134. *The Cleavage of Arylazo-β-naphthylamines by Alcoholic Hydrochloric Acid.*

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Substituted arylazo-β-naphthylamines in which the aryl substituents are *op*-directing are decomposed by alcoholic hydrochloric acid into β-naphthylamine and an aryldiazonium compound, which in turn is decomposed by the alcohol. When the aryl substituents are *m*-directing (*e.g.*, the nitro-group), no decomposition occurs. The reaction appears to be a two-point attack by hydrochloric acid at the bond connecting nitrogen with the 1-carbon of the β-naphthylamine residue.

The decomposition of azo-compounds by mineral acids has often been investigated (see *inter alia* Rowe and Dangerfield, *J. Soc. Dyers and Col.*, 1936, **52**, 48). Azobenzene with hydrochloric acid yields benzidine (Zinin, *Annalen*, 1866, **137**, 376) and aniline and chloroaniline (Schmitt, *J. pr. Chem.*, 1879, **19**, 314). By keeping a methyl-alcoholic solution of azobenzene saturated with hydrogen chloride for 12 hours and then boiling it, Jacobson (*Annalen*, 1909, **367**, 304) isolated 2 : 3 : 5 : 4′-tetrachloro-4-aminodiphenylamine. Aniline and *p*-phenylenediamine, together with benzoquinone and various chlorobenzoquinones, were obtained by refluxing 4-aminoazobenzene with concentrated hydrochloric acid (Wallach and Kolliker, *Ber.*, 1884, **17**, 395). Those of the above authors who referred to the nature of the decomposition regarded it as primarily reduction, followed by oxidation and chlorination of some of the fission products by liberated chlorine. This point of view is not confirmed by the present investigation. Benzeneazo-α-naphthylamine, heated with 80% acetic acid at 130° under pressure, gave β-anilino-α-naphthaquinone, as did also benzeneazo-α-naphthol when refluxed with glacial acetic acid for 8—10 hours (Fischer and Hepp, *Ber.*, 1892, **25**, 2732).

Arylazo-β-naphthylamines in their behaviour with hydrochloric acid resemble diazoamino-compounds in that β-naphthylamine and the diazonium salt of the diazotised amine component are formed. This recalls the action of fuming nitric acid on azo-dyes (Meldola and Morgan, J., 1889, **55**, 608; Schmidt, *Ber.*, 1905, **38**, 3201; Charrier and Ferreri, *Gazzetta*, 1914, **44**, 165, 405; Rowe and Levin, *J. Soc. Dyers and Col.*, 1924, **40**, 226) in which a diazonium nitrate of the first component and a nitro-derivative of the coupling component are generally formed.

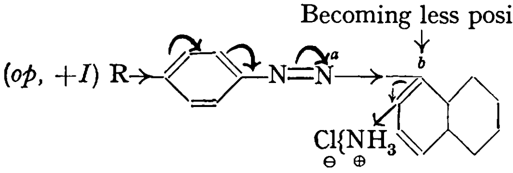
In order to facilitate the decomposition and promote solubility of the reactants, alcohol was used; where reaction occurred, therefore, the regenerated diazonium salt of the original amine was converted into either the deaminated compound or the alkoxy-compound.

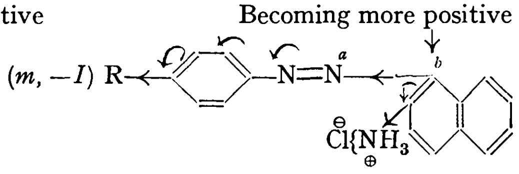
Fifteen arylazo-β-naphthylamines were refluxed (see Table) with a mixture of alcohol and hydrochloric acid (*d* 1·16) for 2—24 hours. The six azo-compounds which reacted readily (in 2—7 hours) afforded β-naphthylamine in 83·0—91·4% yield and had for first component either the free amine (aniline, α-naphthylamine, etc.) or an amine containing an *op*-directing (electron-repelling) group. *o*- and *p*-Methoxybenzeneazo-β-naphthylamines required 9 hours for half decomposition, the influence of the (—*I*) inductive effect of the methoxyl group in retarding decomposition thus being indicated, and *p*-chlorobenzeneazo-β-naphthylamine, in which the (—*I*) inductive effect is more intense, required 10 hours for quarter decomposition.

Diazotised amine.	Medium.	Time, hrs.	% Yield of β-naphthylamine.	Other products.
p-Anisidine	HCl + EtOH	9	53·5	Anisole
o-Anisidine	,,	8	58·0	Anisole
Aniline	,,	7	83·0	Phenetole
p-Toluidine	HCl + MeOH	2	84·8	*p*-Tolyl methyl ether
o-Toluidine	,,	2	87·0	*o*-Tolyl methyl ether
p-Aminophenol ...	HCl + EtOH	7	85·0	Phenol and *pp'*-azophenol
p-Chloroaniline ...	,,	10	25·0	Chlorobenzene
α-Naphthylamine	HCl + MeOH	4	91·0	Naphthalene, α-naphthyl methyl ether
β-Naphthylamine	,,	4	91·4	Naphthalene, β-naphthyl methyl ether
p-Anisidine	Cu_2Cl_2, HCl, EtOH	2	58·0	*p*-Chloroanisole

2-Chloro- and 2 : 5-dichloro-benzeneazo-β-naphthylamines, in which the —*I* effect is still more pronounced, and also *o*-, *m*-, and *p*-nitrobenzeneazo-β-naphthylamines did not decompose at all within 24 hours.

