CCLXXIII.—*Nitrosation of Phenols. Part III. Nitrosation of 4-Halogeno-*o*- and -*m*-cresols and Oximation of the 4-Halogeno-2 : 5-toluquinones.*

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The 5-nitroso-derivatives which have been obtained from 4-chloro-, 4-bromo-, and 4-iodo-*o*-cresol dissolve in aqueous sodium hydroxide without frothing and exist each in only one modification which preserves its identity whether crystallised from hot aqueous mineral acid or precipitated from alkaline solution (compare J., 1923, **123**, 2499; 1925, **127**, 2260). Since the m. p.'s of 3-chloro-4-nitrosophenol and 5-nitroso-*o*-cresol are 135° and 134—135°, respectively, whilst 4-chloro- and 4-bromo-5-nitroso-*o*-cresol both melt at 197°, our previous conclusions with regard to the relation between m. p. and constitution (*loc. cit.*, p. 2260) lead us to the opinion that the latter two compounds are quinoneoximes. Support for this view was found in the fact that in the case of the chloro- and bromo-compounds the substance produced by the nitrosation of the 4-halogeno-*m*-cresol was the same as that formed by the action of hydroxylamine hydrochloride on the 4-halogeno-2 : 5-toluquinone. No indication of stereoisomerism was observed—and this is remarkable, since Kehrmann, Tichvinsky, and Rüst (*Annalen*, 1898, **303**, 16) have described stereoisomeric 4-chloro-2 : 5-toluquinoneoximes, m. p. 170° and 165°, and stereoisomeric 4-bromo-2 : 5-toluquinoneoximes, m. p. 186° and 178—180°. Our method of preparing the toluquinones—by the oxidation of 4-chloro- and 4-bromo-5-amino-*o*-cresol—ensured their purity, since any isomeric 4-chloro- and 4-bromo-6-amino-*m*-cresol present would have given the same toluquinones. It is significant that none of Kehrmann's 3-halogeno-2 : 5-toluquinones exhibits stereoisomerism.

The difficulties met with in the preparation of 2-iodo-4-nitrosophenol (*loc. cit.*, p. 2263) were again encountered in the nitrosation of 4-iodo-*m*-cresol. The final product decomposed at 170° (the iodonitroso-compounds do not melt), whereas the product of the oximation of 4-iodo-2 : 5-toluquinone decomposed at 181°; this difference is ascribed to the presence of impurities and not to isomerism.

In general, the m. p.'s of the halogenated compounds described in this paper decrease with increasing atomic weight of the halogen.

EXPERIMENTAL.

Preparation of the 4-*Halogeno*-o-*cresols*.—The 4-halogeno-2-nitrotoluene ($\frac{1}{3}$ g.-mol.) was reduced by a boiling solution of sodium sulphide (3 parts) in water (200 c.c.), and the 4-halogeno-*o*-toluidine distilled in steam. Concentrated sulphuric acid (75 c.c.) was added to the distillate, which was then evaporated until, on rapid cooling, it set to a paste of the crystalline sulphate. This was diazotised in the usual way, the excess of nitrous acid destroyed by carbamide, and the filtered solution decomposed by boiling dilute sulphuric acid through which a current of steam was passing; the 4-halogeno-*o*-cresols distilled in yields of about 75% calculated on the weight of the nitro-compound taken. They all crystallise from light petroleum in white needles.

4-Chloro-*o*-cresol has m. p. 73° (Auwers and Deines, *Zentr.*, 1924, II, No. 18, give m. p. 73—74°). 4-*Bromo*-o-*cresol* has m. p. 78° (Found: Br, 42·6. C_7H_7OBr requires Br, 42·8%), and 4-*iodo*-o-*cresol*, m. p. 65° (Found: I, 53·8. C_7H_7OI requires I, 54·2%).

Nitrosation of the 4-*Halogeno*-o-*cresols*.—The method used for the preparation of 3-chloro-4-nitrosophenol (J., 1923, **123**, 2502) was employed, the temperature being 0—10°. The product was filtered off after 12 hours and extracted with hot benzene to remove unchanged cresol (yield about 4 g. from 4 g. of 4-halogeno-*o*-cresol).

4-*Chloro*-5-*nitroso*-o-*cresol* crystallised from alcohol and from dilute hydrochloric acid in small, pale yellow, feathery needles, and from benzene in somewhat deeper yellow needles; m. p. 196°, 195°, and 197° (decomp.), respectively (Found: Cl, 20·5; N, 8·1; *M*, cryoscopic in phenol, 165. $C_7H_6O_2NCl$ requires Cl, 20·7; N, 8·2%; *M*, 171·5). The three samples appeared uniform under the microscope.

