CCXXXIV.—*The Action of Phosphorus Pentachloride on Ethyl Tartrate.*

By THOMAS STEWART PATTERSON and ALEXANDER ROBERTUS TODD.

ACCORDING to the literature, the action of phosphorus pentachloride on tartaric acid yields chloromaleyl chloride (Perkin and Duppa, *Compt. rend.*, 1860, **50**, 441), which, however, Perkin later showed to be in reality chlorofumaryl chloride (J., 1888, **53**, 695), or a mixture of chlorofumaric and dichlorosuccinic acids (Walden, *Ber.*, 1893, **26**, 210); whereas on ethyl tartrate in the homogeneous condition it produces ethyl chlorofumarate (Henry, *Compt. rend.*, 1870, **71**, 316), and on the ester in the presence of chloroform, it gives rise to ethyl β-chloromalate (Walden, *Ber.*, 1895, **28**, 1291). In connexion with some other experiments, we have recently found it necessary to re-examine the direct action of phosphorus pentachloride on ethyl tartrate.

To 200 g. of pure phosphorus pentachloride contained in a round-bottomed flask, fitted with a reflux condenser and cooled in water, 50 g. of ethyl tartrate $[\alpha_{5461}^{18^\circ}$ (100 mm.) $= 9{\cdot}5^\circ]$ were added in two portions through the condenser: the second portion was added as soon as the very vigorous initial reaction had subsided. After some 15 minutes the flask was heated on the water-bath. Vigorous reaction again set in at a temperature of about 75°, and was completed by heating on the boiling water-bath for 7—8 hours, after which time evolution of hydrogen chloride had practically ceased, and a homogeneous solution had been formed, although some phosphorus pentachloride crystallised out on cooling. The mixture was then gradually poured into water with constant stirring, the temperature being kept below 40°. The mixture was extracted with chloroform, the extract dried, and the chloroform removed on a water-bath, 20—25 g. of a thick, dark liquid remaining.

The product from 400 g. of ethyl tartrate treated in this way was distilled under 12—14 mm. pressure, and three distinct fractions were obtained: (1) 118—125°, a solid (*ca.* 16—20 g.); (2) 127—132°, a liquid (*ca.* 60 g.); (3) 160—165°, another solid (*ca.* 16—20 g.).

Fraction 1 was recrystallised several times from light petroleum (b. p. 60—80°); it formed fine glittering plates which softened about 112° and melted sharply at 117—118° (Found: Cl, 43%). In chloroform solution the compound was optically inactive. It dissolved slowly in water to yield a strongly acid solution, which decolorised potassium permanganate solution immediately, and bromine water very slowly.

By the addition of a solution of ammoniacal silver nitrate to the aqueous acid solution, a silver salt was prepared as a white crystalline precipitate; this was recrystallised from hot water (Found: Ag, 53·8%). The original substance would therefore seem to be dichloromaleic anhydride (Calc.: Cl, 42·6%), from which, by hydrolysis, a silver salt should be obtained which requires Ag, 54·1%.

Fraction 2 formed a colourless mobile liquid of $\alpha_{5461}^{17^\circ}$ (100 mm.) = − 22·43°, and decolorised potassium permanganate solution. After nine distillations under reduced pressure, the rotation of a portion of b. p. 128—129°/12—14 mm. became constant at $\alpha_{5461}^{15^\circ}$ (100 mm.) = − 27·2° (Found: Cl, 27·7%).

This liquid, hydrolysed by boiling with 30% sulphuric acid, yielded a white solid, m. p. *ca.* 170—175°, which, after repeated recrystallisation from glacial acetic acid, gave a product of m. p. 193° (Found: Cl, 23·68%). This substance decolorised potassium permanganate solution and appeared to be chlorofumaric acid (Calc.: Cl, 23·6%), which suggested the presence of ethyl chlorofumarate (Calc.: Cl, 17·2%; b. p. 127°/10 mm., Ruhemann and Tyler, J., 1896, **69**, 532) in the original volatile fraction.

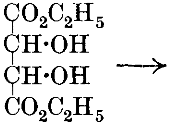
The rotation of the fraction must be due to some other substance, and the most probable would appear to be ethyl dichlorosuccinate, which has b. p. 128°/12—13 mm. (Wood and Nicholas, J., 1928, 1691), and requires Cl, 29·2%. It is obvious that fractional distillation could not separate these two substances.

We were unable, however, to isolate a definite derivative of dichlorosuccinic acid, in spite of the fact that, since the proportion of chlorine (27·7%) in the fraction of b. p. 128—129°/12—14 mm. lies nearer to the theoretical value for ethyl dichlorosuccinate (29·2%) than to that for ethyl chlorofumarate (17·2%), there should have been a considerably greater proportion of the former substance present. This, we think, is mainly or entirely due to the fact that boiling with acid not merely hydrolyses the ethyl dichlorosuccinate, but also converts the resulting dichlorosuccinic acid into chlorofumaric acid (or first converts ethyl dichlorosuccinate into ethyl chlorofumarate), as is corroborated by the following experiment.

