CLI.—3 : 5-*Dichloro-o-xylene and 3 : 5-Dichloro-o-phthalic Acid.*

By ARTHUR WILLIAM CROSSLEY and HENRY RONDEL LE SUEUR.

IN a recent communication to the Society (Trans., 1902, 81, 827), it was shown that when phosphorus pentachloride acts on dimethyldihydroresorcin, there is obtained about 80 per cent. of the theoretical quantity of 3 : 5-dichloro-1 : 1-dimethyl- $\Delta^{2:4}$ -dihydrobenzene (I), to-

gether with a small quantity of a substance of higher boiling point, which has since been proved to consist of 3:5-dichloro-*o*-xylene (II).

It would appear that this substance is a normal product of the action of phosphorus pentachloride on dimethyldihydroresorcin, the amount obtainable being influenced, first, by the presence of excess of the pentachloride, and second, by the length of time during which the mixture is heated. When pure dichlorodimethyldihydrobenzene is heated with excess of phosphorus pentachloride in chloroform solution, it is almost completely transformed into dichloro-*o*-xylene. The position of the chlorine atoms in this substance is doubtless the same as in dichlorodimethyldihydrobenzene, namely, 3:5, and this is confirmed by the numbers obtained for the magnetic rotation; it may also be mentioned that when 3:5-dichlorodihydrobenzene,

is treated with phosphorus pentachloride it is converted into 3:5-dichlorobenzene (details not yet published).

The conversion of the hydroaromatic into the aromatic dichloride necessitates, however, the wandering of a methyl group, and the main point to be decided was the position taken up by this group. This is readily shown to be the ortho-position, for on oxidation with nitric acid the dichloroxylene is converted into a dichlorophthalic acid,

which, as it gives the fluorescein reaction and also a characteristic anhydride, can only be 3:5-dichloro-*o*-phthalic acid.

EXPERIMENTAL.

The accumulated fractions of high boiling point (b. p. above 100° under 23 mm. pressure), obtained by the action of phosphorus pentachloride on dimethyldihydroresorcin, were distilled in a vacuum, when after the third distillation nearly the whole passed over at 128–129° under 23 mm. pressure. This substance gave the following numbers on analysis :

0.1330 gave 0.2643 CO₂ and 0.0566 H₂O. C = 54.30; H = 4.73.

0.2266 required 0.4346 AgNO₃. Cl = 40.05.

C₈H₈Cl₂ requires C = 54.85; H = 4.57; Cl = 40.57 per cent.

3:5-Dichloro-*o*-xylene is a faintly yellow, highly refractive liquid

with a slight aromatic odour. It boils at 129° under 23 mm. or at 226° under the ordinary pressure, and on cooling solidifies to a mass of flaky needles which melt at $3-4^{\circ}$. Unlike dichlorodimethyl-dihydrobenzene, which does not solidify on cooling in a freezing mixture, it does not decolorise a solution of bromine in chloroform, or decompose on standing.

Claus and Kautz (*Ber.*, 1885, 18, 1368) have described a dichloro-*o*-xylene boiling at 227° and melting at 3° , but this substance cannot be identical with the above, as on oxidation (Claus and Groneweg, *J. pr. Chem.*, 1891, [ii], 43, 252) it yields the entirely different 4 : 5-dichloro-*o*-phthalic acid.

Densities, Magnetic Rotation, and Refractive Values of Dichloro-o-xylene.

The authors desire to express their thanks to Dr. W. H. Perkin, sen., for kindly determining the following physical data :

Densities : $d\ 4^{\circ}/4^{\circ} = 1.2472$; $d\ 15^{\circ}/15^{\circ} = 1.2374$; $d\ 25^{\circ}/25^{\circ} = 1.2301$.

Magnetic Rotation.

<i>t.</i>	Sp. rot.	Mol. rot.
15.1°	1.9614	15.411

The influence of chlorine displacing hydrogen in this compound may be seen as follows :

Mol. rot. 3 : 5-dichloro- <i>o</i> -xylene	15.411
„ <i>o</i> -xylene (Trans., 1896, 69, 1241)...	13.345
Cl ₂ displaces H ₂	$\frac{2}{2.066}$
Cl displaces H	1.033

This amount is small, but is due to the position of the chlorine atoms (*ibid.*, 1131), and the rotation is therefore confirmatory of the conclusion that the dichloro-*o*-xylene is a 3 : 5-derivative.

Refractive Values.

Density : $16.2^{\circ}/4^{\circ} = 1.23529$.

Line.	<i>t.</i>	μ .	$\mu - 1$.	$\frac{\mu - 1}{d} p$.
H _a	16.2°	1.54492	0.44112	77.197
H _{β}	16.2	1.56194	0.45491	79.608
H _{γ}	16.2	1.57295	0.46380	81.168

Dispersion : $H_{\gamma} - H_a = 3.971$.

Action of Phosphorus Pentachloride on Dichlorodimethyldihydrobenzene.

