231. *Esters Containing Phosphorus. Part II.*

By H. G. Cook, H. McCombie and B. C. Saunders.

Several more alcohols have been converted into the dialkyl hydrogen phosphites and thence into the corresponding chlorophosphonates by the method described in Part I (this vol., p. 380). In particular, ethyl lactate can be converted into *di*-(1-*carbethoxyethyl*) *chlorophosphonate* by this method. *Di*-(1-*carbethoxyethyl*) *anilinophosphonate* is readily prepared from the chlorophosphonate.

In Part I (this vol., p. 380) a convenient method for obtaining diethoxyphosphoryl chlorides (dialkyl chlorophosphonates) by the direct chlorination of dialkyl hydrogen phosphites was described. The method proves to be general for alkyl compounds and an account is now given of the conversion into the corresponding dialkyl phosphoryl chlorides (dialkyl chlorophosphonates) of the following alcohols: *iso*butyl, 3-methyl-*n*-butyl, 1 : 3-dimethyl-*n*-butyl, 1-ethyl-*n*-propyl. Ethyl lactate also readily responds to the standard treatment giving di-(1-carbethoxyethyl) hydrogen phosphite (I), on the addition of phosphorus trichloride in the absence of a tertiary base. This hydrogen phosphite then gives di-(1-carbethoxyethyl) phosphoryl chloride (III) on chlorination. (I) probably reacts as the tautomeric phosphonate (II) during chlorination.

$$3EtO_2C\cdot CHMe\cdot OH \xrightarrow{PCl_3} (EtO_2C\cdot CHMe\cdot O)_3P \xrightarrow{HCl} EtO_2CC\cdot HCl\cdot Me + (EtO_2C\cdot CHMe\cdot O)_2P\cdot OH$$

$$\text{(I.)} \downarrow$$

$$(EtO_2C\cdot CHMe\cdot O)_2(PhNH)P{:}O \xleftarrow{PhNH_2} (EtO_2C\cdot CHMe\cdot O)_2ClP{:}O \xleftarrow{Cl_2} (EtO_2C\cdot CHMe\cdot O)_2HP{:}O.$$

(IV.) (III.) (II.)

The compound (III) was further characterised by the formation of the crystalline di-(1-carbethoxyethyl) anilinophosphonate (IV) on treatment with aniline.

Although 1 : 3-dichlorohydrin did not give analytically pure di-(1 : 3-dichloro*iso*propyl) hydrogen phosphite because of a tendency to decompose on distillation, the crude hydrogen phosphite was readily converted into the chlorophosphonate, which again showed a tendency to decompose. The di-(1 : 3-dichloro*iso*propyl) anilinophosphonate obtained from the chlorophosphonate was, however, stable and could be obtained in an analytically pure condition (cf. Atherton, Openshaw and Todd, this vol., p. 382, who showed that the unstable dibenzyl hydrogen phosphite could be converted through the unstable chlorophosphonate into the stable aminophosphonate).

Experimental.

Di-(1 : 3-*dimethyl*-n-*butyl*) *Hydrogen Phosphite.*—Phosphorus trichloride (27·5 g., 0·2 mol.) in carbon tetrachloride (10 c.c.) was added slowly to 1 : 3-dimethyl-*n*-butyl alcohol (61·2 g., 0·6 mol.) also dissolved in carbon tetrachloride (60 c.c.). Air was drawn through the mixture for 2 hours and the temperature meanwhile slowly raised to 85°. After all the hydrogen chloride and carbon tetrachloride had been removed, the reaction mixture gave, on distillation, a fraction (44·5 g., 89%) of b. p. 81°/0·2 mm. (Found : C, 56·8; H, 10·4. $C_{12}H_{27}O_3P$ requires C, 57·6; H, 10·8%).

The reaction was also carried out in ethereal solution, the hydrogen chloride being removed by passing ammonia through the reaction product, and separating the precipitated ammonium chloride by filtration; yield 90%.

Di-(1 : 3-*dimethyl*-n-*butyl*) *Chlorophosphonate.*—The hydrogen phosphite (25 g.) was cooled in ice, and a stream of chlorine was passed through the liquid until a faint permanent green coloration was produced. Air was drawn through the liquid to remove the excess of chlorine and most of the hydrogen chloride. The last traces of hydrogen chloride were eliminated by the addition of lead carbonate and filtration through a layer of kieselguhr. The resulting liquid was dried over sodium sulphate, and on distillation gave a fraction (13 g., 46%) having b. p. 72·5—73·5°/0·01 mm. (Found : Cl, 12·6. $C_{12}H_{26}O_3ClP$ requires Cl, 12·5%).

Di-(1-*carbethoxyethyl*) *Hydrogen Phosphite.*—This was prepared as above from ethyl lactate (70·8 g., 0·6 mol.), dissolved in carbon tetrachloride (70 c.c.), and phosphorus trichloride (27·5 g., 0·2 mol.) also in carbon tetrachloride (10 c.c.). After working up in the usual way two fractions were obtained. (i) Ethyl 1-chloropropionate, b. p. 52—54°/18 mm. (21 g., 79%); this was redistilled at 145°/760 mm. (ii) *Di-*(1-*carbethoxyethyl*) *hydrogen phosphite*, b. p. 135°/0·2 mm. (31 g., 55%) (Found : C, 43·2; H, 6·81. $C_{10}H_{19}O_7P$ requires C, 42·6; H, 6·74%).

