CCCXXXV.—*Chloro*-o-*xylenols. Part II.* 3-*Chloro*-o-4-*xylenol, the Dichloro*-o-4-*xylenols and* 4 : 5-*Dichloro*-o-3-*xylenol.*

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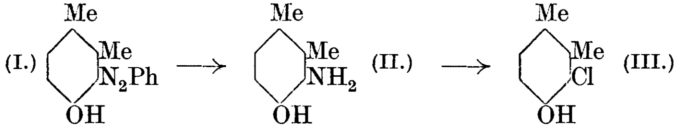
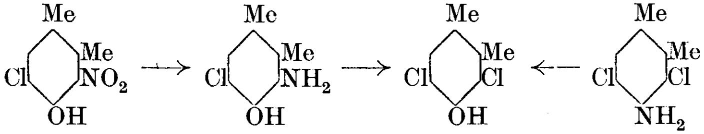
In previous communications (J., 1923, **123**, 2968; 1924, **125**, 1847) six chloro-*o*-xylenols have been described; the syntheses of five of the eight remaining chloro-*o*-xylenols have now been completed.

The synthesis of 3-chloro-*o*-4-xylenol was achieved through *o*-4-xylenol, which was coupled with benzenediazonium chloride (Diepolder, *Ber.*, 1909, **42**, 2918; 1911, **44**, 2498), the 3-benzeneazo-*o*-4-xylenol (I) being separated from the accompanying 5-benzeneazo-*o*-4-xylenol, and reduced to 3-*amino*-o-4-*xylenol* (II), which was converted into 3-*chloro*-o-4-*xylenol* (III) in the normal manner.



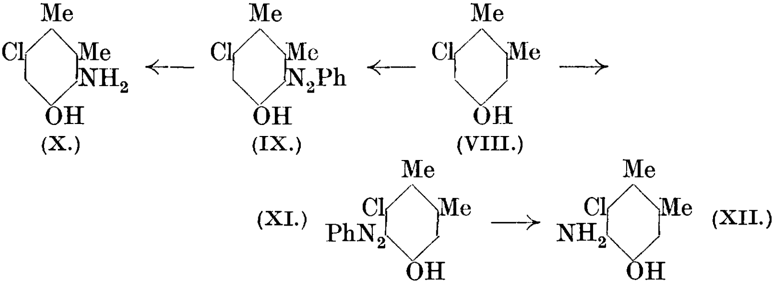
3 : 5-*Dichloro*-o-4-*xylenol* was synthesised through 5-chloro-*o*-4-xylenol (Hinkel, Collins, and Ayling, J., 1923, **123**, 2973). The latter did not couple with benzenediazonium chloride, and was

therefore nitrated, and the resulting 5-*chloro*-3-*nitro*-o-4-*xylenol* (IV) reduced to 5-*chloro*-3-*amino*-o-4-*xylenol* (V). Replacement of the amino-group by chlorine did not yield a homogeneous product, although the similar action with 3-amino-*o*-4-xylenol (II) proceeded normally. The mixture of chloro-xylenols obtained from (V) probably resulted from either a partial elimination of the amino-group or its partial replacement by a second hydroxyl group instead of by chlorine. From the mixture a pure dichloro-*o*-4-xylenol was isolated, which was identical with 3 : 5-dichloro-*o*-4-xylenol (VI) subsequently prepared from 3 : 5-dichloro-*o*-4-xylidine (VII) (this vol., p. 1878), thus confirming the position of the nitro-group in (IV).



(IV.) (V.) (VI.) (VII.)

In an attempted synthesis of 5 : 6-dichloro-*o*-4-xylenol, 6-chloro-*o*-4-xylenol (VIII) (Hinkel, J., 1924, **125**, 1852) was coupled with benzenediazonium chloride, and the resulting azo-compound reduced to the corresponding amine, but attempted replacement of the amino-group by chlorine resulted in its unexpected elimination with regeneration of the starting material. Since, in the latter, both ortho-positions to the hydroxyl group are free, the coupling of the diazonium chloride can yield either of the azo-compounds (IX) and (XI), the product on reduction being either of the amines (X) and (XII).



In (X) the amino-group is situated similarly to those in (II) and (V), in which the amino-group can be replaced by chlorine. This serves in a measure to establish the constitutions of the azo-compound and the amine as 5-*benzeneazo*- (XI) and 5-*amino*-6-*chloro*-o-4-*xylenol* (XII) respectively, and the fact that 5-chloro-*o*-4-xylenol does not couple with benzenediazonium chloride (compare p. 2529), whilst *o*-4-xylenol couples mainly in position 5 (compare Diepolder, *loc. cit.*), supports this view.

