

S 40. *The Preparation of Halogeno-compounds by a New Modification of the Sandmeyer Reaction.*

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Aryl nitroso-compounds, and in particular *p*-nitroso- and *m*-halogeno-*p*-nitroso-phenols, react with hydroxylamine salts in the presence of cuprous salts and the relevant acid with replacement of the nitroso-group by halogen.

FOLLOWING Bamberger's observation (*Ber.*, 1895, **28**, 1218; cf. also O. Fischer, *ibid.*, 1899, **32**, 247) that free hydroxylamine reacts with nitroso-compounds to give diazo-compounds which, however, were not isolated but allowed to couple *in situ*, one of the present authors (Hodgson, *J.*, 1931, 1494) found that 3-chloro-4-nitrosophenol reacted very slowly with hydroxylamine hydrochloride but rapidly when a substance was present with which the diazo-compound when formed could couple, *e.g.*, β -naphthylamine, to form an azo-dye. In continuation of the above results, it has now been found that the 3-halogeno-4-nitrosophenols react rapidly in dilute hydrochloric or hydrobromic acid suspension with hydroxylamine salts at ordinary temperatures in the presence of cuprous salts to form the corresponding dihalogeno-phenols; *e.g.*, 3-chloro-4-nitrosophenol affords 3:4-dichlorophenol in at least 70% yield; the reaction occurs more sluggishly in the presence of copper bronze. At ordinary temperatures, *p*-nitrosophenol itself and still more so nitrosobenzene react much less readily than the chloro-derivative above, but when the reaction mixtures are heated to *ca.* 70°, rapid evolution of nitrogen begins, and replacement of the nitroso-group takes place. When potassium iodide alone is added in the cold instead of the cuprous salts, no reaction occurs even with the *m*-halogeno-*p*-nitrosophenols, thereby affording evidence in support of the previous observation of Hodgson, Birtwell, and Walker (*J.*, 1941, 770) that the reaction of diazonium salts with potassium iodide proceeds *via* the tri-iodide, KI₃, and that the reducing effect of the hydroxylamine salt present is to prevent tri-iodide formation; when heated with excess potassium iodide to *ca.* 70°, however, reaction occurs with liberation of iodine, and formation of an iodo-substituted phenol.

The method now described is therefore useful for the rapid preparation of chloro- and bromo-phenols (less so for the iodophenols) otherwise difficult of access, since the direct Sandmeyer reaction only gives poor yields with aminophenols. In like manner, *p*-nitrosodimethylaniline has been found to afford *p*-chloro- and *p*-bromo-dimethylaniline respectively.

EXPERIMENTAL.

General Procedure.—The nitroso-compound (1 part) is suspended at room temperature in a solution of hydroxylamine hydrochloride or sulphate (equivalent parts) and water (10 parts), and finely powdered cuprous chloride (or cuprous bromide) in excess is stirred into the mixture. On addition of hydrochloric acid (10 parts, *d* 1.18) (or the corresponding amount of hydrobromic acid, *d* 1.7), nitrogen is at once evolved with the halogenonitrosophenols, but only on heating with the less reactive nitroso-compounds. The halogeno-products are then removed either by steam distillation or by solvent extraction. The yields of halogenophenols have been determined by bromination to their water-insoluble halogenobromophenols.

Individual Reactions.—(a) *With cuprous chloride.* (i) Nitrosobenzene reacted at 70–80° and afforded chlorobenzene in 15–20% yields (several experiments).

(ii) *p*-Nitrosophenol (2.5 g.) reacted at 20°, but more vigorously at 50°, and gave on steam-distillation a yield of 61% of *p*-chlorophenol, determined by conversion into 4-chloro-2:6-dibromophenol (3.5 g.), whose *benzoate* crystallised from 25% aqueous alcohol in colourless needles, m. p. 84° (Found: Cl + Br, 29.4. $C_{13}H_7O_2ClBr_2$ requires Cl + Br, 29.6%).

(iii) 3-Chloro-4-nitrosophenol (0.5 g.) reacted at room temperature to give a 74.7% yield of 3:4-dichlorophenol, determined as 3:4-dichloro-2:6-dibromophenol (0.8 g.), m. p. 99° (Found: Cl + Br, 71.7. $C_6H_2OCl_2Br_2$ requires Cl + Br, 71.9%).

(iv) 3-Bromo-4-nitrosophenol (0.5 g.) reacted as in (iii) to give 4-chloro-3-bromophenol (0.3 g.), which crystallised from light petroleum in colourless prisms, m. p. 57° (Found: Cl + Br, 55.4. C_6H_4OClBr requires Cl + Br, 55.6%). 4-Chloro-2:3:6-tribromophenol separated from 25% aqueous alcohol in colourless needles, m. p. 96° (Found: Cl + Br, 75.1. $C_6H_2OClBr_3$ requires Cl + Br, 75.4%). 4-Chloro-5-bromo-2-nitrophenol, obtained by the action of nitrous acid on 4-chloro-3-bromophenol, separated from water in very pale yellow plates, m. p. 70° (Found: Cl + Br, 45.4. $C_6H_3O_2NClBr$ requires Cl + Br, 45.7%), which give a scarlet sodium salt.

