426. *Dichloro-*o*-xylenes. Part II.*

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BY dichlorination of *o*-xylene, Hinkel, Ayling, and Bevan (J., 1928, 1874) isolated three dichloro-derivatives, the constitutions of two of them being established as 4 : 5- and 3 : 4-dichloro-*o*-xylene by their reactions. The remaining isomeride, produced only in small amount, was not fully investigated and was assumed to be 3 : 6-dichloro-*o*-xylene. Its synthesis, together with those of the 4 : 5- and the 3 : 4-derivative, has therefore been undertaken.

3 : 6-*Dichloro*-o-*xylene* was synthesised from aceto-*o*-3-xylidide through 6-chloro-*o*-3-xylidine (Hinkel, Collins, and Ayling, J., 1923, **123**, 2972; compare this vol., p. 284), by replacement of the amino-group of the latter by chlorine. It was not identical with the previously suggested 3 : 6-dichloro-*o*-xylene. On dinitration and subsequent reduction it yielded an *o*-diamine (phenanthraquinone test) and on chlorination it furnished the anticipated 3 : 4 : 5 : 6-tetrachloro-*o*-xylene. Its mononitro-derivative was identical with 3 : 6-*dichloro*-4-*nitro*-o-*xylene* prepared from 6-chloro-4-nitro-*o*-3-xylidine (this vol., p. 285). The third dichloro-derivative, m. p. 68°, obtained by Hinkel, Ayling, and Bevan (*loc. cit.*) is therefore not the 3 : 6-isomeride, but may be a chloroxylyl chloride (although two of its derivatives, *viz.*, amino- and hydroxy-, do not react with alcoholic silver nitrate) and it and its derivatives previously described (J., 1928, 1878, 2533) must, for the time being, be regarded as xylene derivatives of unknown constitution.

The syntheses of 4 : 5- and 3 : 4-dichloro-*o*-xylene were accomplished with aceto-*o*-4-xylidide, which on monochlorination yields the 5- and the 3-chloro-derivative (compare this vol., p. 283), the corresponding amines giving the respective dichloro-*o*-xylenes when submitted to the diazo-reaction. Both 4 : 5-dichloro-*o*-xylene and its 3-nitro-derivative, m. p. 117°, were identical with the compounds regarded as having these constitutions by Hinkel, Ayling, and Bevan (*loc. cit.*). Similarly, the chloro-compound obtained from 4-chloro-*o*-3-xylidine yielded, on dinitration, a compound identical with the previously described 3 : 4-dichloro-5 : 6-dinitro-*o*-xylene (*ibid.*) and the correctness of the orientations assigned to these two dichloro-*o*-xylenes is therefore fully confirmed.

Claus and Groneweg (*J. pr. Chem.*, 1891, **43**, 352), by the bromination of an impure 4 : 5-dichloro-*o*-xylene obtained by Claus and Kautz (*Ber.*, 1885, **18**, 1367; compare Villiger, *ibid.*, 1909, **42**, 3529), obtained 4 : 5-dichloro-3-bromo-*o*-xylene, m. p. 90°. This compound has now been synthesised from 4 : 5-dichloro-*o*-3-xylidine by the diazo-reaction, its much higher m. p. (111°) indicating that Claus and Groneweg did not obtain it in a pure state. Similarly, the 4 : 5-dichloro-3 : 6-dinitro-*o*-xylene and the corresponding diamine prepared from 4 : 5-dichloro-*o*-xylene by Hinkel, Ayling, and Bevan have higher melting points than the compounds prepared by Claus, Raps, Herfeldt, and Berkefeld (*J. pr. Chem.*, 1891, **43**, 563) from the impure 4 : 5-dichloro-*o*-xylene of Claus and Kautz.

The only dichloro-*o*-xylenes formed in the chlorination of *o*-xylene are thus the 3 : 4- and the 4 : 5-derivative and it appeared probable that they must be formed through the 3- and the 4-chloro-*o*-xylene respectively. The latter two compounds are both formed by the action of chlorine on *o*-xylene, but can only be separated by indirect methods (Kruger, *Ber.*, 1885, **18**, 1755; Claus and Baeyer, *Annalen*, 1893, **274**, 304), and have now been prepared from the corresponding *o*-xylidines.

Chlorination of 3- and 4-chloro-*o*-xylene yielded only 3 : 4- and 4 : 5-dichloro-*o*-xylene respectively in accordance with the above view.

EXPERIMENTAL.