The first runnings from the distillations of Fraction 2 [having $\alpha = ca. - 22\cdot5°$ ($l = 1$)] were boiled with 30% aqueous sulphuric acid until all had gone into solution (about 7 hours). The solution thus obtained had no observable rotation in a 400-mm. tube, and the solid (m. p. 192—193°) obtained from it by extraction with ether had also no observable rotation either before or after crystallisation. From the facts that the original, strongly active, fraction decolorised permanganate solution and had a chlorine content too low for ethyl dichlorosuccinate, and that only chlorofumaric acid could be obtained on hydrolysis of the liquid, we are, we think, justified in concluding that Fraction 2 was composed of ethyl chlorofumarate and ethyl dichlorosuccinate.

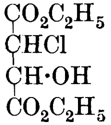
Fraction 3. This product was purified by several distillations under reduced pressure, b. p. 161—163°/12—14 mm., and by two crystallisations from light petroleum (b. p. 40—60°). It then melted at 52—53°, forming small, rod-like, white crystals (Found : Cl, 19·86%), fairly soluble in water, giving an acid solution which decolorised potassium permanganate solution instantaneously. It was optically inactive and could be recrystallised from boiling water. Boiled with 30% sulphuric acid for several hours, this substance yielded a solid unsaturated acid, m. p. 193° (Found : Cl, 23·62. Calc. for chlorofumaric acid : Cl, 23·60%), and its identity was confirmed by a mixed melting point with authentic chlorofumaric acid. Fraction 3 is therefore presumably ethyl hydrogen chlorofumarate (Calc. : Cl, 19·9%). It may be mentioned that ethyl hydrogen fumarate has b. p. 147°/16 mm. and m. p. 66° (Anschütz and Drugmann, *Ber.*, 1897, **30**, 2651; Shields, J., 1891, **59**, 738, gives m. p. 70°).

The results obtained confirm and, inasmuch as a greater number of products have been isolated, amplify previous work. The reaction probably proceeds in stages, the products obtained depending on the conditions of reaction. The first product is probably ethyl β-chloromalate (II), and the second, ethyl dichlorosuccinate (III), the latter



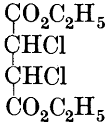
$$\begin{array}{l}\mathrm{CO_2C_2H_5}\\ |\\ \mathrm{CH\cdot OH}\\ |\\ \mathrm{CH\cdot OH}\\ |\\ \mathrm{CO_2C_2H_5}\end{array} \longrightarrow$$

(I.)



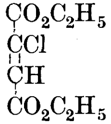
$$\begin{array}{l}\mathrm{CO_2C_2H_5}\\ |\\ \mathrm{CHCl}\\ |\\ \mathrm{CH\cdot OH}\\ |\\ \mathrm{CO_2C_2H_5}\end{array}$$

(II.)



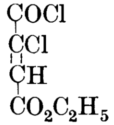
$$\begin{array}{l}\mathrm{CO_2C_2H_5}\\ |\\ \mathrm{CHCl}\\ |\\ \mathrm{CHCl}\\ |\\ \mathrm{CO_2C_2H_5}\end{array}$$

(III.)



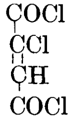
$$\begin{array}{l}\mathrm{CO_2C_2H_5}\\ |\\ \mathrm{CCl}\\ \|\\ \mathrm{CH}\\ |\\ \mathrm{CO_2C_2H_5}\end{array}$$

(IV.)



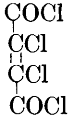
$$\begin{array}{l}\mathrm{COCl}\\ |\\ \mathrm{CCl}\\ \|\\ \mathrm{CH}\\ |\\ \mathrm{CO_2C_2H_5}\end{array}$$

(V.)



$$\begin{array}{l}\mathrm{COCl}\\ |\\ \mathrm{CCl}\\ \|\\ \mathrm{CH}\\ |\\ \mathrm{COCl}\end{array}$$

(VI.)



$$\begin{array}{l}\mathrm{COCl}\\ |\\ \mathrm{CCl}\\ \|\\ \mathrm{CCl}\\ |\\ \mathrm{COCl}\end{array}$$

(VII.)

by loss of hydrogen chloride passing, to a large extent, into ethyl chlorofumarate (IV). The ethyl dichlorosuccinate and chlorofumarate form our Fraction 2. Ethyl chlorofumarate, which was the product obtained by Henry, may then be attacked by phosphorus pentachloride giving ethyl chlorofumaryl chloride (V) (and probably ethyl chloride and phosphorus oxychloride). This compound, when the reaction mixture is poured into water, would give rise to ethyl hydrogen chlorofumarate, of which our Fraction 3 consists. Further action of phosphorus pentachloride on ethyl chlorofumaryl chloride may give chlorofumaryl dichloride (VI), which, either by direct chlorination by the pentachloride or by addition of two atoms of chlorine and subsequent elimination of hydrogen chloride, might give dichlorofumaryl (or dichloromaleyl) chloride (VII), and this, in turn, by subsequent treatment with water followed by distillation, would produce dichloromaleic anhydride, our Fraction 1.

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