When the reaction was carried out in ethereal solution, and the hydrogen chloride removed by ammonia, the yield of the hydrogen phosphite was 86%.

Di-(1-*carbethoxyethyl*) *Chlorophosphonate.*—The hydrogen phosphite (80 g.) was cooled in ice, and dry chlorine passed through the liquid until a faint permanent green coloration was produced. The excess of chlorine and hydrogen chloride were removed sufficiently by drawing air through the product. After drying over sodium sulphate, the liquid was distilled and had b. p. 120°/0·02 mm. (72 g., 80%) (Found : Cl, 11·36. $C_{10}H_{18}O_7Cl$ requires Cl, 11·24%).

Di-(1-*carbethoxyethyl*) *Anilinophosphonate.*—The chlorophosphonate (10 g.) was added to aniline (5·87 g.) cooled in ice. Heat was evolved and the reaction mixture solidified. The solid was extracted with boiling benzene, the solution evaporated and the residual syrup then crystallised on standing. It was recrystallised from alcohol–water (1 : 3) and obtained in long white needles, m. p. 91° (Found : N, 3·98. $C_{16}H_{24}O_7NP$ requires N, 3·75%).

Di-(1-*ethyl*-n-*propyl*) *Hydrogen Phosphite.*—This was prepared in the usual way from 1-ethylpropyl alcohol (*i.e.*, *sec.*-amyl alcohol, 52·8 g., 0·6 mol.) in carbon tetrachloride (53 c.c.) and phosphorus trichloride (27·5 g., 0·2 mol.) in carbon tetrachloride (10 c.c.). The fraction (33 g., 75%) had b. p. 72°/0·2 mm. (Found : C, 54·04; H, 10·42. $C_{10}H_{23}O_3P$ requires C, 54·05; H, 10·36%).

Di-(1-*ethyl*-n-*propyl*) *Chlorophosphonate.*—This was prepared from the corresponding hydrogen phosphite and obtained in 63·5% yield. It had b. p. 73·5°/0·1 mm. (Found : Cl, 13·98. $C_{10}H_{22}O_3ClP$ requires Cl, 13·84%).

Di-(3-*methyl*-n-*butyl*) *Hydrogen Phosphite.*—Prepared in the usual manner from 3-methyl-*n*-butyl alcohol (*iso*amyl alcohol). Yield 85%, b. p. 75°/0·15 mm. (Found : C, 53·5; H, 10·2. $C_{10}H_{23}O_3P$ requires C, 54·05; H, 10·36%).

Di-(3-*methyl*-n-*butyl*) *chlorophosphonate*, prepared in 49% yield from the above hydrogen phosphite, had b. p. 74°/0·02 mm. (Found : Cl, 13·86. $C_{10}H_{22}O_3ClP$ requires Cl, 13·84%).

*Di-*iso*butyl hydrogen phosphite*, obtained in 90% yield by the usual procedure, had b. p. 105·6—106·5°/12 mm. (Found : C, 49·76; H, 9·92. $C_8H_{19}O_3P$ requires C, 49·5; H, 9·8%).

*Di-*iso*butyl chlorophosphonate* was prepared in theoretical yield from the hydrogen phosphite. It had b. p. 57°/0·1 mm. (Found : Cl; 15·8. $C_{10}H_{18}O_3ClP$ requires Cl, 15·54%). By the action of aniline this chlorophosphonate was converted into *di-*iso*butyl anilinophosphonate*. When recrystallised from methanol, it was obtained in short colourless needles, m. p. 43·5—45° (Found : C, 58·75; H, 8·62; N, 5·06. $C_{14}H_{24}O_3NP$ requires C, 58·95; H, 8·42; N, 4·91%).

Di-(1 : 3-*dichloro*iso*propyl*) *anilinophosphonate.*—Phosphorus trichloride (13·75 g.) was added to mechanically stirred 1 : 3-dichlorohydrin (38·7 g.) kept at below 3° by addition of solid carbon dioxide. Alternatively, the reaction was carried out in carbon tetrachloride solution. Air was drawn through the mixture to remove hydrogen chloride and the residue was fractionated. The hydrogen phosphite had b. p. *ca.* 180°/2 mm., but it was advisable to omit the distillation owing to incipient decomposition. The undistilled hydrogen phosphite prepared from dichlorohydrin (155 g.) and phosphorus trichloride (55 g.) was chlorinated in the usual way and air drawn through the mixture and then distilled. It had b. p. 182—186°/2 mm., with a marked tendency to decompose (69 g., 50%).

The chlorophosphonate was added to aniline (2 mol.). A vigorous reaction took place and the mixture became almost solid. After filtration, the solid was extracted with boiling benzene, and the cold benzene solution run through a column of alumina. The benzene was removed and the solidified *anilinophosphonate*, recrystallised from aqueous acetic acid, was obtained in small colourless needles, m. p. 81° (Found : C, 36·66; H, 4·06; N, 3·7. $C_{12}H_{16}O_3NCl_4P$ requires C, 36·46; H, 4·05; N, 3·54%).

We are grateful to the Director General of Scientific Research Development for permission to publish this work.

University Chemical Laboratory, Cambridge. [*Received, August 20th*, 1945.]