3 : 6-*Dichloro*-o-*xylene*.—6-Chloro-*o*-3-xylidine hydrochloride (Hinkel, Collins, and Ayling, *loc. cit.*; cf. this vol., p. 284) was dissolved in boiling 4*N*-hydrochloric acid and the suspension obtained on cooling was diazotised at 10°. Treatment with cuprous chloride, followed by distillation in steam, yielded a pale yellow, low-melting solid, which was extracted with ether, and the ethereal solution washed with sodium hydroxide and water and dried.* Evaporation

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* This procedure was used in the following diazotisations and Sandmeyer reactions for which details are not recorded.

of the ether yielded 3 : 6-*dichloro*-o-*xylene* (yield, 70%), which crystallised from well-cooled methyl alcohol in white iridescent crystals, m. p. 29°, b. p. 234°/760 mm. (Found : Cl, 40·85. $C_8H_8Cl_2$ requires Cl, 40·6%). Its chlorination as described by Hinkel (J., 1920, **117**, 1300) gave a quantitative yield of 3 : 4 : 5 : 6-tetrachloro-*o*-xylene, m. p. and mixed m. p. 226°.

3 : 6-*Dichloro*-4-*nitro*-o-*xylene*.—3 : 6-Dichloro-*o*-xylene was nitrated under the conditions described by Hinkel, Ayling, and Bevan (*loc. cit.*, p. 1876); the solid obtained crystallised from methyl alcohol in small white needles, m. p. 84°, unchanged by admixture with 3 : 6-*dichloro*-4-*nitro*-o-*xylene* prepared as described below (Found : Cl, 32·7. $C_8H_7O_2NCl_2$ requires Cl, 32·3%).

3 : 6-*Dichloro*-o-4-*xylidine*.—A mixture of 3 : 6-dichloro-4-nitro-*o*-xylene (3 g.), iron filings (10 g.), and 5% acetic acid (100 c.c.) was heated under reflux on a steam-bath for 4 hours and then basified. The solid product (2·5 g.; 96%) isolated by steam-distillation crystallised from aqueous alcohol in clusters of long silky needles, m. p. 54° (Found : Cl, 37·35. $C_8H_9NCl_2$ requires Cl, 37·3%). The *acetyl* derivative crystallised from aqueous alcohol in long needles, m. p. 146° (Found : Cl, 30·8. $C_{10}H_{11}ONCl_2$ requires Cl, 30·6%).

3 : 6-*Dichloro*-4 : 5-*dinitro*-o-*xylene*, prepared from 3 : 6-dichloro-*o*-xylene by the method described by Hinkel, Ayling, and Bevan (*loc. cit.*, p. 1876), crystallised from alcohol in prismatic needles, m. p. 174° (Found : Cl, 27·0. $C_8H_8O_4N_2Cl_2$ requires Cl, 26·8%).

3 : 6-*Dichloro*-4 : 5-*diamino*-o-*xylene*.—3 : 6-Dichloro-4 : 5-dinitro-*o*-xylene was reduced in alcoholic solution by means of sodium hydrosulphite. The solid obtained after removal of the alcohol under reduced pressure crystallised from alcohol in small hair-like crystals, m. p. 176° (Found : Cl, 34·7. $C_8H_{10}N_2Cl_2$ requires Cl, 34·6%). The diamine and phenanthraquinone in acetic acid gave a yellow precipitate of the *phenazine* derivative, which crystallised from acetic acid in small fine needles, m. p. above 250° (Found : Cl, 18·7. $C_{22}H_{14}N_2Cl_2$ requires Cl, 18·8%).

3 : 6-*Dichloro*-4 : 5-*dibromo*-o-*xylene*.—3 : 6-Dichloro-*o*-xylene was brominated according to the method of Crossley (J., 1904, **85**, 284); the product crystallised from alcohol in slender needles, m. p. 238° (Found : Cl, 21·8; Br, 48·1. $C_8H_6Cl_2Br_2$ requires Cl, 21·3; Br, 48·05%).

Conversion of 6-*Chloro*-4-*nitro*-o-3-*xylidine into* 3 : 6-*Dichloro*-4-*nitro*-o-*xylene*.—6-Chloro-4-nitro-*o*-3-xylidine (this vol., p. 285) (2 g.) was dissolved in warm hydrochloric acid (20 c.c.) and water (10 c.c.), diazotised at 8°, and added to cuprous chloride solution (20 c.c.). The resulting solid (2·0 g.; 90%) crystallised from methyl alcohol in small fine needles, m. p. 84°, unchanged by admixture with the above 3 : 6-dichloro-4-nitro-*o*-xylene (Found : Cl, 32·1%).

4 : 5-*Dichloro*-o-*xylene*.—A solution of 5-chloro-*o*-4-xylidine (this vol., p. 286) (1 g.) in warm hydrochloric acid (4 c.c.) and water (3 c.c.) was cooled, diazotised at − 10°, treated with cuprous chloride, and the mixture distilled in steam. The resulting white solid (0·8 g.; 71%) crystallised from methyl alcohol in long transparent needles, m. p. 76°, unchanged by admixture with 4 : 5-dichloro-*o*-xylene (Hinkel, Ayling, and Bevan, *loc. cit.*).