5 : 6-Dichloro-*o*-4-xylenol was finally prepared from 5 : 6-dichloro-*o*-4-xylidine (this vol., p. 1877) and is identical with the compound described by Hinkel (J., 1924, **125**, 1851).

4 : 5-*Dichloro*-o-3-*xylenol* and 3 : 6-*dichloro*-o-4-*xylenol* were prepared similarly from the respective dichloro-xylidines (this vol., p. 1876), although in no case does the replacement of the amino-group proceed smoothly.

EXPERIMENTAL.

3-*Amino*-o-4-*xylenol*.—3-Benzeneazo-*o*-4-xylenol, prepared according to Diepolder (*loc. cit.*), was finally purified by several crystallisations from light petroleum (b. p. 60—80°) and obtained as dark red crystals, m. p. 70°. The azo-compound was reduced in alcoholic solution with sodium hydrosulphite, and on removal of the alcohol under reduced pressure, a white solid separated which crystallised from benzene in small crystals, m. p. 126° (Found : N, 10·2. $C_8H_{11}ON$ requires N, 10·2%).

3-*Chloro*-o-4-*xylenol*.—3-Amino-*o*-4-xylenol was diazotised and treated with cuprous chloride in the usual way. Distillation with steam yielded an oil, which was extracted with ether, and the extract washed with sodium hydroxide solution. The xylenol, recovered from the alkaline solution by acidification and extraction with ether, crystallised from light petroleum (b. p. 40—60°) in transparent crystals, m. p. 27° (Found : Cl, 22·4. C_8H_9OCl requires Cl, 22·7%). The *benzoyl* derivative, prepared in the usual manner, crystallised from dilute alcohol in prisms, m. p. 87° (Found : Cl, 13·4. $C_{15}H_{13}O_2Cl$ requires Cl, 13·6%).

5-*Chloro*-3-*nitro*-o-4-*xylenol*.—To 1 g. of 5-chloro-*o*-4-xylenol (Hinkel, Collins, and Ayling, *loc. cit.*) in 10 c.c. of glacial acetic acid, 0·5 c.c. of nitric acid in 10 c.c. of glacial acetic acid was slowly added. After standing for 20 minutes, the mixture was poured on ice, and the precipitated solid distilled in steam. The solid distillate crystallised from benzene in yellow plates, m. p. 127·5° (Found : Cl, 17·6. $C_8H_8O_3NCl$ requires Cl, 17·6%).

5-*Chloro*-3-*amino*-o-4-*xylenol*.—5-Chloro-3-nitro-*o*-4-xylenol was reduced in alcoholic solution with sodium hydrosulphite. On removal of the alcohol under reduced pressure, a white solid was precipitated which crystallised from alcohol in very fine needles, m. p. 175°, with considerable darkening just below the m. p. (Found : Cl, 20·3. $C_8H_{10}ONCl$ requires 20·7%).

3 : 5-*Dichloro*-o-4-*xylenol*.—(1) 5-Chloro-3-amino-*o*-4-xylenol (2 g. in 240 c.c. of hydrochloric acid) was diazotised at 0°, poured into

cuprous chloride solution, distilled with steam, and the distillate extracted with ether. The extract was washed with sodium hydroxide solution, and the alkaline solution yielded a mixture of xylenols which, on fractional crystallisation from light petroleum (b. p. 60—80°), yielded mainly 3 : 5-*dichloro*-o-4-*xylenol* as feathery crystals, m. p. 52°, the constitution being confirmed by the synthesis described below (Found : Cl, 36·8. $C_8H_8OCl_2$ requires Cl, 37·2%). The *benzoyl* derivative crystallised from light petroleum (b. p. 40—60°) as white crystals, m. p. 89° (Found : Cl, 23·6. $C_{15}H_{12}O_2Cl_2$ requires Cl, 24·1%).

(2) 3 : 5-Dichloro-*o*-4-xylidine (this vol., p. 1878), dissolved in concentrated sulphuric acid, was diazotised at 0°, poured into dilute sulphuric acid, and steam-distilled. The distillate, which consisted mainly of 3 : 5-dichloro-*o*-xylene (4 : 6-dinitro-derivative, m. p. 175° ; compare Crossley and Renouf, J., 1904, **85**, 284) together with a small quantity of the xylenol, was extracted with ether, and the extract washed with sodium hydroxide solution. The xylenol, obtained from the alkaline solution in the usual manner and purified from light petroleum (b. p. 60—80°), was identical with the 3 : 5-dichloro-*o*-4-xylenol described above.

