100. *The Relative Directive Powers of the Carboxyl and the Quaternary Ammonium Group.*

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The action of nitric acid upon *p*-aldehydophenyltrimethylammonium chloride resulted in oxidation of the aldehyde group. On nitration of p-*carboxyphenyltrimethylammonium chloride* the nitro-group entered the *o*-position relative to the

carboxyl group, since the product gave 2-*nitro*-4-*dimethylaminobenzoic acid* on decomposition with alcoholic sodium ethoxide.

WITH the object of comparing the relative directive powers of the aldehydo- and the quaternary ammonium group in one and the same nucleus the nitration of *p*-aldehydophenyltrimethylammonium chloride was attempted. Mixtures of concentrated nitric and sulphuric acids had no action in the cold, and at a higher temperature the aldehydo-group suffered oxidation and p-*carboxyphenyltrimethylammonium chloride* was formed (potassium permanganate produced the same result). This salt on decomposition with alcoholic sodium ethoxide gave *p*-dimethylaminobenzoic acid.

On nitration of *p*-carboxyphenyltrimethylammonium chloride the nitro-group entered the *o*-position relative to the carboxyl group. This was proved by decomposing the product with alcoholic sodium ethoxide, 2-*nitro*-4-*dimethylaminobenzoic acid* being obtained. This acid on decarboxylation in boiling hydrochloric acid afforded *m*-nitrodimethylaniline.

Attempts to prepare 2-nitro-4-carboxyphenyltrimethylammonium iodide from 3-nitro-4-dimethylaminobenzoic acid by the addition of methyl iodide were unsuccessful; even heating under pressure was of no avail. Prolonged heating with methyl sulphate on the water-bath resulted only in esterification of the acid.

EXPERIMENTAL.

p-*Carboxyphenyltrimethylammonium Salts.*—*Picrate.* A solution of *p*-aldehydophenyltrimethylammonium chloride (this vol., p. 350) (1 g.) in a mixture of concentrated nitric acid (7 c.c.) and concentrated sulphuric acid (17 c.c.) was heated on a water-bath for 3 hours, poured into ice-water, neutralised with sodium bicarbonate, and kept in ice for several hours. The inorganic salts were removed and aqueous picric acid was added to the filtrate; a *picrate*, m. p. 206—207°, was precipitated. The same picrate was obtained from the product of refluxing (on a water-bath for 8 hours or on a sand-bath for 3 hours) a solution of *p*-aldehydophenyltrimethylammonium chloride (1 g.) in fuming nitric acid (25 c.c.). It separated from water, in which it was fairly readily soluble, in yellow crystals, m. p. 207° (Found: C, 47·3; H, 4·0; N, 13·8. $C_{16}H_{16}O_9N_4$ requires C, 47·0; H, 4·0; N, 13·7%).

Chloride. The picrate was warmed with concentrated hydrochloric acid and the cooled solution was filtered from picric acid, extracted with ether or benzene to remove the last trace, and evaporated on a water-bath. The residual *chloride* separated from alcohol in colourless crystals, m. p. 240—241°, soluble in water, sparingly soluble in absolute alcohol, and insoluble in acetone, benzene, and ether (Found: C, 55·6; H, 6·5; N, 6·8; Cl, 16·2. $C_{10}H_{14}O_2NCl$ requires C, 55·7; H, 6·5; N, 6·5; Cl, 16·5%).

The *iodide*, obtained in colourless crystals, m. p. 238°, from concentrated solutions of the chloride and potassium iodide, resembled the chloride in solubility (Found: I, 41·3. $C_{10}H_{14}O_2NI$ requires I, 41·3%).

The *perchlorate*, precipitated on addition of 30% perchloric acid to a concentrated aqueous solution of the chloride, crystallised from water in colourless plates, m. p. 284° (Found: Cl, 12·5. $C_{10}H_{14}O_6NCl$ requires Cl, 12·7%).

