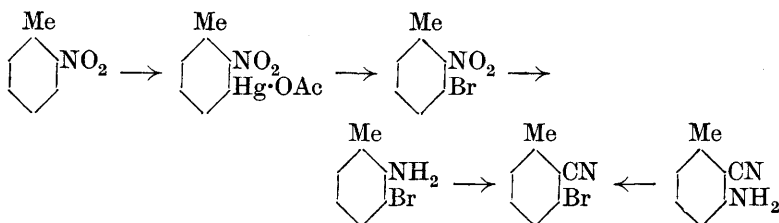


CCXXXVIII.—*Mercuration of o-Nitrotoluene.*

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SOME years ago, experiments were carried out on the mercuration of *o*-nitrotoluene with the object of preparing 3-bromo-2-nitrotoluene according to the scheme



The desired result was attained, the compound being converted into a bromotoluidine which gave a bromotoluenitrile identical with the product from 2-cyano-*m*-toluidine.

Mercuration had, however, taken place in position 4 as well as in position 3 (compare Dimroth, *Ber.*, 1921, **54**, 1504), for sufficient 4-bromo-2-nitrotoluene accompanied the desired isomeride to permit its isolation in a pure condition.* The mercuration of *o*-nitrotoluene takes place in positions 3 and 4, the chlorination, however, in 4 and 6 (Cohn, *Sitzungsber. K. Akad. Wiss.*, 1901, **110**, 391).

An extension of the investigation of this type of substitution was in progress when a paper by Coffey on the mercuration of toluene appeared (*J.*, 1925, **127**, 1029) in which reference is made to a statement of Holleman that the mercuration product of nitrobenzene contains 40% and 50% of the *m*- and *o*-isomerides, respectively. Correspondence with Dr. Coffey elicited the information that he had extended his quantitative studies to the case of *o*-nitrotoluene. The results now recorded are to some extent supplementary to his and it was mutually agreed to publish the two sets of results.

"That the course of mercuration is not dependent solely on the group already present" (Coffey, *loc. cit.*, p. 1030) is evident and the authors direct particular attention to these results in view of recent discussions on the theory of aromatic substitution.

EXPERIMENTAL.

Mercuric acetate (1 part) and *o*-nitrotoluene (5 parts) were heated at 150° for about 4 hours, until solution of the acetate was

* The work of Kharasch and Chalkley (*J. Amer. Chem. Soc.*, 1921, **43**, 601) warrants the assumption of identical orientations for a mercuri-compound and the bromo-derivative prepared from it.

complete and a sample gave no yellow precipitate with aqueous sodium hydroxide. The cooled liquid was filtered from a small quantity of solid matter (probably a dimercurated product), mixed with saturated brine, and distilled in steam to remove unchanged *o*-nitrotoluene. The residual oil solidified on cooling and was then finely ground and shaken (10 parts) with a solution of bromine (5 parts) in a cold saturated aqueous solution of potassium bromide (8 parts). The oil thus obtained, after purification in the usual manner, distilled at 152–170°/32 mm. More than 70% of the distillate boiled almost constantly at 157°/34 mm., but was nevertheless a mixture, since it partly solidified when cooled in a freezing mixture. The solid thus obtained (1.5 g. from 24 g. of oil) melted at 46–47° after being drained on porous earthenware and did not depress the m. p. of authentic 4-bromo-2-nitrotoluene. The residual oil, consisting largely of 3-bromo-2-nitrotoluene, was reduced in glacial acetic acid solution below 50° with stannous chloride and hydrochloric acid, giving impure 3-bromo-*o*-toluidine, b. p. 124–160°/36 mm., from which a pure *acetyl* derivative was readily obtained by means of a mixture of acetic anhydride and acetyl chloride. It separated from benzene in fine needles, m. p. 166° (Found: N, 6.25. $C_9H_{10}ONBr$ requires N, 6.1%). Oxidation of this *acetyl* derivative (5 g.) by a boiling solution of potassium permanganate (15 g.) and magnesium sulphate (10 g.) in water (1000 c.c.) furnished 3-bromo-2-acetylaminobenzoic acid, which separated from alcohol in stout prisms, m. p. 212° (Found: N, 5.45. $C_9H_8O_3NBr$ requires N, 5.4%), and was recovered unchanged after boiling with dilute sulphuric acid of various concentrations. When a mixture of the crude 3-bromo-*o*-toluidine (5 g.), sulphuric acid (6 c.c.), and water (25 c.c.) was diazotised, and the resulting solution added at 80° to another, prepared from copper sulphate (10 g.), potassium cyanide (11 g.), and water (65 g.), 6-bromo-*o*-toluonitrile was produced. After purification by steam distillation, the oil obtained partly solidified in hexagonal crystals, m. p. 99°. It did not depress the m. p. of the pure compound, m. p. 100°, prepared by treating a diazotised solution of 2-cyano-*m*-toluidine (5 g.) in hydrobromic acid (*d* 1.4; 25 c.c.) and water (6 c.c.) with a solution of cuprous bromide (4 g.) in hydrobromic acid (*d* 1.4; 40 c.c.). This product was purified by distillation under reduced pressure and crystallisation from light petroleum (Found: N, 7.4. C_8H_6NBr requires N, 7.1%).

The crude bromonitrotoluene was boiled with nitric acid (*d* 1.37; 3 parts) for several days; the aqueous liquor on evaporation deposited a small amount of 4-bromo-2-nitrobenzoic acid, m. p. 163° (Found: equiv., 244. Calc.: equiv., 246). But when the

oil (10 g.) was oxidised by a boiling solution of potassium permanganate (30 g.) and magnesium sulphate (20 g.) in water (1500 c.c.), a mixture of 3- and 4-bromonitrobenzoic acids was produced, from which the latter was removed by boiling water. The residual, sparingly soluble 3-bromonitrobenzoic acid (2.5 g.) separated from dilute alcohol in prismatic needles, m. p. 250° , as described by Holleman (*Rec. trav. chim.*, 1901, **20**, 215) and earlier workers (Found: N, 5.85. Calc.: N, 5.7%). The *ethyl* ester formed long needles, m. p. 132° (Found: N, 5.5. $C_9H_8O_4NBr$ requires N, 5.1%), and was converted by treatment with an equal weight of copper powder at 180° into *ethyl 2:2'-dinitrodiphenyl-3:3'-dicarboxylate*, which crystallised from light petroleum in iridescent, white plates, m. p. 113° (Found: N, 7.1. $C_{18}H_{16}O_8N_2$ requires N, 7.2%). By hydrolysis with boiling 70% sulphuric acid, the ester was converted into *2:2'-dinitrodiphenyl-3:3'-dicarboxylic acid*, yellow needles, m. p. 286° (decomp.) (Found: N, 8.5; equiv., 165. $C_{14}H_8O_8N_2$ requires N, 8.4%; equiv., 166).

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