

CCXLIII.—*Dichloro-o-xylenes.*

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WITH the exception of 3 : 5-dichloro-*o*-xylene (Crossley, J., 1902, **81**, 1536) there appears to be no trustworthy information concerning the dichloro-*o*-xylenes. The direct chlorination of *o*-xylene was considered by Claus and Kautz (*Ber.*, 1885, **18**, 1367) to yield only a liquid dichloro-derivative, b. p. 227° and solidifying at 3°, which Claus and Groneweg (*J. pr. Chem.*, 1891, **43**, 352) believed to be 4 : 5-dichloro-*o*-xylene. Koch, however, showed (*Ber.*, 1890, **23**, 2321) that the liquid was a mixture, which slowly deposited a dichloro-*o*-xylene, m. p. 73°. Villiger (*Ber.*, 1909, **42**, 3529), moreover, considered the dichlorophthalic anhydride obtained by Claus and Groneweg from the liquid derivative to be a mixture.

Ferrand (*Compt. rend.*, 1901, **133**, 169) claims to have identified three dichloro-derivatives from the chlorination. He regards the solid, m. p. 73°, as the 3 : 4-dichloro-*o*-xylene and the two liquids, b. p. 226—228° and 229.5—231.5°, as mixtures of the 4 : 5- and 3 : 6-dichloro-derivatives; little reliance, however, can be placed on his work, since he employed *o*-xylene containing as much as 10% of *m*-xylene. From the solid, he obtained a dichlorophthalic anhydride, m. p. 186°, corresponding to the 4 : 5- and not the 3 : 4-dichloro-anhydride as he supposed (compare Villiger, *loc. cit.*).

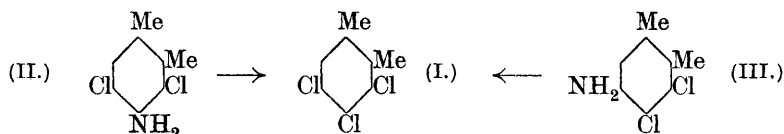
The chlorination of pure *o*-xylene under conditions designed to produce dichloro-derivatives has been studied with the result that all the dichloro-*o*-xylenes can now be described. The only one about which any doubt exists is 3 : 6-dichloro-*o*-xylene. It is produced in such small amount that it has not been possible thoroughly to investigate its properties, but it will be described more fully when experiments now in progress for its synthesis are completed.

The first action of chlorine on *o*-xylene results in the formation of *o*-3- and *o*-4-monochloro-derivatives in the proportion of 1 to 2 (Kruger, *Ber.*, 1885, **18**, 1755; Claus and Baeyer, *Annalen*, 1893, **274**, 304), and on further chlorination the former should yield the 3 : 4- and the 3 : 6- and the latter the 3 : 4- and the 4 : 5-dichloro-derivatives. Dichlorination, therefore, should yield principally 3 : 4- and 4 : 5-dichloro-*o*-xylenes together with a small quantity of 3 : 6-dichloro-*o*-xylene. This has been proved to be the case.

The dichloroxylene of m. p. 76° yields on oxidation a dichlorophthalic anhydride, m. p. 187°, and is therefore 4 : 5-dichloro-*o*-xylene (compare Villiger, *loc. cit.*). On nitration it yields 4 : 5-dichloro-3-nitro-*o*-xylene, reduction of which gives 4 : 5-dichloro-*o*-3-xylylidine.

Diazotisation of the xylydine by the Gattermann process gave an altogether unforeseen result, tetrachloro-*o*-xylene being formed with the expected 3:4:5-trichloro-*o*-xylene. The former probably results from further chlorination occurring in the presence of the cuprous chloride and concentrated hydrochloric acid.