Seven grams of dichlorodimethyldihydrobenzene were heated with 20 grams of phosphorus pentachloride in chloroform solution for 6 hours, during which time a small amount of hydrogen chloride was evolved. On working up the product in the usual way, 4 grams of a liquid were obtained boiling between 224° and 228° and possessing all the properties of 3:5-dichloro-o-xylene.

Oxidation of 3:5-Dichloro-o-xylene to 3:5-Dichloro-o-phthalic Acid.

Sixteen grams of dichloroxylene were heated in quantities of 2 grams at a time with 15 c.c. of dilute nitric acid (35 c.c. of acid in 100 c.c. of water) in sealed tubes at 190 — 200° until the whole of the oil had disappeared. In some instances, on cooling, slender, white needles had separated, but in all cases the contents of the tubes were evaporated in a vacuum over caustic potash, when a solid residue of 18 grams was obtained, which, although purified by repeated crystallisation from water saturated with hydrogen chloride, did not melt sharply. It contracted slightly about 130° , partially sublimed, and finally melted at 164° with evolution of gas.

The whole was therefore heated with excess of acetyl chloride for 3 hours, the latter evaporated, and the solid residue purified by crystallisation from light petroleum and analysed:

0.1718 gave 0.2768 CO_2 and 0.0198 H_2O . $\text{C} = 43.94$; $\text{H} = 1.28$.

0.1382 required 0.2153 AgNO_3 . $\text{Cl} = 32.53$.

$\text{C}_8\text{H}_2\text{O}_3\text{Cl}_2$ requires $\text{C} = 44.24$; $\text{H} = 0.92$; $\text{Cl} = 32.72$ per cent.

3:5-Dichloro-o-phthalic anhydride is readily soluble in benzene, chloroform, or ether in the cold and crystallises from light petroleum (b. p. 80 — 100°) in radiating clusters of glistening needles melting at 89° . When heated with resorcinol and a drop of sulphuric acid, and the residue dissolved in caustic soda and poured into water, a brilliant green, fluorescent solution is obtained.

3:5-Dichloro-o-phthalic Acid.—The anhydride is insoluble in cold water, but on boiling it slowly dissolves to form a strongly acid solution, which, on evaporation in a vacuum, yields the acid as a white solid. It crystallises from water saturated with hydrogen chloride in masses of hair-like needles melting at 164° with evolution of gas, and many degrees below the melting point there is slight contraction and sublimation. The acid is very readily soluble in the cold in water, alcohol, acetone, or ether, but not readily so in benzene or chloroform even on boiling. It gives the fluorescein reaction, and, on heating, sublimes in needles melting at 89° and consisting of the anhydride.

Characteristic is the insolubility of the acid ammonium salt, which is precipitated on adding a solution of the acid to a solution of the neutral ammonium salt. On heating, the precipitate dissolves, and, on cooling, separates in long, slender needles.

The *silver* salt, $C_8H_2O_4Cl_2Ag_2$, is obtained as a white, caseous precipitate on adding silver nitrate in excess to a warm solution of the neutral ammonium salt. The silver was estimated by dissolving the salt in nitric acid and titrating with ammonium thiocyanate:

0.2228 gave 0.1064 Ag. $Ag = 47.78$.

$C_8H_2O_4Cl_2Ag_2$ requires $Ag = 48.10$ per cent.

The *diethyl ester*, $C_8H_2O_4Cl_2(C_2H_5)_2$, prepared by treating the silver salt with ethyl iodide in dry ethereal solution, is an odourless, oily, faintly yellow liquid boiling at $312-313^\circ$ under 760 mm. pressure:

0.1420 gave 0.2582 CO_2 and 0.0530 H_2O . $C = 49.59$; $H = 4.14$.

$C_{12}H_{12}O_4Cl_2$ requires $C = 49.48$; $H = 4.12$ per cent.

The *anil*, $C_{14}H_7O_2NCl_2$, obtained by heating the anhydride and the calculated amount of aniline at 180° until no more gas was evolved, crystallises from alcohol in bunches of silken needles melting at $150-150.5^\circ$. The crystals are insoluble in water, but readily soluble in acetone, chloroform, or benzene, and possess a marked yellow colour which could not be removed by repeated crystallisation (compare Graebe and Gourevitz, *Ber.*, 1900, 33, 2024):

0.2918 gave 12 c.c. moist nitrogen at 18° and 775 mm. $N = 4.83$.

$C_{14}H_7O_2NCl_2$ requires $N = 4.79$ per cent.

The *imide*, $C_8H_3O_2NCl_2$, was prepared by passing dry ammonia gas into the molten anhydride. It is insoluble in water, and only sparingly soluble in benzene, chloroform, or alcohol on warming, and crystallises from the last-named solvent in small, glistening, yellow needles melting at 208° :

0.2746 gave 16.0 c.c. moist nitrogen at 21.5° and 760 mm. $N = 6.62$

$C_8H_3O_2NCl_2$ requires $N = 6.48$ per cent.

The colour of the crystals could not be removed by recrystallisation.

CHEMICAL LABORATORY,
ST. THOMAS'S HOSPITAL, S.E.