

89. *The Analogy Between the Benzidine Change and the Dissociation of Oxides of Nitrogen. A New Reagent for the Recovery of Secondary Bases from Nitrosoamines and for Purifying Amines.*

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In a previous paper, the dissociation of nitrogen tri- and tetra-oxides was regarded as comparable with the initial stage of the isomerisation of hydrazobenzene and symmetrical aromatic hydrazines under the influence of acids, and attributed to heterogeneity (Jones and Kenner, J., 1931, 1848). The nitrosoamines can be regarded as intermediate between the hydrazines and the oxides of nitrogen, and indeed Wieland has emphasised the analogy between diarylnitrosoamines and tetra-arylhydrazines in respect of their isomerisation by acids and their thermal decomposition (*Annalen*, 1911, **381**, 212; 1912, **392**, 127). But whilst providing experimental evidence for his view that in each case the latter change is due to dissociation into radicals (or nitric oxide), Wieland rejected the extension of this interpretation to the decomposition of hydrazobenzene into aniline and azobenzene, because its 4-methyl derivative yielded the two corresponding amines and 4-methylazobenzene, unaccompanied by either azobenzene or 4:4'-dimethylazobenzene (*Ber.*, 1915, **48**, 1098). This argument, however, overlooks the fact that each radical will be generated with another already within its sphere of action and will therefore react with it unless, for example, free molecules of a reducing agent are also available, or—as in the case of the tetra-arylhydrazines or nitric oxide—it is capable of a separate existence.

These considerations, we think, suffice also to meet similar and other objections to regarding the benzidine change as due to dissociation (Wieland, *loc. cit.*; Jacobson, *Annalen*, 1922, **428**, 76). It is significant that Wieland, by heating di- $\beta$ -naphthylnitrosoamine, obtained a semidine, which also resulted when the preparation of tetra- $\beta$ -naphthylhydrazine was attempted; and again 3-nitrocarbazole as a product of the thermal decomposition of nitrosocarbazole.



regard the possibility that the chloride is the source of nitric oxide in our experiments as negated by the behaviour of mixed hydrazo-compounds and the parallelism between these and nitrosoamines. Rather it is the formation of nitrosyl chloride by the union of nascent nitric oxide and chloride ion which supplies the electron requisite to convert the radical in (II) into the secondary base.

By contrast with the above instances, the very slight basic properties of carbazole correspond to the stability of its nitroso-derivative towards cuprous chloride solution, although, as mentioned, it is amenable to the characteristic thermal decomposition.

Incidentally to these experiments, we have also observed that cuprous chloride is able to form well-defined complex salts with the hydrochlorides of bases. Although its use in this connexion has received scarcely any attention, apart from an observation by Saglier (*Compt. rend.*, 1888, **106**, 1423) and from the Sandmeyer reaction, we have found it to provide a ready means of purifying crude monomethyl- and ethyl-anilines, as well as of separating *m*-toluidine from its isomerides, and *vic.-m*-xylylidine from the commercial base remaining after extraction of the *p*- and the 4-*m*-isomerides.

#### EXPERIMENTAL.

*Decomposition of Nitrosoamines.*—The yield of nitric oxide derived from the several nitroso-compounds was determined in the apparatus previously described (Jones and Kenner, *loc. cit.*), by adding excess of a cold solution of cuprous chloride (35 g.) in hydrochloric acid (*d* 1.17; 200 c.c.) to a weighed amount of the nitroso-derivative. Decomposition occurred immediately, but the whole of the nitric oxide was only collected after the mixture had been warmed. In this manner yields of 94, 84, 99.5, 84, and 94.5% respectively were obtained from the nitroso-derivatives of methyl-aniline, ethylaniline (b. p. 93°/0.5 mm.), piperidine (b. p. 85°/0.5 mm.), triacetoneamine, and diphenylamine. The resulting free bases were also isolated in the usual manner and respectively identified by conversion into the hydrochloride, m. p. 122°, hydrochloride, m. p. 178°, hydrochloride, m. p. 243°, hydrate, m. p. 58°, and free base, m. p. 54°. In each case comparison was made with an authentic specimen.

