CLVIII.—*The Action of Caustic Alkalis on the 3-Halogeno-4-nitrosodimethylanilines.*

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In view of the conversion of 4-nitroso-3-chloro- and -3-bromophenols into their tautomerides, the 3-chloro- and 3-bromo-benzoquinone-4-oximes (Hodgson and Moore, J., 1923, **123**, 2499; 1925, **127**, 2260), it appeared desirable to ascertain whether the latter substances could be produced directly by the action of alkali hydroxide on the 3-halogeno-4-nitrosodimethylanilines. This result was obtained with the 3-chloro- and the 3-bromo-compound, but 3-iodo-4-nitrosodimethylaniline lost iodine when boiled with aqueous alkali hydroxide.

3-*Iododimethylaniline* and its 4-*nitroso*-derivative do not appear to have been prepared before. An improved method is described for making the 3-halogenodimethylanilines. The purity of preparations of 3-bromo-4-nitrosodimethylaniline described in the literature has hitherto been in doubt.

EXPERIMENTAL.

Preparation of the 3-Halogenodimethylanilines.—The 3-halogenoaniline (1/20 g.-mol.), methyl alcohol (12 c.c.), and methyl sulphate (15 c.c.) are mixed together, heat being evolved. When this has abated, the mixture is heated for 6 hours in a sealed tube. Dimethylation of 3-chloro- and of 3-bromo-aniline occurs at 165°, but 3-iodoaniline requires a temperature of 175° (it chars at 185°). The product is poured into water and made faintly alkaline, and the oil thus liberated is quickly separated, since otherwise emulsification readily takes place. The oil is washed, dried with calcium chloride, and distilled.

The bulk of the 3-chlorodimethylaniline distils between 230° and 233° and has b. p. 231° (Stadel, *Ber.*, 1883, **16**, 32, and Joubert, *Bull. Soc. chim.*, 1874, **21**, 24, give b. p. 231°) (Found : Cl, 22·7. Calc. : Cl, 22·8%).

3-Bromodimethylaniline distils between 244—245° and at 175°/

120 mm., and has b. p. 245° (Wurster, *Ber.*, 1879, **12**, 1818, gives b. p. 259°) (Found: Br, 40·1. Calc.: Br, 40%).

3-*Iododimethylaniline* has b. p. 215—216°/190 mm., but decomposes when distilled under atmospheric pressure (Found: I, 51·6. $C_8H_{10}NI$ requires I, 51·4%).

The 3-halogenodimethylanilines are viscous liquids which dissolve slowly in dilute mineral acids, but readily in the concentrated acids and then remain in solution on dilution.

Preparation of the 3-*Halogeno*-4-*nitrosodimethylanilines*.—A solution of the 3-halogenodimethylaniline (1/20 g.-mol.) in concentrated hydrochloric acid (16 c.c.) is diluted with water (60 c.c.), cooled to 0°, and treated slowly with sodium nitrite (7 g. in 35 c.c. of water). After an hour's stirring the yellow hydrochloride of the 3-halogeno-4-nitrosodimethylaniline is collected, and the green base is liberated from it and crystallised from methyl alcohol. The three compounds all crystallise in dark green needles.

3-Chloro-4-nitrosodimethylaniline has m. p. 130° (decomp.) (Stadel and Joubert, *locc. cit.*, do not record the m. p.) (Found: Cl, 19·1. Calc.: Cl, 19·2%).

3-Bromo-4-nitrosodimethylaniline has m. p. 129° (decomp.). Wurster (*loc. cit.*) gives m. p. 145°, Vorländer and Siebert (*Ber.*, 1919, **52**, 283) give m. p. 116°, and Kharasch and Piccard (*J. Amer. Chem. Soc.*, 1920, **42**, 1855) give m. p. 148°. The purifying process employed by Kharasch and Piccard is unnecessary when the 3-bromodimethylaniline used has been prepared by the method described above, nitrosation then proceeding smoothly. The above product, m. p. 129°, after treatment according to Kharasch and Piccard, remained unchanged; it still melted at 129°, and did not give the Liebermann nitroso-reaction—the test of purity employed by those authors (Found: Br, 34·7. Calc.: Br, 34·9%). The presence of under-methylated or of unchanged amine appreciably interferes with the nitrosation, and the product then obtained resinifies when kept.

3-*Iodo*-4-*nitrosodimethylaniline* has m. p. 128° (decomp.) (Found: I, 46·1. $C_8H_9ON_2I$ requires I, 46·0%). Like the corresponding chloro- and bromo-analogues, it is soluble with difficulty in methyl or ethyl alcohol, benzene, toluene, or ether, and insoluble in light petroleum or carbon tetrachloride.

Action of Aqueous Alkalis on the 3-*Halogeno*-4-*nitrosodimethylanilines*.—3-Chloro- or 3-bromo-4-nitrosodimethylaniline is boiled with a large excess of 10% halogen-free aqueous sodium or potassium hydroxide until almost complete solution is attained, dimethylamine being expelled. The filtered solution, when rendered just acid in the cold, gives a precipitate of the almost colourless form of 3-chloroor 3-bromo-benzoquinone-4-oxime, m. p. 175° and 190°, respectively (Found : Cl, 22·4. Calc. : Cl, 22·5%. Found : Br, 39·6. Calc. : Br, 39·6%). Comparison of the products, recrystallised from benzene (m. p. 178° and 190°, respectively), with Hodgson and Moore's (*loc. cit.*) preparations made by direct nitrosation of 3-chloro- and 3-bromo-phenol, and subsequent conversion by means of alkalis, established identity.

3-Iodo-4-nitrosodimethylaniline is decomposed by the above treatment into compounds of indefinite character with elimination of iodine. No similar removal of halogen occurs with the 3-chloro- and the 3-bromo-compound.

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