The *chloride perbromide*, obtained from the chloride and a slight excess of bromine in methyl alcohol or acetic acid at 0°, separated in orange-red needles, m. p. 200° after recrystallisation from the same solvent (Found: Cl, 9·0; Br, 41·0. $C_{10}H_{14}O_2NClBr_2$ requires Cl, 9·4; Br, 42·6%).

Decomposition of the chloride. The chloride (2 g.) and alcoholic sodium ethoxide (0·7 g. of sodium in 40 c.c. of absolute alcohol) were refluxed for 3 hours. After dilution and acidification with hydrochloric acid, the solution was washed with ether to extract any *p*-ethoxybenzoic acid, neutralised with sodium bicarbonate, and slightly acidified with acetic acid. The precipitate (1·5 g.) thus obtained crystallised from alcohol in colourless needles, proved by m. p. 234° and mixed m. p. to be *p*-dimethylaminobenzoic acid.

3-*Nitro*-4-*carboxyphenyltrimethylammonium Salts.*—*Picrate.* A mixture of *p*-carboxyphenyltrimethylammonium chloride (5 g.), fuming nitric acid (25 c.c.), and concentrated sulphuric acid (75 c.c.) was heated on a water-bath for 6 hours, poured on ice, neutralised with sodium bicarbonate, and cooled. The liquid was filtered from precipitated inorganic salts, slightly acidified with hydrochloric acid, and evaporated to dryness, and the residue exhaustively extracted with boiling alcohol. The alcohol was distilled off, and an aqueous solution of the residue mixed with aqueous picric acid. The precipitated *picrate* (6·8 g.) crystallised from water in yellow needles, m. p. 198° (Found : C, 42·7; H, 3·4; N, 15·6. $C_{16}H_{15}O_{11}N_5$ requires C, 42·4; H, 3·3; N, 15·5%). Yield, 65%.

The *chloride* separated from absolute alcohol in colourless crystals, m. p. 230—231°, soluble in water (Found : C, 45·8; H, 5·2; N, 10·3; Cl, 13·2. $C_{10}H_{13}O_4N_2Cl$ requires C, 46·1; H, 5·0; N, 10·8; Cl, 13·6%). The *iodide* formed colourless crystals, m. p. 236°, fairly readily soluble in water, sparingly in alcohol (Found : I, 35·5. $C_{10}H_{13}O_4N_2I$ requires I, 36·1%). Both salts were insoluble in benzene, acetone, and ether.

The *perchlorate*, recrystallised from a little water, formed colourless plates, m. p. 259°, which puffed strongly in a flame (Found : Cl, 10·3. $C_{10}H_{13}O_8N_2Cl$ requires Cl, 10·9%).

The *chloride perbromide* separated from acetic acid in orange-red crystals, m. p. 158—159°. When recrystallised from methyl alcohol, it partly decomposed with liberation of bromine (Found : Cl, 8·4; Br, 37·7. $C_{10}H_{13}O_4N_2ClBr_2$ requires Cl, 8·4; Br, 38·0%).

Decomposition of the chloride. This was carried out as in the case already described (chloride, 3 g.; sodium, 1·2 g.; absolute alcohol, 200 c.c.). 2-*Nitro*-4-*dimethylaminobenzoic acid*, precipitated from the final solution acidified with acetic acid, crystallised from alcohol in yellow needles, m. p. 242° after darkening at 225° (Found : C, 51·7; H, 5·0; N, 13·3. $C_9H_{10}O_4N_2$ requires C, 51·4; H, 5·1; N, 13·4%).

Decarboxylation of 2-*Nitro*-4-*dimethylaminobenzoic Acid*.—When the acid (1 g.) was boiled with 12% hydrochloric acid (25 c.c.), carbon dioxide was liberated. The solution was made alkaline with sodium hydroxide; the precipitate obtained crystallised from alcohol in reddish needles, m. p. and mixed m. p. with authentic *m*-nitrodimethylaniline 60—61° (Found : C, 57·8; H, 5·8; N, 16·4. Calc. for $C_8H_{10}O_2N_2$: C, 57·8; H, 6·1; N, 16·9%).

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