*Complex Salts of Cuprous Chloride with Bases.*—The following procedure is typical of that adopted in the preparation of these compounds: methyl-aniline (5 g.) was treated successively with hydrochloric acid (*d* 1.17; 10 c.c.), alcohol (30 c.c.), and cuprous chloride solution (30 c.c.). The complex salt, after collection and rapid washing with concentrated hydrochloric acid, dilute acid, and finally alcohol, was dried in a vacuum desiccator to avoid

oxidation and consequent darkening. Colourless needles, m. p. (with blackening) 210—220°, sparingly soluble in hydrochloric acid, water, and alcohol, were obtained (Found: N, 5.9; Cl, 29.0; Cu, 26.2.  $C_7H_9N, HCl, CuCl$  requires N, 5.8; Cl, 29.2; Cu, 26.2%). From ethylaniline, white felted needles were obtained, m. p. 120—130° (with blackening), sparingly soluble in concentrated hydrochloric acid, moderately easily in dilute acid, water, and alcohol (Found: N, 5.5; Cl, 27.3; Cu, 24.8.  $C_8H_{11}N, HCl, CuCl$  requires N, 5.5; Cl, 27.6; Cu, 24.8%). Aniline yielded colourless needles, which became yellow when dried, m. p. 150—160° (with blackening), somewhat soluble in concentrated hydrochloric acid, more soluble in water, and moderately easily soluble in alcohol (Found: Cl, 31.1; Cu, 27.6.  $C_6H_7N, HCl, CuCl$  requires Cl, 31.0; Cu, 27.8%). From *m*-toluidine, colourless felted needles were obtained: they became greenish-yellow when dried, m. p. 131—140° (with blackening), and were fairly readily soluble in concentrated hydrochloric acid, readily in water and alcohol (Found: Cl, 29.6; Cu, 25.7.  $C_7H_9N, HCl, CuCl$  requires Cl, 29.2; Cu, 26.2%). In neither of these last two cases could satisfactory values for nitrogen be obtained. *vic.-m*-Xylidine yielded crisp prisms, m. p. 180—190° (with blackening), sparingly soluble in hydrochloric acid, water, and alcohol (Found: N, 5.5; Cl, 27.5; Cu, 24.5.  $C_8H_{11}N, HCl, CuCl$  requires N, 5.5; Cl, 27.6; Cu, 24.8%).

*Purification of Bases.—Methylaniline.* Crude methylaniline (50 g) was added to a solution of cuprous chloride (25 g.) in concentrated hydrochloric acid (250 c.c.). The complex salt, having been collected from the cooled mixture and washed, was decomposed with aqueous sodium hydroxide, and the base isolated by steam-distillation. Methylaniline (20 g., b. p. 197° corr.) was obtained. Its content of methylaniline was shown to be 100.0% by analysis with acetic anhydride, whilst dimethylaniline (20 g.), isolated from the liquors, was similarly shown to contain 17.3% of methylaniline (inclusive of any aniline present in the original material).

*Crude ethylaniline.* The sample of crude monoethylaniline (50 g.), kindly supplied by Imperial Chemical Industries, Ltd., was treated with a solution of cuprous chloride (23 g.) in concentrated hydrochloric acid (140 c.c.). The double salt thus obtained yielded pure monoethylaniline (20 g., b. p. 206° corr.), which was found by analysis with acetic anhydride to contain 94.8% of monoethylaniline, as against 79.1% similarly determined and inclusive of aniline in the original crude material.

*m-Toluidine.* The crude base (50 g., and known to contain about 60% of the pure material), supplied by The British Dyestuffs Corporation, was treated with a solution of cuprous chloride (25 g.)

in concentrated hydrochloric acid (85 c.c.). The double salt collected yielded *m*-toluidine (32 g., b. p. 203° corr.), the purity of which was checked by conversion in excellent yield into the benzoyl derivative (m. p. 125°), and comparison of this with an authentic specimen.

*vic.-m-Xylidine*. Commercial xylidine residues (500 c.c.), supplied by the British Dyestuffs Corporation, were treated with concentrated hydrochloric acid (500 c.c.), and then with a solution of cuprous chloride (800 c.c.), prepared by dissolving cuprous chloride (35 g.) in concentrated hydrochloric acid (200 c.c.). The double salt furnished *vic.-m-xylidine* (67 g., b. p. 216.3—216.7° corr.), and the purity of the material was checked by acetylation in benzene solution with acetic anhydride. The acetyl derivative was at once obtained, without recrystallisation, in the practically pure condition (m. p. 174—176°) and in quantitative yield. It was also compared with an authentic specimen.

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