51. *Some Quaternary Ammonium Salts and their Decomposition Products.*

By A. Zaki and H. Fahim.

p-Nitrophenyltrimethylammonium salts, previously reported to be unobtainable, and other quaternary ammonium salts containing substituted phenyl groups have now been prepared. These salts on decomposition by heat and alkali showed different behaviour according to the position and nature of the substituents.

Formation of Quaternary Ammonium Salts.—Of the three nitrodimethylanilines, the *p*-isomer previously failed to give the quaternary ammonium salt when treated with methyl iodide or methyl sulphate (Zaki, J., 1930, 1078). It has now been obtained in satisfactory yield by the use of a large excess of methyl sulphate without other solvent, or with benzene as solvent with prolonged heating.

Of the dinitrodimethylanilines, 3 : 4-dinitrodimethylaniline failed to form a quaternary ammonium salt. The 2 : 4-dinitro-compound gave in toluene solution a product from which a picrate could be precipitated. This gave satisfactory analytical figures for carbon and hydrogen, but too high a value for nitrogen.

5-Nitro-2-dimethylaminobenzenesulphonic acid, which was expected to be less resistant to addition than 2 : 4-dinitrodimethylaniline, did not react with methyl sulphate.

Attempts to get the dinitro-compounds by nitration of quaternary ammonium salts containing mononitrophenyl groups failed (cf. Vorländer and Siebert, *Ber.*, 1919, **52**, 296).

Dimethylanilines with *op*-orienting groups such as methyl and methoxyl added methyl sulphate without difficulty.

Decomposition of Phenyltrimethylammonium Salts.—The quaternary ammonium salts now investigated decomposed on heating in the same way as phenyltrialkylammonium salts (Hofmann, *Annalen*, 1851, **78**, 253; Lossen, *ibid.*, 1876, **181**, 364; Collie and Schryver, J., 1890, **57**, 767), *viz.*, $NPhR'R''R'''X \longrightarrow NPhR'R'' + R'''X$ (where X denotes a halogen and R an alkyl radical). For example, the m- and p-*nitro-*, o-*methoxy-*, o-*methyl-*, *4-nitro-2-methoxy-*, and *4-nitro-2-methyl-phenyltrimethylammonium chlorides* all decomposed with loss of methyl chloride and formation of the tertiary base.

On decomposition by means of sodium ethoxide as recommended by Vorländer and Spreckels (*Ber.*, 1919, **52**, 309), *m*-nitro-, *o*-methoxy-, and *o*-methyl-phenyltrimethylammonium chlorides gave the corresponding tertiary bases and methyl ethyl ether, but *p*-nitro-, 4-nitro-2-methoxy-, and 4-nitro-2-methylphenyltrimethylammonium chlorides gave trimethylamine and the corresponding phenetole derivatives.

o-Nitrophenyltrimethylammonium chloride, which would be expected to decompose with formation of a phenetole derivative, decomposed at once when obtained from the picrate by treatment with concentrated hydrochloric acid, giving *o*-nitrodimethylaniline hydrochloride.

EXPERIMENTAL.

Preparation of the Quaternary Ammonium Salts.—The salts were formed by treating the tertiary bases with methyl sulphate, neutralising the product with sodium carbonate, and finally precipitating the picrates. The chlorides were prepared by decomposing the picrates with concentrated hydrochloric acid on the water-bath, filtering and extracting the picric acid with ether, and evaporating the aqueous solutions to dryness (cf. Groenewoud and Robinson, J., 1934, 1692). The iodides were precipitated on addition of concentrated potassium iodide solution to fairly concentrated aqueous solutions of the chlorides. The perbromides were formed by adding bromine to solutions of the chlorides in glacial acetic acid or other suitable solvent; they readily lost bromine. The perchlorates were obtained by adding concentrated sodium perchlorate solution to concentrated solutions of the chlorides; they exploded above their m. p.'s.

Decomposition of the Quaternary Ammonium Salts.—The quaternary ammonium chlorides were heated above their m. p.'s. Decomposition with alkali was effected by refluxing the quaternary ammonium chloride (1 mol.) with sodium (about 1·5 atom.) dissolved in absolute alcohol. The products of decomposition in both cases were identified by the method of mixed melting points.

p-*Nitrophenyltrimethylammonium picrate*, obtained in 72% yield after *p*-nitrodimethylaniline (50 g.), methyl sulphate (50 g.), and benzene (150 c.c.) had been refluxed for 7½ hours, crystallised from water in yellow needles, m. p. 182—183° (Found: C, 43·9; H, 3·8; N, 17·3. $C_{15}H_{15}O_9N_5$ requires C, 44·0; H, 3·7; N, 17·1%).

