XXIV.—*The Nitration of* m-*Bromophenol.*

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THE systematic study of the direct nitration of *m*-bromophenol does not appear to have been undertaken, although the following derivatives have been obtained by indirect means: 3-bromo-6-nitrophenol (Laubenheimer, *Ber.*, 1876, **9**, 1155), 3-bromo-6- and -4-nitrophenols (Auwers and Deines, *Zentr.*, 1924, II, No. 18), and 3-bromo-4 : 6-dinitrophenol (Körner, *J.*, 1876, **1**, 2317), Tijmstra (*Rec. trav. chim.*, 1902, **21**, 292) has described 3-bromo-2 : 4 : 6-trinitrophenol.

The present investigation on the direct nitration of *m*-bromophenol was carried out on similar lines to that of *m*-chlorophenol (J., 1925, **127**, 1599). 2-, 4-, and 6-Nitro-3-bromophenols, 4 : 6-, 2 : 6-, and 2 : 4-dinitro-3-bromophenols, and 2 : 4 : 6- and 2 : 5 : 6-trinitro-3-bromophenols have been prepared in excellent yield. Their properties are very similar to those of the corresponding chloro-compounds.

3-Bromo-2-nitrophenol forms a remarkably labile, colourless hydrate, m. p. 35°, which changes on keeping, particularly in dry air, to a bright yellow, anhydrous form of m. p. 65—67°; this reverts to the colourless hydrate in moist air. The sensitiveness of the compound is such as to make it an approximate indicator of atmospheric humidity. This behaviour of the substance led to a further examination of the previously reported, colourless 3-chloro-2-nitrophenol (*loc. cit.*, p. 1601), which was found to be likewise a hydrate, but much more stable in air than that of the bromo-compound. Our analyst reported on a sample which he had thoroughly dried, but made no comment on the change of colour. This we ascribed at that time to atmospheric ammonia.) The analytical datum, therefore, is for anhydrous 3-chloro-2-nitrophenol.

Since 3-bromo-5-nitrophenol has been described by Blanksma (*Rec. trav. chim.*, 1892, **21**, 254) and Heller and Kammann (*Ber.*, 1909, **42**, 2191), the anhydrous substance mentioned above must have the only remaining constitution, *viz.*, that of 3-bromo-2-nitrophenol.

The order of increasing solubility in water of the three dinitro-compounds is : 2 : 6-, 4 : 6-, and 2 : 4-. They form characteristic silver salts, that of 3-bromo-4 : 6-dinitrophenol existing in three forms (two yellow and one red); Körner's observation (*loc. cit.*) is thus confirmed and supplemented.

The orientations tentatively proposed for the dinitro-compounds follow from the modes of preparation and by analogy with the corresponding chloro-compounds (*loc. cit.*). In addition is the following evidence : (1) All three dinitro-compounds are convertible into 3-bromo-2 : 4 : 6-trinitrophenol; the two nitro-groups in each compound are therefore in the meta-position with respect to each other. (2) The constitution of 3-bromo-4 : 6-dinitrophenol is definitely settled by its preparation from 3-bromo-4- and -6-nitrophenols and from 1 : 3-dibromo-4 : 6-dinitrobenzene. (3) 3-Bromo-2 : 6- and -2 : 4-dinitrophenols not only differ in melting point and solubility and in the properties of their silver salts, but the former can be prepared from both 3-bromo-2- and -6-nitrophenols, whereas the 2 : 4-dinitro-compound is obtainable only from a sulphonated 3-bromo-2-nitrophenol. (4) The 2 : 6- and 2 : 4-dinitro-compounds both yield 2 : 4-dinitro-*m*-phenylenediamine when heated in a sealed tube with ammonia, and each specimen of this compound gives 2 : 4-dinitroresorcinol when boiled with aqueous sodium hydroxide. The vicinal positions of the four atoms or groups in each of these two bromodinitrophenols are thus established. Also these two compounds are converted into 2 : 4-dinitroresorcinol by boiling alkalis.

After prolonged sulphonation followed by treatment with excess of nitric acid, *m*-bromophenol gives a trinitro-sulphonic acid; this on hydrolysis yields 3-bromo-2 : 5 : 6-trinitrophenol, which is volatile in steam.

