

XXIX.—*Action of Acetylene Tetrabromide on Organic Bases.*

By JAMES DAVIDSON FULTON.

THE present investigation, in which the reagents were allowed to react in the absence of a solvent, was suggested by the action of nicotine on acetylene tetrabromide. The rotation of the solution changed rapidly from negative to positive and the solution became hot and coloured; after a few days a solid separated, whilst some oily matter remained. The latter, usually small in amount, was discarded in this and subsequent experiments.

The interaction of aniline and acetylene tetrabromide at the ordinary temperature was investigated by Sabanejev (*Annalen*, 1875, **178**, 125), who obtained a number of products including acetylenetriphenyltriamine, $C_{20}H_{17}N_3$. Schoop (*Ber.*, 1880, **13**, 2196) obtained octamethyltetra-aminotetraphenylethane by heating dimethylaniline with acetylene tetrabromide for 8 days. Elbs and Neumann (*J. pr. Chem.*, 1898, **58**, 250) failed to substantiate all the findings of Sabanejev. In the above cases, the hydrobromide of the base also was obtained. Dehn (*J. Amer. Chem. Soc.*, 1912, **34**, 286) has shown that the reaction of bases and acetylene tetrabromide in dry ether furnishes the hydrobromide and tribromoethylene quantitatively and that sunlight accelerates the reaction.

In the present instance, in the case of tertiary bases additive compounds of the hydrobromide with acetylene tetrabromide were obtained. The influence of sunlight on their formation was not marked. Abnormal bromoaurates were obtained from nicotine and quinine.

EXPERIMENTAL.

Acetylene tetrabromide (usually 2 or 3 mols.) was added to the base (1 mol.) in the cold. Solid hydrobromides were immediately precipitated from primary and secondary amines. With tertiary bases, a solid separated after a day or two. In the case of α -picoline, although reaction was apparent, no crystals appeared for weeks until the mixture was cooled in liquid air and again left. The solid product was filtered off, freed from oily matter, and crystallised from alcohol. The well-crystallised substances thus obtained were all soluble in cold methyl or ethyl alcohol and very soluble in the hot solvent; repeated crystallisation brought about a partial change to the hydrobromide. A single crystallisation from acetone or chloroform effects this change almost completely. The compounds are slightly or not at all soluble in other common organic solvents. The total bromine and the ionisable bromine were estimated.

Water decomposes these compounds. Acetylene tetrabromide is liberated, and the supernatant aqueous solution contains the hydrobromide of the base, which was recognised, in the case of pyridine and quinoline, by analysis and melting point.

The bromoaurates separated when hot alcoholic solutions of the additive compounds, to which auric bromide in alcohol had been added, were allowed to cool.

Nicotine: $C_{10}H_{14}N_2, 2HBr, 2C_2H_2Br_4$, needles, or rhombs by slow crystallisation, m. p. 178—180° (decomp.), softening at 140° (Found: total Br, 79.0, Br', 15.9. Calc., 78.7 and 15.7%, respectively). $[\alpha]_{D}^{25} + 3.21^\circ$ in alcohol ($c = 5.6025$).

The *bromoaurate*, $C_{10}H_{14}N_2, 2HBr, AuBr_3$, forms dark red crystals, m. p. 183°, which are soluble in alcohol and slightly soluble in water (Found: Au, 26.05. Calc., Au, 25.9%).

A more stable, less soluble compound, $[\alpha]_{D}^{25} + 6.96^\circ$ in alcohol ($c = 5.6025$), m. p. 182—183° (decomp.), giving the same bromoaurate (Found: Au, 26.0%), was obtained by repeated crystallisation of the above and also from 1 mol. of the base and 1 mol. of acetylene tetrabromide [Found: total Br, 64.4; Br', 32.3. ($C_{10}H_{14}N_2, 2HBr$)₂, $C_2H_2Br_4$ requires Br, 64.4; Br', 32.2%].

Pyridine: $C_5H_5N, HBr, C_2H_2Br_4$, colourless crystals, m. p. 108—109° (Found: total Br, 79.15; Br', 16.05. Calc., Br, 79.05; Br', 15.8%).

The *bromoaurate* forms brownish-red crystals, m. p. 318—319° (Found: Au, 33.0. $C_5H_5N, HBr, AuBr_3$ requires Au, 33.0%).

Quinoline: The product was washed with a little alcohol and ether. It softened at 115° and melted at 136° [Found: total Br, 62.4; Br', 21.2. (C_9H_7N, HBr)₂, $C_2H_2Br_4$ requires Br, 62.7; Br', 20.9%]. This substance is analogous to the lead compound, (C_9H_7N, HBr)₂, $PbBr_4$ (Classen and Zahorski, *Z. angew. Chem.*, 1891, 4, 107).

The *bromoaurate* forms dark red crystals, m. p. 171—172°, which are soluble in alcohol and slightly soluble in water [Found: Au, 23.0. (C_9H_7N, HBr)₂, $AuBr_3$ requires Au, 23.0%]. It is analogous to Fenner and Tafel's chloro-compound (*Ber.*, 1899, 32, 3227).

isoQuinoline gave mostly its hydrobromide, m. p. 207° (Found: Br, 38.0. Calc., Br, 38.1%). The additive compound, m. p. 155—156°, was almost colourless and not quite pure [Found: total Br, 61.4; Br', 22.5. (C_9H_7N, HBr)₂, $C_2H_2Br_4$ requires Br, 62.7; Br', 20.9%].

The bromoaurate, obtained from the hydrobromide in dark red crystals, m. p. 223°, was normal (Found: Au, 30.25. Calc. for $C_9H_7N, HBr, AuBr_3$, Au, 30.5%).

Lutidine, b. p. 153—156° (regarded as 2:4-dimethylpyridine):

Colourless crystals, m. p. 135—140° [Found : total Br, 66·7; Br', 22·3. (C₇H₉N, HBr)₂, C₂H₂Br₄ requires Br, 66·5; Br', 22·2%].

α-Picoline : C₆H₇N, HBr, C₂H₂Br₄, colourless needles, m. p. 104—105° (Found : total Br, 76·8; Br', 15·4. Calc., Br, 76·9; Br', 15·4%).

Interaction of acetylene tetrabromide and piperidine, coniine, homopiperonylamine, menthylamine, hexamethylenetetramine, and phenylhydrazine gave rise to the hydrobromide only. Antipyrine dissolved in hot acetylene tetrabromide crystallised unchanged on cooling. Pyrrole also did not react.

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THE UNIVERSITY, GLASGOW.

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