CLIII.—*The Nitration of* 2 : 4 : 6-*Trimethylbenzaldehyde.*

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The nitration of 2 : 4 : 5-trimethylbenzaldehyde has been recorded (Gattermann, *Annalen*, 1906, **347**, 377), but the nitration of the 2 : 4 : 6-isomeride does not appear to have been described. The latter has been studied and a noteworthy feature is the partial replacement of the aldehyde group under certain conditions.

Partial replacement of the aldehyde group during nitration has previously been observed with piperonal and veratraldehyde (Salway, J., 1909, **95**, 1163) and complete replacement with 6-chloro- and 6-bromo-piperonal (Orr, Robinson, and Williams, J., 1917, **111**, 951; Jones and Robinson, *ibid.*, p. 908; compare Parijs, *Rec. trav. chim.*, 1930, **49**, 17). With mesitylene derivatives, replacement, during nitration, of the sulphonic group (Rose, *Annalen*, 1872, **164**, 53; Blanksma, *Rec. trav. chim.*, 1902, **21**, 336; Gibson, J., 1920, **117**, 949), of bromine (Süssenguth, *Annalen*, 1882, **215**, 249; Blanksma, *Rec. trav. chim.*, 1902, **21**, 285), and of iodine (Töhl and Eckel, *Ber.*, 1893, **26**, 1099) has been observed. Of these examples, that most analogous to the replacement now described is the conversion of mesitylenesulphonic acid into a mixture of dinitromesitylenesulphonic acid and trinitromesitylene (Gibson, *loc. cit.*).

Nitration of 2 : 4 : 6-trimethylbenzaldehyde with fuming nitric acid and acetic acid gives the *mononitro-* and with concentrated nitric and sulphuric acids the *dinitro*-derivative. More vigorous treatment with fuming nitric and concentrated sulphuric acids leads to the formation of a mixture of the dinitro-compound and trinitromesitylene. The constitutions of the *nitro-aldehydes* have been confirmed by oxidation to the corresponding nitrotrimethylbenzoic acids and the successive conversion, aldehyde ⟶ nitro-aldehyde ⟶ dinitro-aldehyde ⟶ trinitromesitylene, has been accomplished.

EXPERIMENTAL.

Nitration of 2 : 4 : 6-*Trimethylbenzaldehyde.*—(1) *With fuming nitric and glacial acetic acids.* 2 : 4 : 6-Trimethylbenzaldehyde (1 g.) was added drop by drop, with constant shaking, to a mixture of nitric acid (*d* 1·5) (10 c.c.) and glacial acetic acid (5 c.c.). The mixture, poured on ice after 5 minutes, yielded 3-*nitro*-2 : 4 : 6-*trimethylbenzaldehyde* as a white solid (92%), which crystallised from aqueous alcohol in colourless needles, m. p. 61° (Found : N, 7·4. $C_{10}H_{11}O_3N$ requires N, 7·3%).

The *phenylhydrazone*, prepared by heating the nitro-aldehyde (1 g.) in alcohol (20 c.c.) with phenylhydrazine (5 c.c.) and glacial acetic acid (5 c.c.) for 1 hour, crystallised from aqueous alcohol in yellow needles, m. p. 102° (Found : C, 67·1; H, 6·1. $C_{16}H_{17}O_2N_3$ requires C, 67·8; H, 6·0%).

(2) *With concentrated nitric and sulphuric acids.* 2 : 4 : 6-Trimethylbenzaldehyde (1 g.) was gradually added with shaking to a mixture (20 c.c.) of equal volumes of nitric (*d* 1·42) and concentrated sulphuric acids. Separation of a white solid began almost immediately, dilution with water and crystallisation from aqueous alcohol yielding 3 : 5-*dinitro*-2 : 4 : 6-*trimethylbenzaldehyde* (75%) in colourless needles, m. p. 166° (Found: C, 50·4; H, 4·2. $C_{10}H_{10}O_5N_2$ requires C, 50·4; H, 4·2%).

The *phenylhydrazone*, prepared in a manner similar to that described above, crystallised from aqueous alcohol in orange-red plates, m. p. 209° (Found : C, 57·9; H, 4·9. $C_{16}H_{16}O_4N_4$ requires C, 58·5; H, 4·9%).

(3) *With fuming nitric and concentrated sulphuric acids.* 2 : 4 : 6-Trimethylbenzaldehyde (1 g.) was gradually added to an ice-cooled mixture (10 c.c.) of equal volumes of nitric (*d* 1·5) and concentrated sulphuric acids. A vigorous reaction occurred and the mixture was poured on ice as soon as all the aldehyde had been added, a white solid, m. p. 192°, being obtained, which on crystallisation from alcohol yielded trinitromesitylene, m. p. 235°. Concentration of the solution yielded a small quantity of 3 : 5-dinitro-2 : 4 : 6-trimethylbenzaldehyde.

Nitration of 3-*Nitro*-2 : 4 : 6-*trimethylbenzaldehyde.*—The aldehyde (0·5 g.) was gradually added to an ice-cooled mixture (14 c.c.) of equal volumes of nitric (*d* 1·42) and concentrated sulphuric acids. Solution rapidly occurred and on standing a white solid separated, which proved to be identical with the above dinitro-compound, m. p. 166°.

Oxidation of the Nitrotrimethylbenzaldehydes.—3-Nitro-2 : 4 : 6-trimethylbenzaldehyde (0·5 g.) was mixed with 0·5*N*-sodium hydroxide solution (30 c.c.) and heated on a steam-bath, and dilute potassium permanganate solution added until oxidation was complete. Filtration and acidification yielded 3-nitro-2 : 4 : 6-trimethylbenzoic acid, m. p. 182° (compare Küster and Stallberg, *Annalen*, 1894, **278**, 217) (Found : equiv. by titration with baryta, 210·0. Calc., 209·0).

Similar treatment of 3 : 5-dinitro-2 : 4 : 6-trimethylbenzaldehyde yielded 3 : 5-dinitro-2 : 4 : 6-trimethylbenzoic acid, m. p. 230° (compare Küster and Stallberg, *loc. cit.*; Kunckell and Hildebrandt, *Ber.*, 1901, **34**, 1827) (Found : equiv., 253·3. Calc., 254·0).

Action of Fuming Nitric and Concentrated Sulphuric Acids on 3 : 5-*Dinitro*-2 : 4 : 6-*trimethylbenzaldehyde.*—The dinitro-aldehyde (0·5 g.) was cautiously added to an ice-cooled mixture of nitric acid (*d* 1·5; 10 c.c.) and concentrated sulphuric acid (8 c.c.), and the whole was warmed on a water-bath to 50° and poured on ice. Crystallisation of the resulting solid (93%) yielded only trinitromesitylene, m. p. 235°.

Trinitromesitylene was prepared, for comparison, by addition of an ice-cooled solution of mesitylene (2 g.) in concentrated sulphuric acid (10 c.c.) to ice-cooled nitric acid (*d* 1·5; 20 c.c.). A white solid rapidly separated, crystallisation of which from aqueous alcohol yielded trinitromesitylene, m. p. 235° (compare Blanksma, *Rec. trav. chim.*, 1902, **21**, 336).

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