4-*Bromo*-5-*nitroso*-o-*cresol* crystallised from benzene, alcohol, and hot dilute hydrochloric acid in yellow, feathery needles, m. p. 197°, 197°, and 195° (decomp.), respectively (Found: Br, 36·9; N, 6·5; *M*, cryoscopic in phenol, 210. $C_7H_6O_2NBr$ requires Br, 37·0; N, 6·5%; *M*, 216).

4-*Iodo*-5-*nitroso*-o-*cresol* crystallised from aqueous alcohol and benzene in brown plates, m. p. 200° (decomp.) (Found: I, 48·0; N, 5·6; *M*, cryoscopic in phenol, 257. $C_7H_6O_2NI$ requires I, 48·3; N, 5·3%; *M*, 263).

In the Liebermann reaction the 4-halogeno-5-nitroso-*o*-cresols develop a deep green colour; this becomes greenish-brown when the solution is diluted and made alkaline.

Reduction of the 4-*Halogeno*-5-*nitroso*-o-*cresols to the* 4-*Halogeno*-5-*amino*-o-*cresols*.—To a solution of the nitroso-compound in aqueous sodium carbonate, solid sodium hyposulphite was added until the colour was discharged. The amine precipitated was crystallised from alcohol, 4-*chloro*-5-*amino*-o-*cresol*, m. p. 217° (Found: Cl, 22·5. C_7H_8ONCl requires Cl, 22·5%), 4-bromo-5-amino-*o*-cresol, m. p. 189° (Gattermann, *loc. cit.*, gives m. p. 180°) (Found: Br, 39·5. Calc.: Br, 39·6%), and 4-*iodo*-5-*amino*-o-*cresol*, m. p. 170° (Found: I, 51·4. C_7H_8ONI requires I, 51·0%), being thus obtained in colourless plates which turned brown on keeping.

Preparation of the 4-*Halogeno*-m-*cresols*.—On account of the labile nature of the halogen atom in the 4-halogeno-*m*-nitrotoluenes, these cannot be reduced with sodium sulphide. The chloro- and bromo-compounds were reduced with tin and hydrochloric acid, and the iodo-compound with iron and acetic acid as in the preparation of 2-iodoaniline (J., 1925, **127**, 2263). The resulting 4-halogeno-*m*-toluidines, m. p. 30°, 46°, and 37·5°, respectively (Beilstein gives 29—30°, 35°, and 188—189° ?), were converted into the 4-halogeno-*m*-cresols by the method described above in the case of the 4-halogeno-*o*-cresols; the diazotised 4-iodo-*m*-toluidine sulphate, however, was dropped into boiling water instead of boiling dilute sulphuric acid, to avoid splitting off iodine. These 4-halogeno-*m*-cresols have very characteristic odours quite different from those of the 4-halogeno-*o*-cresols. 4-*Chloro*-m-*cresol* has m. p. 45° (Found: Cl, 24·8. C_7H_7OCl requires Cl, 24·9%), and 4-*bromo*-m-*cresol* m. p. 38° (Found: Br, 42·5. C_7H_7OBr requires Br, 42·8%).

In describing the preparation of 2-iodophenol (yield 91%) from 2-iodoaniline (J., 1925, **127**, 2263) we regret that we omitted mention of the very similar method of Holleman and Rinkes (*Rec. trav. chim.*, 1911, **30**, 94), which gives a yield of 80%.

Nitrosation of 4-*Chloro- and* 4-*Bromo*-m-*cresols*.—This was readily effected by the general method (*loc. cit.*). 4-*Chloro*-6-*nitroso*-m-*cresol* crystallised from alcohol, aqueous alcohol, benzene, toluene, and hot dilute hydrochloric acid in needles which varied in shade from yellow to brown and in m. p. (decomp.) from 187° to 191° (Found: Cl, 20·6; N, 8·3%; *M*, cryoscopic in phenol, 156. $C_7H_6O_2NCl$ requires Cl, 20·7; N, 8·2%; *M*, 171·5). 4-*Bromo*-6-*nitroso*-m-*cresol* behaved similarly on crystallisation, the m. p. (decomp.) varying from 187° to 190° (Found: Br, 36·8. $C_7H_6O_2NBr$ requires Br, 37·0%). In both cases the samples crystallised from alcohol had the lowest m. p. and the deepest colour.

Nitrosation of 4-*Iodo*-m-*cresol*.—The general method having proved useless, tarry matter only being formed (compare the nitrosation of 2-iodophenol; *loc. cit.*, p. 2263), the alternative method described in the same place was employed (4-iodo-*m*-cresol, 4 g.; water, 2000 c.c.; sodium nitrite, 10 g.; glacial acetic acid, 5 c.c.; water, 50 c.c.; time of keeping, 16 hours; ethereal extract shaken with aqueous sodium carbonate). The 4-*iodo*-6-*nitroso*-m-*cresol* produced on acidification was obtained, after several recrystallisations from alcohol, in brownish-yellow plates), m. p. 170° (decomp.) (Found: I, 47·9. $C_7H_6O_2NI$ requires I, 48·3%).