6-*Chloro*-5-*benzeneazo*-o-4-*xylenol*.—The requisite amount of benzenediazonium chloride solution was coupled with 2·6 g. of 6-chloro-*o*-4-xylenol (Hinkel, *loc. cit.*) in slightly alkaline solution. The precipitate crystallised from alcohol in red needles, m. p. 143° (Found : Cl, 13·6. $C_{14}H_{13}ON_2Cl$ requires Cl, 13·4%).

6-*Chloro*-5-*amino*-o-4-*xylenol*.—The foregoing azo-compound was reduced in aqueous-alcoholic solution with sodium hydrosulphite ; removal of the alcohol under reduced pressure precipitated a white solid, which crystallised from dilute alcohol in fluffy needles, m. p. 144·5° (Found : Cl, 20·1. $C_8H_{10}ONCl$ requires Cl, 20·7%). Diazotisation of the amine and treatment with cuprous chloride in the usual manner, followed by distillation with steam, yielded a white solid, which was extracted with ether, and then crystallised from light petroleum (b. p. 60—80°) in fine needles, m. p. 98°, unchanged by admixture with 6-chloro-*o*-4-xylenol, m. p. 98°.

5 : 6-*Dichloro*-o-4-*xylenol*.—5 : 6-Dichloro-*o*-4-xylidine (this vol., p. 1877), 0·5 g. at a time, was dissolved in 5 c.c. of sulphuric acid ; the sulphate was precipitated in a finely divided state by the addition of 10 c.c. of water, diazotised at 0°, and gently warmed to 40° until a clear solution was obtained. The diazotised solution was treated according to the method of Heinichen (*Annalen*, 1889, **253**, 281 ; compare Cain and Norman, J., 1906, **89**, 19) by the addition of 20 c.c. of concentrated sulphuric acid, but modified by heating the acid solution for 1 hour on a steam-bath. Other methods of treat-

ment (compare Cain and Norman) result in the formation of much red solid, which is reduced to a minimum by the above procedure. The acid solution was distilled with steam, the solid distillate treated with dilute sodium hydroxide solution, the solution filtered, and the xylenol recovered in the usual manner; it crystallised from well-cooled light petroleum (b. p. 60—80°) in tiny rosettes, m. p. 102·5° (Found: Cl, 36·6. Calc. for $C_8H_8OCl_2$: Cl, 37·2%). The benzoyl derivative crystallised from dilute alcohol in stellate groups, m. p. 97·5° (Found: Cl, 23·8. Calc. for $C_{15}H_{12}O_2Cl_2$: Cl, 24·1%). These m. p.'s were unchanged by admixture with the corresponding compounds described by Hinkel (J., 1924, **125**, 1851).

3 : 6-*Dichloro*-o-4-*xylenol.*—3 : 6-Dichloro-*o*-4-xylidine (this vol., p. 1878) was dissolved by heating in 30% sulphuric acid. The finely divided sulphate obtained on cooling was diazotised at 40°, poured into boiling 40% sulphuric acid, and distilled with steam. The solid distillate was treated with dilute sodium hydroxide solution, the solution filtered, acidified, and extracted with light petroleum (b. p. 40—60°). The xylenol crystallised in long, flat needles, m. p. 84° (Found: Cl, 36·8. $C_8H_8OCl_2$ requires Cl, 37·2%). The *benzoyl* derivative crystallised from methyl alcohol in transparent, flat needles, m. p. 124° (Found: Cl, 23·8. $C_{15}H_{12}O_2Cl_2$ requires Cl, 24·1%).

4 : 5-*Dichloro*-o-3-*xylenol.*—4 : 5-Dichloro-*o*-3-xylidine (this vol., p. 1876) was treated exactly as in the preceding case, and the xylenol, recovered in the usual manner, crystallised from light petroleum (b. p. 60—80°) in stellate masses, m. p. 90° (Found: Cl, 36·5. $C_8H_8OCl_2$ requires Cl, 37·2%). The *benzoyl* derivative crystallised from dilute alcohol in prisms, m. p. 133° (Found: Cl, 24·3. $C_{15}H_{12}O_2Cl_2$ requires Cl, 24·1%).

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[*Received, July* 24*th*, 1928.]