

386. The Action of Sodium Nitrite on *p*-Nitrodimethylaniline in Hydrobromic Acid.

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BROMINATION in the 2-position occurs when *p*-nitrodimethylaniline is treated with hydrobromic acid and nitrous acid at 0°, the excess acid being 5*N*. The brown substance precipitated is a *perbromide* of 2-bromo-4-nitrodimethylaniline hydrobromide, the orientation of which was established by Norton and Allen (*Ber.*, 1885, **18**, 1996). 2-Bromo-4-nitrodimethylaniline *perbromide*, treated with hot aqueous alcohol, gives 2-bromo-4-nitrodimethylaniline, which with sodium nitrite in dilute hydrochloric acid forms 2-bromo-4-nitrophenylmethylnitrosoamine. Elimination of the nitroso-group by hot concentrated hydrochloric acid yields 2-bromo-4-nitromethylaniline, which on nitration with nitric acid (*d* 1.43) gives 2-bromo-4 : 6-dinitrophenylmethylnitrosoamine; this, when boiled with phenol and water, is converted into 2-bromo-4 : 6-dinitromethylaniline.

To ascertain at what concentration of hydrogen bromide mixtures of nitrous and hydrobromic acids act as a brominating agent, small quantities of phenyltrimethylammonium bromide were added to the nitrous-hydrobromic acid mixtures. Above 0.36*N* the orange *perbromide* $NPhMe_3Br_3$ was precipitated, solutions 0.305—0.358*N* were cloudy, and solutions weaker than 0.3*N* remained clear.

The limiting bromine concentration is about 0.003 gram-mol. per litre as detected by formation of *perbromide*. The presence of alkali bromide or hydrobromic acid diminishes this sensitivity to about one half when the ratio of bromide to bromine is 5. This observation is significant, because the *perbromide* dissolves less easily in solutions containing small amounts of bromides than it does in water alone. The precipitated *perbromide* passes into solution at the rate of about $\frac{1}{2}$ gram in 24 hours. The dissolution is accompanied by decomposition, during which a part of the bromine escapes by volatilisation, a part enters the benzene nucleus in the *m*-position with formation of hydrogen bromide, and only a small amount is available to liberate iodine from slightly acidified potassium iodide. The greater part of the bromine, however, is probably present as bromate (the production of which takes place as readily in nitrogen as in air), for the solution, after being warmed with concentrated hydrochloric acid and diluted, liberates 0.4 equiv. of iodine from potassium iodide. As a check on the value 0.3*N* below which no bromine was liberated in the hydrobromic-nitrous acid mixtures, air or carbon dioxide was aspirated through the mixtures at 0° into acidified silver nitrate solutions for 6 hours. Experiments in which the sodium nitrite was omitted, or sodium nitrate was used instead of sodium nitrite, gave no silver bromide below a hydrogen bromide concentration of 7.25*N*.

EXPERIMENTAL.

Perbromide of 2-Bromo-4-nitrodimethylaniline Hydrobromide.—This substance was precipitated as a dark brown powder when sodium nitrite (4 mols.) in a little water was added at 0° to *p*-nitrodimethylaniline (1 mol.) dissolved in hydrobromic acid of concentration exceeding 4*N*. After recrystallisation from glacial acetic acid, it formed brown plates, m. p. 157°, soluble in ether, acetone, hot ethyl alcohol, or concentrated mineral acids (with decomp.). When wetted, the substance liberated iodine from starch-iodide paper [Found : C, 19.8; H, 1.85; N, 5.8; Br (ionisable), 49.5; Br (total), 66.0. $C_8H_{10}O_2N_2Br_4$ requires C, 19.9; H, 2.05; N, 5.8; Br (ionisable), 49.6; Br (total), 66.1%].

2-Bromo-4-nitrodimethylaniline.—When the *perbromide* was heated with aqueous alcohol, this substance crystallised in yellow needles, m. p. 74°, soluble in ether, acetone, or hot alcohol, not easily soluble in dilute acids, but moderately readily soluble in cold concentrated acids (Found : C, 39.2; H, 3.7; N, 11.4; Br, 32.65. $C_8H_9O_2N_2Br$ requires C, 39.1; H, 3.6; N, 11.4; Br, 32.8%).

2-Bromo-4-nitrophenylmethylnitrosoamine was precipitated in a few hours at 0° from a hydrochloric acid solution of the tertiary amine on addition of sodium nitrite (3 mols.). After crystallisation from alcohol, it formed nearly white needles, m. p. 95°, which gave the Liebermann reaction for nitroso-compounds, were little soluble in strong acids, but dissolved in ether,

acetone, or hot alcohol (Found : C, 32.3; H, 2.3; N, 16.15; Br, 30.8. $C_7H_6O_3N_3Br$ requires C, 32.4; H, 2.3; N, 16.0; Br, 30.6%).

2-Bromo-4-nitromethylaniline.—The nitrosoamine was heated with concentrated hydrochloric acid; after cooling and addition of water, the secondary *amine* separated as a powder, which crystallised from alcohol in long yellow needles, m. p. 115° (Found : C, 36.4; H, 3.1; N, 12.1; Br, 34.7. $C_7H_7O_2N_2Br$ requires C, 36.3; H, 3.1; N, 12.3; Br, 34.7%).

2-Bromo-4 : 6-dinitrophenylmethylnitroamine was prepared from the preceding amine by heating it gently with concentrated nitric acid; the powder obtained on cooling crystallised from alcohol in white plates, m. p. 126°. It gave a positive nitroamine reaction, and contained three nitro-groups (by reduction with titanous chloride). Being unstable to heat, it was not further analysed.

2-Bromo-4 : 6-dinitromethylaniline.—After removal of the nitro-group of the nitroamine by boiling with phenol, this substance was obtained as a yellow solid, m. p. 153° (after crystallisation from alcohol) alone or mixed with an authentic specimen (Korner, *Jahresb. Chem.*, 1875, 337).

Decomposition of Phenyltrimethylammonium Perbromide in Water.—*m*-Bromophenyltrimethylammonium bromide was identified among the decomposition products of phenyltrimethylammonium perbromide in water by removing bromine by an air blast, evaporating the aqueous solution to dryness, and recrystallising the white residue from absolute alcohol; m. p. 233° [Found : Br (ionisable), 27.2; Br (total), 54.2. Calc. for $C_6H_4Br \cdot NMe_3Br$: Br (ionisable), 27.1; Br (total), 54.2%]. Its perbromide melted at 94° (decomp.), its periodide at 109° (decomp.), its iodide at 202°, and its picrate at 150°, in agreement with the m. p.'s recorded by Vörländer and Siebert (*Ber.*, 1919, 52, 283).

The Indicator.—Phenyltrimethylammonium bromide was prepared by the action of anhydrous acetone on the corresponding quaternary ammonium perbromide in the manner described by McCombie and Reade (*J.*, 1923, 123, 148). The aqueous solution used in the experiments contained 0.108 g. per c.c.

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