The liquid dichloro-*o*-xylene, b. p. 234°, on nitration gave as the main product a *mononitro*-derivative. Substitution of chlorine for the amino-group in the corresponding amine (m. p. 63°) gave 3:4:5-trichloro-*o*-xylene, m. p. 96° (I) (compare Hinkel, J., 1920, 117, 1296). This trichloro-compound could theoretically be obtained from all the dichloro-*o*-xylenes except the 3:6-isomeride; consequently, since the constitution of the 4:5-isomeride has been established, the liquid compound must have the chlorine atoms either in the 3:4- or the 3:5-positions and the dichloro-*o*-xylydine, m. p. 63°, must therefore be represented by (II) or (III).



3:5-Dichloro-*o*-4-xylydine (II) has been synthesised by Crossley from *o*-4-acetoxylidide (J., 1904, 85, 264) and has now been obtained more conveniently from 3:5-dichloro-*o*-xylene. The melting points of the amine so prepared and of its acetyl derivative have been raised to 47.5° and 196°, respectively. The amine of m. p. 63° must consequently be 5:6-dichloro-*o*-4-xylydine (III), and the liquid of b. p. 234° 3:4-dichloro-*o*-xylene. This orientation has been substantiated by the conversion of 3:4-dichloro-*o*-xylene into the corresponding dichloro-*o*-diamine, which gave the characteristic test for *o*-diamines with phenanthraquinone.

The constitutions of three out of the four possible dichloro-*o*-xylenes are thus definitely established and the fourth isomeride, m. p. 68°, must therefore be 3:6-dichloro-*o*-xylene. Reduction of its mononitro-derivative gave the corresponding xylydine. Replacement of the amino-group by chlorine in the usual manner gave, instead of 3:4:6-trichloro-*o*-xylene (compare Hinkel, *loc. cit.*), a mixture of chloro-compounds which, owing to the small quantity available, could not be further investigated.

The three dichloro-*o*-xylenes yield the same tetrachloro-*o*-xylene on further chlorination.

#### EXPERIMENTAL.

Chlorine was passed into pure *o*-xylene (b. p. 143.5°) at -10° in presence of iron filings until the gain in weight corresponded to

2 atoms of chlorine. After being washed with water and with sodium hydroxide solution, the liquid was dried and distilled; on boiling, a vigorous evolution of hydrogen chloride occurred due to the decomposition of intermediate additive compounds. Three main fractions were ultimately collected: (i) 225—230°; (ii) 230—236°; (iii) 236—246°.

Fraction (i), when cooled in ice, deposited 3 : 6-*dichloro-o-xylene*, which crystallised from methyl alcohol in white, iridescent flakes, m. p. 68°, b. p. 227° (corr.) (Found: Cl, 40.9.  $C_8H_8Cl_2$  requires Cl, 40.6%).

Fraction (ii) gave 3 : 4-*dichloro-o-xylene*, b. p. 234° (corr.). This solidified when cooled in a mixture of ice and salt and melted at 9° (Found: Cl, 40.7%).

Fraction (iii), when cooled in ice, gave 4 : 5-*dichloro-o-xylene*, which crystallised from methyl alcohol in long, transparent needles, m. p. 76°, b. p. 240° (corr.) (Found: Cl, 40.6%).

*Conversion of the Dichloro-o-xylenes into Tetrachloro-o-xylene.*—Each of the dichloro-*o*-xylenes was chlorinated as described by Hinkel (J., 1920, **117**, 1300). Repeated crystallisation from alcohol or ethyl acetate of the tetrachloro-*o*-xylene so prepared does not entirely remove the last trace of any trichloro-*o*-xylene formed during the chlorination, but this can be readily achieved by crystallisation from carbon tetrachloride containing a small quantity of chloroform. The pure compound so obtained melts at 227°.

*Oxidation of 4 : 5-Dichloro-o-xylene.*—2 G. of 4 : 5-dichloro-*o*-xylene were heated with 15 c.c. of nitric acid (*d* 1.15) in a sealed tube for 7 hours at 180°. The resulting liquid was evaporated to dryness over solid caustic soda in a vacuum. The acid obtained melted at 199—200° after crystallisation from water. The anhydride, prepared by heating the acid with acetyl chloride, separated from carbon tetrachloride in small crystals, m. p. 187° (compare Villiger, *loc. cit.*).