The *chloride* crystallised from absolute alcohol–ether in white needles, m. p. 183—184° (decomp.) (Found: C, 49·8; H, 6·3; Cl, 16·3. $C_9H_{13}O_2N_2Cl$ requires C, 49·9; H, 6·0; Cl, 16·4%). The *iodide* crystallised from water in yellow prisms, m. p. 161° (decomp.) (Found: I, 41·05. $C_9H_{13}O_2N_2I$ requires I, 41·2%). The perbromide formed yellow needles from absolute alcohol, m. p. 154—157° (decomp.). The *perchlorate*, crystallised from acetone–ether, had m. p. 181—182° (Found: Cl, 12·5. $C_9H_{13}O_6N_2Cl$ requires Cl, 12·65%).

o-*Nitrophenyltrimethylammonium picrate*, obtained after *o*-nitrodimethylaniline (35 g.) had been heated with methyl sulphate (140 c.c.) on the water-bath for 4 hours, formed yellow needles from water, m. p. 167—168° (decomp.) (Found: C, 44·2; H, 3·8; N, 17·4%).

m-Nitrophenyltrimethylammonium picrate, obtained in 67% yield after *m*-nitrodimethylaniline (10 g.) and methyl sulphate (10 g.) had been heated in benzene (30 c.c.) on the water-bath for 7½ hours, crystallised from water in yellow needles, m. p. 150—151° (Vorländer and Siebert, *Ber.*, 1919, **52**, 295).

The *chloride* crystallised from water in white needles, m. p. 230—235° (decomp.) (Found: C, 49·8; H, 6·1; Cl, 16·3. $C_9H_{13}O_2N_2Cl$ requires C, 49·9; H, 6·0; Cl, 16·4%). The perbromide formed yellow plates, m. p. 120° (decomp.).

o-Methoxyphenyltrimethylammonium chloride, as separated in aqueous solution in the manner described above, could not be freed from adhering hydrochloric acid (cf. Groenewoud and Robinson, J., 1934, 1695).

The *perchlorate* separated from alcohol in white feathery crystals, m. p. 224—225° (Found: Cl, 13·2. $C_{10}H_{16}O_5NCl$ requires Cl, 13·4%).

4-*Nitro-2-methoxyphenyltrimethylammonium picrate*, obtained after 5-nitrodimethyl-*o*-anisidine (19 g.) had been heated with methyl sulphate (50 c.c.) on the water-bath for 7 hours (dilution with benzene or toluene inhibited addition altogether), crystallised from water in yellow needles, m. p. 174—175° (Found: C, 43·8; H, 4·0; N, 16·1. $C_{16}H_{17}O_{10}N_5$ requires C, 43·7; H, 3·9; N, 15·9%).

The *chloride* crystallised from alcohol–ether in white needles, m. p. about 183° (decomp.) (Found: C, 48·6; H, 6·15; Cl, 13·9. $C_{10}H_{15}O_3N_2Cl$ requires C, 48·7; H, 6·1; Cl, 14·4%), and the *iodide* in yellow needles, m. p. 156—157° (decomp.) (Found: I, 37·8. $C_{10}H_{15}O_3N_2I$ requires I, 37·6%). The *perchlorate* crystallised from acetone–ether in white prisms, m. p. 207—208° (Found: Cl, 11·3. $C_{10}H_{15}O_7N_2Cl$ requires Cl, 11·4%). The perbromide crystallised from absolute alcohol in orange needles, m. p. 135° (decomp.).

o-Tolyltrimethylammonium chloride separated with adhering hydrochloric acid. It crystallised from absolute alcohol–ether in cubic crystals which were still impure and melted at 84—85° (cf. Groenewoud and Robinson, *loc. cit.*).

The iodide crystallised from water in long, pale yellow prisms which volatilised at 225° (Found : C, 43·3; H, 5·8; I, 45·8. Calc. for $C_{10}H_{16}NI$: C, 43·3; H, 5·8; I, 45·85%) (cf. Braun, *Ber.*, 1916, **49**, 1107). The *perchlorate*, crystallised from acetone–ether, had m. p. 198—199° (Found : Cl, 14·1. $C_{10}H_{16}O_4NCl$ requires Cl, 14·2%).

4-*Nitro*-2-*methylphenyltrimethylammonium picrate*, obtained after 5-nitrodimethyl-*o*-toluidine (19 g.) had been heated with methyl sulphate (70 c.c.) and a little magnesium oxide on the water-bath for 10 hours, crystallised from acetone–ether in tiny yellow needles, m. p. 197—198° (decomp.) (Found : C, 45·5; H, 4·0; N, 16·6. $C_{16}H_{17}O_9N_5$ requires C, 45·4; H, 4·0; N, 16·5%).

The *chloride* crystallised from absolute alcohol–ether in white feathery needles, m. p. 174—175° (decomp.) (Found : C, 52·1; H, 6·8; Cl, 15·45. $C_{10}H_{15}O_2N_2Cl$ requires C, 52·1; H, 6·5; Cl, 15·4%), the *iodide* from absolute alcohol in yellow fan-like crystals, m. p. about 145° (decomp.) (Found : I, 39·0. $C_{10}H_{15}O_2N_2I$ requires I, 39·4%), the *perchlorate* from water in white needles, m. p. 186—187° (Found : Cl, 12·3. $C_{10}H_{15}O_6N_2Cl$ requires Cl, 12·05%), and the perbromide from glacial acetic acid in orange crystals, m. p. 121—122° (decomp.).

Fouad I University, Cairo, Egypt.

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