(v) Only a very small amount of 4-chloro-3-iodophenol was obtained from 3-iodo-4-nitrosophenol in the steam distillation owing to decomposition of the iodo-compound, but it was identified by conversion into the more readily steam-volatile 4-chloro-5-iodo-2-nitrophenol, which separated from water in yellow crystals, m. p. 71° (Found: Cl + I, 54.0. $C_6H_3O_2NClI$ requires Cl + I, 54.2%); the latter was brominated to give 4-chloro-2-bromo-3-iodo-6-nitrophenol, which separated from 25% aqueous alcohol in yellow crystals, m. p. 102° (Found: Cl + Br + I, 63.8. $C_6H_2O_3NClBrI$ requires, Cl + Br + I, 64%).

(b) *With cuprous bromide.* *p*-Nitrosophenol (0.6 g.) gave a yield of 84% of *p*-bromophenol, determined as 2:4:6-tribromophenol (1.4 g.).

(vii) 3-Chloro-4-nitrosophenol (2.5 g.) was suspended in a solution of hydroxylamine sulphate (5 g.), hydrobromic acid (20 c.c., 30%), and water (20 c.c.), and cuprous bromide (5 g.) stirred into the mixture. An appreciable evolution of nitrogen occurred at room temperature, which increased at 40–50°, and was completed by heating on the water-bath. On steam distillation, 3-chloro-4-bromophenol passed over and solidified; it crystallised from light petroleum in colourless silver plates, m. p. 63° (Found: Cl + Br, 55.5. C_6H_4OClBr requires Cl + Br, 55.6%), which had a very penetrating phenolic odour; it was converted by bromine water into 3-chloro-2:4:6-tribromophenol, which crystallised from aqueous alcohol in stout colourless prisms, m. p. and mixed m. p. with a specimen prepared by bromination of *m*-chlorophenol, 130° (Found: Cl + Br, 75.1. $C_6H_2OClBr_3$ requires Cl + Br, 75.4%). Nitrous acid converted 3-chloro-4-bromophenol into 5-chloro-4-bromo-2-nitrophenol, which was volatile in steam and crystallised from 25% aqueous alcohol in pale yellow plates, m. p. 68° (Found: Cl + Br, 45.5. $C_6H_3O_2NClBr$ requires Cl + Br, 45.7%), and gave a red sodium salt; on bromination, it yielded 3-chloro-2:4-dibromo-6-nitrophenol, which crystallised from methanol in pale yellow hexagonal prisms, m. p. 147° (Found: Cl + Br, 58.7. $C_6H_2O_3NClBr_2$ requires Cl + Br, 59.0%).

(viii) With details as for (vii), 3-bromo-4-nitrosophenol gave 3:4-dibromophenol, which crystallised from carbon tetrachloride in colourless prisms, m. p. 80° (Hodgson and Walker, *J.*, 1933, 1054, give m. p. 80°; Schiff, *Monatsh.*, 1890, 11, 347, gives m. p. 79–80°) (Found: Br, 63.2. Calc. for $C_6H_4OBr_2$: Br, 63.5%); it was brominated to give 2:3:4:6-tetrabromophenol, m. p. 113° (Found: Br, 77.7. Calc. for $C_6H_2OBr_4$: Br, 78.0%).

(c) *With potassium iodide.* (ix) By the general procedure, using hydroxylamine sulphate and potassium iodide in place of cuprous salts, *p*-nitrosophenol afforded a small amount of *p*-iodophenol which was identified by bromination of the steam distillate to give 2:6-dibromo-4-iodophenol, which separated from light petroleum in needles, m. p. 105° (King and McCombie, *J.*, 1913, 103, 221, give m. p. 105°).

(x) With details as for (vii), except that excess potassium iodide was added in place of cuprous bromide, and by heating to 70–80°, much iodine was liberated and passed over in the subsequent steam distillation together with a small amount of 3-chloro-4-iodophenol; this was purified by digestion with aqueous sodium hydrogen sulphite; it then crystallised from light petroleum in almost colourless plates, m. p. 40° (Found: Cl + I, 63.5. C_6H_4OClI requires Cl + I, 63.8%). Treatment of the compound with bromine gave 3-chloro-2:6-dibromo-4-iodophenol, which separated from 25% aqueous alcohol in crystals, m. p. 94° (Found: Cl + Br + I, 77.9. $C_6H_2OClBr_2I$ requires Cl + Br + I, 78.2%).

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