4 : 5-*Dichloro-3-nitro-o-xylene.*—2 G. of 4 : 5-dichloro-*o*-xylene were added to 20 c.c. of a mixture of fuming nitric acid (3 vols.) and glacial acetic acid (1 vol.) and heated on a steam-bath for 7 minutes. The solution was poured into water; the solid which separated crystallised from alcohol in fine white needles, m. p. 117° (Found: Cl, 32.5.  $C_8H_7O_2NCl_2$  requires Cl, 32.3%).

4 : 5-*Dichloro-3 : 6-dinitro-o-xylene.*—1 G. of 4 : 5-dichloro-*o*-xylene was heated for 10 minutes with 5 c.c. of sulphuric acid and 3 c.c. of nitric acid. The white solid that separated crystallised from alcohol in colourless prisms, m. p. 210° (Found: Cl, 26.65.  $C_8H_6O_4N_2Cl_2$  requires Cl, 26.8 %).

4 : 5-*Dichloro-o-3-xylylidine.*—A mixture of 3 g. of 4 : 5-dichloro-

3-nitro-*o*-xylene, 9 g. of iron filings, and 30 c.c. of glacial acetic acid was heated with frequent stirring for several hours on a steam-bath. The resulting solid was made alkaline and distilled with steam. The solid product crystallised from aqueous alcohol in long, silky needles, m. p. 88° (Found : Cl, 37·2.  $C_8H_9NCl_2$  requires Cl, 37·3%). The *acetyl* derivative, prepared in the usual manner, crystallised from aqueous alcohol in small rosettes, m. p. 197° (Found : Cl, 30·8.  $C_{10}H_{11}ONCl_2$  requires Cl, 30·6%).

*Conversion of 4 : 5-Dichloro-o-3-xyldine into 3 : 4 : 5-Trichloro-o-xylene.*—The amine, 0·5 g. at a time, was dissolved by heating in 10 c.c. of concentrated hydrochloric acid and 25 c.c. of water. The finely divided hydrochloride obtained on cooling was diazotised, and the whole was poured into a solution of cuprous chloride and distilled in steam. The solid obtained, after crystallising from methyl alcohol, softened at 95° and melted completely at 105°. It was obviously a mixture, although not consisting of 3 : 5 : 6- and 3 : 4 : 5-trichloro-*o*-xylenes, which melt at 47·5° and 96° respectively. Repeated fractional crystallisation from carbon tetrachloride containing varying amounts of chloroform resolved the mixture into 3 : 4 : 5-trichloro-*o*-xylene, m. p. 96°, and tetrachloro-*o*-xylene, m. p. 227°.

4 : 5-Dichloro-3 : 6-diamino-*o*-xylene.—4 : 5-Dichloro-3 : 6-dinitro-*o*-xylene was reduced in alcoholic solution by means of sodium hydrosulphite. After removal of the alcohol under reduced pressure, the solid was crystallised from alcohol, the *diamine* separating in small, white needles, m. p. 186°, decomp. 187° (Found : Cl, 34·4.  $C_8H_{10}N_2Cl_2$  requires Cl, 34·6%).

3 : 4-Dichloro-5-nitro-*o*-xylene.—3 : 4-Dichloro-*o*-xylene was nitrated as described on p. 1876. The solid obtained was crystallised from alcohol, and separated from a small quantity of the 6-nitro-isomeride by washing with light petroleum (b. p. 40—60°) at 0°. It finally crystallised from light petroleum in clumps of hard, prismatic needles, m. p. 78° (Found : Cl, 32·0.  $C_8H_7O_2NCl_2$  requires Cl, 32·3%).

3 : 4-Dichloro-5 : 6-dinitro-*o*-xylene.—3 : 4-Dichloro-*o*-xylene was nitrated as described on p. 1876. The resulting solid crystallised from ethyl acetate in prismatic needles, m. p. 172° (Found : Cl, 27·1.  $C_8H_6O_4N_2Cl_2$  requires Cl, 26·8%).

