiary base showed no tendency either to combine additively with benzenesulphonyl-p-phenylenediazoimide, or to couple with benzenesulphonyl-p-aminobenzenediazonium chloride in dilute alcoholic solution.

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