EXPERIMENTAL.

Unless otherwise stated, the methods of preparation of the 3-bromonitrophenols are those of the corresponding chloro-compounds (*loc. cit.*) with appropriate modifications.

Mononitration of m-*Bromophenol.*

(a) *By Sodium Nitrate and Sulphuric Acid* (loc. cit., p. 1600).—3-*Bromo*-6-*nitrophenol* (yield 8·9 g. from 29 g. of *m*-bromophenol) is volatile in steam and crystallises from light petroleum in yellow prisms, m. p. 42°, having a characteristic odour (Auwers and Deines, m. p. 41·5—42·5°) (Found : Br, 36·7. Calc., Br, 36·7%). The methyl ether forms colourless plates, m. p. 85·5°, the benzoate crystallises in cream-coloured needles, m. p. 104°, and the sodium salt in scarlet needles. [The corresponding derivatives of 3-chloro-6-nitrophenol form colourless plates, m. p. 72°, colourless needles, m. p. 91°, and scarlet needles, respectively.]

3-*Bromo*-4-*nitrophenol* (yield 18 g.) is non-volatile in steam and crystallises from light petroleum in yellowish-white, odourless needles, m. p. 131° (Found : Br, 36·6. Calc., Br, 36·7%). It is also formed readily by oxidation of 4-nitroso-3-bromophenol (J., 1925, **127**, 2262). The methyl ether crystallises in short, colourless needles, m. p. 45°, the benzoate in cream-coloured needles, m. p. 102°, and the sodium salt in amber needles. [3-Chloro-4-nitrophenol : methyl ether, short, colourless needles, m. p. 56·5°; benzoate, colourless needles, m. p. 96°; orange sodium salt.]

(b) *By Nitric Acid in Oleum* (loc. cit., p. 1600).—On dilution of the nitration mixture and hydrolysis in a current of steam, the first distillates were oily, but from the later ones almost colourless needles separated on cooling; m. p. 35° (yield 13 g. or 60%). The product at first separated from light petroleum in bright yellow, curly needles, m. p. 65—67°, but later crystals were admixed with the colourless product, which when separated mechanically had m. p. 33°. The yellow compound dissolves in aqueous sodium hydroxide to a red solution, from which the colourless variety is precipitated on acidification in the cold.

The yellow variety is anhydrous 3-*bromo*-2-*nitrophenol* (Found : Br, 36·6. $C_6H_4O_3NBr$ requires Br, 36·7%). It has a characteristic odour distinct from that of 3-bromo-6-nitrophenol. The *sodium* salt crystallises in red needles, the *methyl ether* from dilute alcohol in white needles, m. p. 73° (Found : Br, 34·2. $C_7H_6O_3NBr$ requires Br, 34·4%), and the *benzoate* from alcohol in white, feathery needles, m. p. 133° (Found : Br, 24·7. $C_{13}H_8O_4NBr$ requires Br, 24·8%).

The colourless variety could not be dried in sufficient quantity for analysis owing to its ready conversion into the anhydrous form and in consequence its degree of hydration has not been determined.

3-*Chloro*-2-*nitrophenol*.—The *anhydrous yellow variety*, after prolonged drying over concentrated sulphuric acid, melts at 45—47° (Found : Cl, 20·6. $C_6H_4O_3NCl$ requires Cl, 20·5%).

The hydrated white variety, crystallised from light petroleum, had m. p. 37·5—38° (Found : Cl, 18·5. $C_6H_4O_3NCl,H_2O$ requires Cl, 18·5%). On desiccation over concentrated sulphuric acid, 1·2108 g. lost 0·1128 g. after 20 hours and 0·1136 g. after 24 hours. The calculated loss for 1 mol. H_2O is 0·1138 g. (M, cryoscopic in phenol, 99. $C_6H_4O_3NCl$ requires M, 173·5; and $C_6H_4O_3NCl$, H_2O requires M, 96 if the water is completely abstracted by phenol).

Dinitration of m-*Bromophenol.*

The mixed acid referred to below contained 98% sulphuric acid (15 vols.), 70% nitric acid (12 vols.), and water (9 vols.).