5 : 6-Dichloro-*o*-4-xyldine.—3 : 4-Dichloro-5-nitro-*o*-xylene was reduced as described on p. 1876. The solid product crystallised from aqueous alcohol in a felt-like mass of white needles, m. p. 63° (Found : Cl, 37·1.  $C_8H_9NCl_2$  requires Cl, 37·3%). The *acetyl* derivative crystallised from aqueous alcohol in fine needles, m. p. 147° (Found : Cl, 30·6.  $C_{10}H_{11}ONCl_2$  requires Cl, 30·6%).

3 : 4-Dichloro-5 : 6-diamino-*o*-xylene.—3 : 4-Dichloro-5 : 6-dinitro-*o*-xylene was reduced with sodium hydrosulphite as described on p. 1877. The diamine obtained crystallised from aqueous alcohol in hair-like crystals, m. p. 176° (Found : Cl, 34·8.  $C_8H_{10}N_2Cl_2$  requires Cl, 34·6%). The diamine and phenanthraquinone in acetic acid gave a yellow precipitate.

3 : 6-Dichloro-4-nitro-*o*-xylene.—3 : 6-Dichloro-*o*-xylene was nitrated under the conditions described on p. 1876. The solid obtained crystallised from methyl alcohol in small, white needles, m. p. 95° (Found : Cl, 32·2.  $C_8H_7O_2NCl_2$  requires Cl, 32·3%).

3 : 6-Dichloro-4 : 5-dinitro-*o*-xylene, prepared from 3 : 6-dichloro-*o*-xylene by the method described on p. 1876, crystallised from alcohol in small, transparent, colourless prisms, m. p. 220° (Found : Cl, 26·4.  $C_8H_6O_4N_2Cl_2$  requires Cl, 26·8%).

3 : 6-Dichloro-*o*-4-xylydine, obtained by reduction of 3 : 6-dichloro-4-nitro-*o*-xylene as described on p. 1876, crystallised from aqueous alcohol in white, silky needles, m. p. 82° (Found : Cl, 37·2.  $C_8H_9NCl_2$  requires Cl, 37·3%). It could not be acetylated by the ordinary methods, but when it was heated for 1 hour on the water-bath with acetic anhydride-acetyl chloride the diacetyl derivative was obtained. This crystallised from alcohol in transparent prisms, m. p. 141° (Found : Cl, 25·8.  $C_{12}H_{13}O_2NCl_2$  requires Cl, 25·9%).

3 : 5-Dichloro-4-nitro-*o*-xylene.—5 G. of 3 : 5-dichloro-*o*-xylene prepared according to Crossley (J., 1902, 81, 1533) were heated for 30 minutes on a water-bath with 125 c.c. of a mixture of fuming nitric acid (3 vols.) and glacial acetic acid (1 vol.). The solid obtained by pouring the mixture into water crystallised from alcohol in a felt-like mass, m. p. 92°, which became waxy when pressed. It could not be freed from the small quantity of the 6-nitro-isomeride also formed during the nitration (Found : Cl, 32·1.  $C_8H_7O_2NCl_2$  requires Cl, 32·3%).

3 : 5-Dichloro-*o*-4-xylydine.—The crude 3 : 5-dichloro-4-nitro-*o*-xylene (m. p. 92°) (5 g.) was reduced with iron filings and acetic acid as described on p. 1876. The solid produced was dissolved in alcohol; a few yellowish-white needles, m. p. 171°, then separated. The filtrate from these crystals (which were probably 3 : 5-dichloro-6-amino-*o*-xylene and were not further examined) was diluted slightly with water; the fine needles that separated crystallised from aqueous alcohol in small rosettes, m. p. 47·5°. The acetyl derivative, prepared in the usual manner, crystallised from boiling water in fine needles, m. p. 196° (Crossley gives m. p. 44·5° and 186°, respectively).