The decomposition appears to be direct cleavage due to a two-point attack by the hydrochloric acid at the azo-nitrogen atom and the 1-carbon atom in the β-naphthylamine residue to which it is attached (*ab*) :





Since excess of hydrochloric acid is always present, the azo-structure might reasonably be assumed to be the predominant form owing to the tendency for salt formation at the amino-group. If the imino-hydrazone structure obtained, the hydrochloric acid would be expected to hydrolyse the imino-group, whereas no β-naphthol or derivative of it has been detected such as occurs in the case of the action of sodium nitrite on glacial acetic acid solutions of some of these amines.

An *op*-directing substituent will tend to reduce the positive character of (*b*) and so render it more prone to attack by positive hydrogen, whereas an electron-attracting substituent will tend to increase the positivity of (*b*) and so enable it to resist attack. Amphoteric groups such as methoxyl and *p*-chlorine have a retarding as well as a promoting effect, and the latter in three examples gradually prevails.

p-Methoxybenzeneazo-β-naphthylamine was decomposed by alcoholic hydrochloric acid in the presence of cuprous chloride; the products were β-naphthylamine and *p*-chloroanisole. In this reaction, as also in the others recorded, 1-chloro-2-naphthylamine could not be detected, thereby indicating the two-point attack to be at the points stated. This result is also in accordance with the data of Rowe and Dangerfield (*loc. cit.*), who assert that all the evidence for the fission of azo-compounds by hot aqueous sulphuric acid is in favour of hydrolysis rather than the reduction of the azo-group (see above for the latter point of view). Finally, the fact that diazonium salts are produced in the cleavage was established by stopping the reaction with *p*-methoxybenzeneazo-β-naphthylamine after one hour; then after dilution with water and filtration into alkaline β-naphthol, *p*-methoxybenzeneazo-β-naphthol was formed.

EXPERIMENTAL.

General Procedure.—The fifteen arylazo-β-naphthylamines were treated as follows: The azo-compound (2 g.) was dissolved in boiling alcohol (75 c.c.), hydrochloric acid (10 c.c., *d* 1·16) added, and the mixture refluxed until the precipitate which had formed had passed into solution. A further addition (2 g.) of the azo-compound was then made, together with more hydrochloric acid (10 c.c., *d* 1·16), and the process repeated until 8 g. in all of the azo-compound had been decomposed. The colour of the solution changed from deep red to purple. Spotting tests were made at intervals with an alkaline solution of β-naphthol, a positive test being obtained after 15 minutes' heating, and a negative test after a period depending on the particular azo-compound used, the decomposition then being complete. The solution was cooled, filtered, and made alkaline with 20% aqueous sodium hydroxide; β-naphthylamine and other products of the cleavage were precipitated and removed, and the filtrate steam-distilled to remove alcohol and any steam-volatile products; the residue in the flask was discarded. The precipitate above was transferred to a flask, alcohol being used if necessary, and distilled with steam for the removal and subsequent identification of steam-volatile cleavage products, *e.g.*, in the case of *p*-methoxybenzeneazo-β-naphthylamine anisole is a steam-volatile product and comes over rapidly. The β-naphthylamine formed in the reaction passed over last with the steam and was collected, dried, and weighed. The first portion of the distillate containing the alcohol was diluted with water and extracted with chloroform, and the extract shaken with 10% sulphuric acid, whereby any β-naphthylamine which passed over with the alcohol was precipitated as sulphate and removed. The chloroform portion was washed with water and dried with anhydrous calcium chloride, the chloroform removed by distillation, and the residue identified.

In the special case of *p*-methoxybenzeneazo-β-naphthylamine, the azo-compound (4 g.) was refluxed with alcohol (35 c.c.) and hydrochloric acid (20 c.c., *d* 1·16) for just over 1 hour, the solution cooled, filtered, diluted with twice its volume of water, and finally filtered into a well-stirred solution of β-naphthol (2 g.) in 10% aqueous sodium hydroxide (150 c.c.). The precipitate of *p*-methoxybenzeneazo-β-naphthol was allowed to settle, removed, and crystallised from ethyl alcohol, red needles, m. p. 137°, being obtained (Charrier and Ferreri, *Gazzetta*, 1912, **42**, 132, 134, give m. p. 137°).

Decomposition of p-*Methoxybenzeneazo*-β-*naphthylamine by Alcoholic Hydrochloric Acid in the Presence of Cuprous Chloride.*—The azo-compound (4 g.) was refluxed with alcohol (70 c.c.) to which cuprous chloride (3 g.), dissolved in hydrochloric acid (10 c.c., *d* 1·16), had been added. After 2 hours the mixture was made alkaline with 20% aqueous sodium hydroxide and steam-distilled; the earlier distillate contained the alcohol and *p*-chloroanisole, the later portion contained the β-naphthylamine. 1-Chloro-2-naphthylamine (which is slowly volatile in steam) was not obtained.

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