3-*Bromo*-4 : 6-*dinitrophenol*.—(*a*) *m*-Bromophenol (4·4 g.) was added gradually to a mixture of 90·5% nitric acid (5 c.c.) and glacial acetic acid (5 c.c.), and after 12 hours the red solution was warmed for 30 minutes on the water-bath, poured into water, and steam-distilled. A little 3-bromo-6-nitrophenol passed over, followed by the main product, which solidified in colourless crystals, m. p. 90° (yield 2 g.). Recrystallised from light petroleum, this melted at 92° (Found : N, 10·7; Br, 30·4. Calc. for $C_6H_3O_5N_2Br$: N, 10·6; Br, 30·4%).

(*b*) 3-Bromo-6- and -4-nitrophenols (2 g.) were each added gradually to the mixed acid (8 c.c.) cooled in running water, the mixture was kept 2 hours, heated at 80° for 15 minutes, diluted, and steam-distilled. The product extracted from the distillate by ether crystallised from water or light petroleum in white needles,

m. p. 92°, in both cases. The liquor in the steam flask deposited in each case, on cooling, 3-bromo-2 : 4 : 6-trinitrophenol.

(*c*) 1 : 3-Dibromo-4 : 6-dinitrobenzene (3 g.) was boiled for 6 hours with aqueous sodium carbonate (3 g. in 20 c.c. of water), and the solution filtered hot and made just acid. The precipitate was crystallised from water; m. p. 92°.

The identity of the products in (*a*), (*b*), and (*c*) was established by the melting points of their mixtures.

The *silver* salt formed as a voluminous, yellow, gelatinous precipitate when a neutral solution of the ammonium salt was treated with aqueous silver nitrate. It gradually changed to a red, crystalline variety on keeping (the transition being accelerated by rubbing with a glass rod) which was but sparingly soluble in aqueous ammonia and in the presence of which conversion into a yellow, crystalline form occurred (Found : Ag, 29·0. Calc., Ag, 29·2%).

3-*Bromo*-2 : 6-*dinitrophenol.*—(*a*) This was obtained from a mixture of 1 g. of 3-bromo-2-nitrophenol and 4 c.c. of mixed acid (*loc. cit.*, p. 1602). The steam-volatile product solidified as a feathery, crystalline mass, m. p. 124°, and crystallised from light petroleum in colourless needles, m. p. 131° (Found : Br, 30·6. $C_6H_3O_5N_2Br$ requires Br, 30·4%). A non-volatile product was 3-bromo-2 : 4 : 6-trinitrophenol.

(*b*) 3-Bromo-6-nitrophenol (4 g.) was slowly added to 7 c.c. of oleum (27% SO_3) with cooling. The deep red solution was kept for 3 hours at 10°, then nitrated with 0·8 c.c. of nitric acid (90·5%) in 4 c.c. of oleum (27% SO_3), and, after 1 hour, the mixture was poured into water.

Much decomposition occurred on hydrolysis but a small quantity of 3-bromo-2 : 6-dinitrophenol was obtained, m. p. 131° (Found : Br, 30·3%).

By the same procedure 3-chloro-2 : 6-dinitrophenol was obtained from 3-chloro-6-nitrophenol.

The red, crystalline *silver* salt is fairly easily soluble in water and readily in ammonia (Found : Ag, 29·1%).

3-*Bromo*-2 : 4-*dinitrophenol* was prepared as was 3-chloro-2 : 4-dinitrophenol (*loc. cit.*, p. 1602). The steam distillate deposited 3-bromo-2 : 6-dinitrophenol (0·7 g.), which was identified by its red silver salt, m. p. 131°, and by analysis (Found : Br, 30·5%). The filtrate gave to ether 0·8 g. of a product, probably 3-bromo-2 : 4-dinitrophenol, which crystallised from water in fine, silky, cream-coloured needles, m. p. 175° (Found : Br, 30·6. $C_6H_3O_5N_2Br$ requires Br, 30·4%).

The yellow, crystalline *silver* salt was insoluble in ammonia (Found : Ag, 29%).

Attempts to prepare 3-bromo-2 : 4-dinitrophenol from 3-bromo-4-nitrophenol were unsuccessful owing to its decomposition during the sulphonation–nitration process described under (*b*) above.