The 6-nitroso-compounds give characteristic colours in the Liebermann nitroso-reaction very similar to those of the 5-nitroso-isomerides.

Reduction of 4-*Halogeno*-6-*nitroso*-m-*cresols to* 4-*Halogeno*-6-*amino*-m-*cresols*.—Reduction was effected as in the preparation of 4-halogeno-5-amino-*o*-cresols. The products crystallised from alcohol in faintly brownish-white plates: 4-Chloro-6-amino-*m*-cresol, m. p 227° (slight decomp.) [Kehrmann, *loc. cit.*, gives m. p. 205° and later 218—220° (*Ber.*, 1916, **49**, 1213)]; 4-bromo-6-amino-*m*-cresol, m. p. 222° (slight decomp.) (Kehrmann, *loc. cit.*, gives m. p. 205—208°; Gattermann, *loc. cit.*, gives 215°); 4-*iodo*-6-*amino*-m-*cresol*, prepared from the quinoneoxime, has m. p. 208° (slight decomp.) (Found: I, 50·2. C_7H_8ONI requires I, 51·0%).

Preparation of the 4-*Halogeno*-2 : 5-*toluquinones*.—The 4-halogeno-5-amino-*o*-cresol or 4-halogeno-6-amino-*m*-cresol (5 g.) was dissolved in dilute sulphuric acid (1 : 3), and manganese dioxide (3—4 g.) added. On steam distillation the 4-halogeno-2 : 5-toluquinone was obtained as a yellow solid (yield about 4 g.). Ferric chloride also can be used for the oxidation.

4-Chloro-2 : 5-toluquinone crystallised from alcohol in long, yellow needles, m. p. 104—105° (Vorländer and Schrodter, *Ber.*, 1901, **34**, 165, give m. p. 102°; Schniter, *Ber.*, 1887, **20**, 2286, gives m. p. 105°), 4-bromo-2 : 5-toluquinone in fine, yellow needles, m. p.

105° (Schniter, *loc. cit.*, gives m. p. 105°; Gattermann, *Ber.*, 1894, **27**, 1931, gives m. p. 106°), and 4-*iodo*-2 : 5-*toluquinone* from dilute alcohol in stout needles, m. p. 92°, having the colour of potassium dichromate (Found: I, 51·0. $C_7H_5O_2I$ requires I, 51·2%).

Preparation of the 4-*Halogenotoluquinone*-5-*monoximes*.—Kehrmann and Tichvinsky's procedure (*loc. cit.*) was followed where data were available, but complete details are now given because of the issue raised. The 4-halogeno-2 : 5-toluquinone (1/50 g.-mol.) was dissolved in warm alcohol (80 c.c.), and hydroxylamine hydrochloride (1·4 g.) added gradually with vigorous shaking. The yellow solution darkened to orange and after 18 hours the separated oxime was filtered off.

4-*Chlorotoluquinone*-5-*oxime*. The crude product, yellowish-brown needles, m. p. 183° (decomp.), on crystallisation from toluene gave yellow, feathery needles which, alone or mixed with the corresponding nitroso-compound, melted at 190°. This product corresponds to Kehrmann's sparingly soluble isomeride of m. p. 170°. The alcoholic filtrate, on dilution with water as in Kehrmann's procedure, gave a precipitate which crystallised from alcohol in yellowish-brown needles, from benzene and toluene in yellow, feathery needles, and from hot dilute hydrochloric acid in small, yellow needles, m. p. (decomp.) 187°, 191°, 189°, and 191°, respectively. No trace of Kehrmann's product of m. p. 165° was obtained, and the yield of oxime was quantitative (Found: Cl, 20·6. $C_7H_6O_2NCl$ requires Cl, 20·7%).

4-*Bromotoluquinone*-5-*oxime*. The crude product, m. p. 185°, on crystallisation from benzene or toluene, gave small, yellowish-brown, feathery needles, m. p. 190°. The material obtained by diluting the alcoholic filtrate with water also melted at 190° after recrystallisation. No isomerism was detected (Found: Br, 37·1. $C_7H_6O_2NBr$ requires Br, 37·0%).

4-*Iodotoluquinone*-5-*oxime* crystallises from dilute alcohol in shimmering, golden plates, m. p. 181° (decomp.) (Found: I, 48·1; N, 5·5; *M*, cryoscopic in phenol, 256. $C_7H_6O_2NI$ requires I, 48·3; N, 5·3%; *M*, 263).

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