4 : 5-*Dichloro*-3-*bromo*-o-*xylene*.—4 : 5-Dichloro-*o*-3-xylidine (1 g.) was dissolved in warm concentrated hydrobromic acid (5 c.c.) and water (3 c.c.) and diazotised at − 5°, and the solution poured into cuprous bromide (1 g.) in concentrated hydrobromic acid (10 c.c.) and distilled in steam. The white solid obtained (1 g.; 80%) crystallised from alcohol in slender needles, m. p. 111° (Found : Cl, 27·75; Br, 31·3. Calc. : Cl, 27·95; Br, 31·5%).

4 : 5-*Dichloro*-3 : 6-*dibromo*-o-*xylene*.—4 : 5-Dichloro-*o*-xylene was brominated according to the method of Crossley (*loc. cit.*). The 4 : 5-*dichloro*-3 : 6-*dibromo*-o-*xylene* obtained crystallised from alcohol in long needles, m. p. 232° (Found : Cl, 21·7; Br, 40·2. $C_8H_6Cl_2Br_2$ requires Cl, 21·3; Br, 40·05%).

3 : 4-*Dichloro*-o-*xylene*.—From 3-chloro-*o*-4-xylidine (this vol., p. 286) (2 g.), in warm hydrochloric acid (6 c.c.) and water (3 c.c.), and diazotised at 0° by the normal procedure, 3 : 4-dichloro-*o*-xylene was obtained as a colourless oil (1·5 g.; 68%), which was immediately converted into 3 : 4-dichloro-5 : 6-dinitro-*o*-xylene by the method of Hinkel, Ayling, and Bevan (*loc. cit.*, p. 1876). The resulting solid crystallised from alcohol in needles, m. p. 172°, unchanged by admixture with an authentic specimen.

3-*Chloro*-o-*xylene*.—*o*-3-Xylidine (10 g., obtained by hydrolysis of pure aceto-*o*-3-xylidide), in warm concentrated hydrochloric acid (30 c.c.) and water (10 c.c.) and diazotised at − 10°, gave by the normal procedure 3-chloro-*o*-xylene as a colourless refractive liquid, b. p. 191°/765 mm., which did not solidify at − 20° [Kruger, *loc. cit.*, records b. p. 189·5° (corr.)].

4-Chloro-*o*-xylene, prepared from *o*-4-xylidine in a similar manner, was a colourless refractive liquid, b. p. 194°/755 mm., f. p. − 6·25° [Kruger, *loc. cit.*, records b. p. 191·5° (corr.), liquid at − 20°; Claus and Groneweg, *loc. cit.*, record b. p. 195°].

Chlorination of 3- *and* 4-*Chloro*-o-*xylene*.—Chlorine was passed into 3-chloro-*o*-xylene at − 10° in presence of iron filings until the gain in weight corresponded to the substitution of one chlorine atom. After being washed with water and boiled under reflux with 10% sodium hydroxide solution for 1 hour to decompose xylyl derivatives, the liquid was dried and fractionally distilled; it was thereby separated into (i) 3 : 4-dichloro-*o*-xylene, b. p. 234°, m. p. 8—9° (compare Hinkel, Ayling, and Bevan, *loc. cit.*), which yielded, on nitration, 3 : 4-dichloro-5 : 6-dinitro-*o*-xylene (compare p. 1946), and (ii) a small amount of unchanged 3-chloro-*o*-xylene; no indication was obtained of the presence of 4 : 5-dichloro-*o*-xylene.

Similar treatment of 4-chloro-*o*-xylene yielded 4 : 5-dichloro-*o*-xylene, m. p. 76°, b. p. 240° (compare Hinkel, Ayling, and Bevan, *loc. cit.*), and a small amount of unchanged 4-chloro-*o*-xylene, no indication being obtained of the presence of 3 : 4-dichloro-*o*-xylene.

Nitration of 4-*Chloro*-o-*xylene* (compare Claus and Groneweg, *loc. cit.*).—4-Chloro-*o*-xylene (1 vol.) was added gradually to well-cooled nitric acid (*d* 1·5; 2—3 vols.), and the mixture warmed for 30 minutes on a water-bath and then poured into water. The yellow oil produced was extracted in ether, washed with sodium hydroxide solution and water, dried, and distilled. The distillate slowly deposited a pale yellow solid, which crystallised from alcohol in flat sheaves, m. p. 111°, and was probably a dinitro-4-chloro-*o*-xylene. Distillation of the residual liquid in steam yielded 4-chloro-5-nitro-*o*-xylene, m. p. 63°, unchanged by admixture with an authentic specimen (this vol., p. 287) (Claus and Groneweg, *loc. cit.*, record m. p. 73° for the compound, obtained, as the sole product, by nitration of 4-chloro-*o*-xylene, as described above, which they considered to be 4-chloro-5-nitro-*o*-xylene).

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