Separation of a Mixture of 3-*Bromo*-2 : 6- *and* -2 : 4-*dinitrophenols.*—The mixture was converted, by the method described under 3-bromo-4 : 6-dinitrophenol above, into silver salts, which were digested with cold aqueous ammonia. The red silver salt of 3-bromo-2 : 6-dinitrophenol dissolved completely, the yellow isomeride was insoluble. The pure phenols liberated by hydrochloric acid had m. p. 131° and 175°, respectively.

Action of Ammonia on 3-*Bromo*-2 : 6- *and* -2 : 4-*dinitrophenols.*—These (1·3 g.) were separately heated in a sealed tube with concentrated ammonia (5 c.c.) to 150° during 2 hours. On cooling, the products were obtained quantitatively as brownish-yellow needles (0·9 g.) in each case, m. p. 258°. Recrystallised from water or glacial acetic acid, they melted, separately or mixed, at 258°. The substance was sparingly soluble in water, alcohol, ether, or glacial acetic acid (Found : N, 28·1 and 28·5, respectively. Calc. for $C_6H_6O_4N_4$: N, 28·3%). Barr states (*Ber.*, 1888, **21**, 1545) that 2 : 4-dinitro-*m*-phenylenediamine melts at 250° with partial decomposition. 4 : 6-Dinitro-*m*-phenylenediamine melts at about 300° (Nietzki and Schedler, *Ber.*, 1897, **30**, 1667).

The 2 : 4-dinitroresorcinol obtained from each of these products by the action of boiling aqueous sodium hydroxide melted, alone or mixed with the other, at 146° (Beilstein gives m. p. 142°) (Found : N, 14·1 and 13·9, respectively. Calc. for $C_6H_4O_6N_2$: N, 14·0%). Each product gave a red, gelatinous silver salt.

Mixtures of 3-bromo-2 : 6- and -2 : 4-dinitrophenols gave 2 : 4-dinitro-*m*-phenylenediamine when heated with ammonia as above, and 2 : 4-dinitroresorcinol on subsequent boiling with aqueous sodium hydroxide. Barr's statement (*loc. cit.*) that conversion into 2 : 4-dinitroresorcinol does not occur is therefore disproved.

Finally 3-bromo-2 : 6- and -2 : 4-dinitrophenols when separately boiled with aqueous sodium hydroxide gave the same 2 : 4-dinitroresorcinol of m. p. 146° and mixed m. p. 146°.

Trinitration of m-*Bromophenol.*

3-*Bromo*-2 : 4 : 6-*trinitrophenol*, prepared as was the corresponding chloro-compound (*loc. cit.*, p. 1603), is non-volatile in steam and crystallises from water in characteristic clusters of colourless, leaf-like forms, m. p. 149° (Tijmstra, *loc. cit.*, gives 144° for the m. p. of the compound crystallised from acetic acid) (Found : Br, 25·8. Calc., Br, 26·0%).

The same compound was also obtained by nitrating 3-bromo-

4 : 6-, -2 : 6-, and -2 : 4-dinitrophenols : 0·5 g. of each was dissolved, by gentle warming, in 98% sulphuric acid (3 c.c.), and the cooled solution treated with 70% nitric acid (1 c.c.) in 98% sulphuric acid (2 c.c.). After 3 hours, the solution was warmed on the water-bath for a few minutes and poured into water. On passage of steam, no volatile product was detected, and the solution, on cooling, deposited crystals of m. p. 149°. The yellow silver salt was insoluble in ammonia.

3-*Bromo*-2 : 5 : 6-*trinitrophenol* was prepared as was the chloro-compound (*loc. cit.*, p. 1603). It is volatile in steam and crystallises from water in fern-like clusters, m. p. 146° (Found : Br, 26·0. $C_6H_2O_7N_3Br$ requires Br, 26·0%). The yellow silver salt is soluble in water but insoluble in ammonia.

Potassium 3-*bromo*-2 : 5 : 6-*trinitrophenol*-4-*sulphonate*, isolated during the above preparation, gave characteristic, yellow crystals from alcohol which exploded when heated [Found : S, 6·7 ; Br, 17·4. Calc. for $C_6Br(OK)(NO_2)_3{\cdot}SO_3K$: S, 6·8 ; Br, 17·2%].

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