

### 394. Interaction of Phosphorus Trichloride with Alcohols and with Hydroxy-esters.

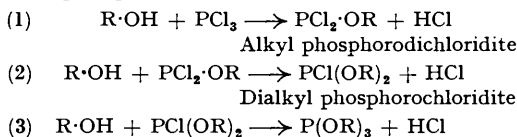
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Phosphorus trichloride is used both for the replacement of hydroxyl by chlorine and for the formation of esters of phosphorus; these two functions are correlated, and the sequence of reactions is studied. Addition of an alcohol such as *n*-butyl alcohol to the trichloride leads to rapid stepwise alkoxylation of phosphorus, followed by dealkylation of the trialkyl phosphite to dialkyl hydrogen phosphite. Yields of the last, dichloridite,  $\text{PCl}_2\cdot\text{OR}$ , and chloridite,  $\text{PCl}(\text{OR})_2$ , depend mainly on the relative amount of alcohol added. Most of the alkyl chloride is formed during the first few minutes, and is mainly due to dealkylation (one group) of the trialkyl phosphite by means of hydrogen chloride. Later, the dialkyl hydrogen phosphite, the chloridite, and to a much less degree the dichloridite are dealkylated.

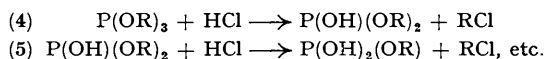
The ethyl esters of glycolic,  $\beta$ -hydroxypropionic, and malic acids behaved as does *n*-butyl alcohol. Esters could not be isolated by the interaction of *tert*-butyl alcohol and the trichloride alone, owing to the rapid formation of alkyl chloride and phosphorous acid, but in the presence of pyridine the dialkyl hydrogen phosphite was obtained.

PHOSPHORUS TRICHLORIDE is used both for the preparation of esters containing phosphorus (Railton, *J.*, 1854, 7, 216; Wichelhaus, *Annalen*, 1868, Suppl. 6, 257; Arbusov, *J. Russ. Phys. Chem. Soc.*, 1906, 38, 687; Milobendzki and Sachnowski, *Chem. Polski*, 1917, 15, 34; Gerrard, *J.*, 1940, 1464; 1944, 85; McCombie, Saunders, and Stacey, *J.*, 1945, 380; Kosolopoff, "Organophosphorus Compounds," Wiley, New York, 1950) and for the replacement of hydroxyl by chlorine (cf. Clark and Streight, *Proc. Roy. Soc. Canada*, 1929, 23, 77; Kenyon and Phillips, *Trans. Faraday Soc.*, 1930, 26, 451). Trichloride-alcohol systems are considered from both these aspects, and the following description applies to hydroxy-compounds which behave similarly to *n*-butyl alcohol.

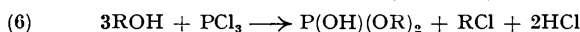
During the dropwise addition of the alcohol to the trichloride at about 0° there is a quick, stepwise alkoxylation of phosphorus:



By the time the alcohol (1 mol.) has been added to the trichloride (1 mol.), in addition to the main product (dichloridite), the chloridite and even some tri-ester have been formed, and a corresponding amount of trichloride remains. The trialkyl phosphite is readily dealkylated (1 group) by hydrogen chloride (reaction 4) (cf. Gerrard and Whitbread, *J.*, 1952, 914), and this is an irreversible reaction belonging to a different sequence; for dealkylation can proceed through the second step (slow) and even through the extremely slow third step:



By stopping the addition of alcohol before 1 mol. has been added, a good yield of dichloridite can be obtained, but chloridite and hydrogen phosphite are also formed. At the 2-mol. stage the yield of chloridite has increased, but so has that of hydrogen phosphite, and it is difficult to get a pure specimen of chloridite from this mixture. The third mol. of alcohol completes the alkoxylation of the phosphorus and produces dialkyl hydrogen phosphite and alkyl chloride in fair agreement with equation (6):



This is the standard procedure for the preparation of hydrogen phosphites; but to increase the yield of alkyl chloride beyond 33% requires longer times and higher temperatures and, to convert all the halogen into alkyl chloride, hydrogen chloride must be conserved.

The dealkylation of *n*-butyl phosphorodichloridite by hydrogen chloride was slow at 17°, but quicker at 65°, and there was no indication that the dichloridite can itself give alkyl chloride even on being heated. The chloridite was more quickly dealkylated than the dichloridite at 17°, and at 65° it was completely so after 48 hours. The conclusion is that for the 3ROH + PCl<sub>3</sub> system the reaction which is almost entirely responsible for the formation of alkyl chloride in the first few minutes is the dealkylation of the trialkyl phosphite to dialkyl hydrogen phosphite. Longer reaction times would allow the dealkylation of the latter to proceed, but there are no chloro-esters in the system to make any contribution. In the systems 2ROH + PCl<sub>3</sub> and ROH + PCl<sub>3</sub>, the alcohol being added to the trichloride, the amount of alkyl chloride quickly formed will be less than in the previous system, because complete alkoxylation of all the phosphorus cannot occur. The slow dealkylation of the chloro-esters, however, can give some alkyl chloride.

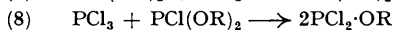
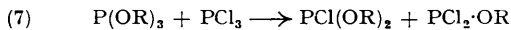
To determine the maximum loss (expressed as yield % of alkyl chloride) of easily hydrolysable chlorine without unproductive loss of hydrogen chloride, reagents were allowed to react in sealed tubes. At 18° there was a comparatively small increase in yield of alkyl chloride when the reaction time was extended from 24 to 72 hours. In the alcohol-trichloride system (Table 1), the yield of alkyl chloride was greatest for the ratio 3ROH : PCl<sub>3</sub>, and even then only about 50% of the chlorine was converted into alkyl chloride. As the proportion of trichloride was increased, so the yield of alkyl chloride decreased. In pentane and benzene, as solvents, the yield of alkyl chloride was not more than about 33% for the 3 : 1 ratio, although for the ratio ROH : PCl<sub>3</sub> the yield was the same as when no solvent was used. It is supposed that the solvent in some way hinders the dealkylation of the hydrogen phosphite, and this effect is particularly noticeable with ether. Data in Table 2 show that in the alcohol-dichloridite system, the ratio being < 2ROH : PCl<sub>2</sub>·OR, about 50% of the chlorine was converted, and this is in accord with equations (2), (3), and (4). As the proportion of the dichloridite was increased to 1 : 1, the yield of alkyl chloride decreased, because not all the dichloridite could be converted into tri-ester. Solvents again had the effect mentioned.

In the chloridite-alcohol system (Table 3), any proportion of alcohol greater than R·OH : PCl(OR)<sub>2</sub> can effect complete dechlorination, and therefore lead to a complete removal of easily hydrolysable chlorine by the reaction R·OH + PCl(OR)<sub>2</sub> → RCl + P(OH)(OR)<sub>2</sub>. That only 90% of complete removal was quickly achieved is attributed to the withholding of hydrogen chloride either by the excess of alcohol, when this was used, or by the hydrogen phosphite, a known property of these compounds.

Table 4 contains data from a series of experiments in which the reaction mixtures were analysed after shorter time intervals. The speed of removal of the last chlorine atom and of the first dealkylation reaction is amply illustrated by the fact that within 2 minutes of mixing of the alcohol (1 mol.) with the chloridite (1 mol.) 90% of the chlorine had been converted into alkyl chloride.

To prepare di-*n*-butyl phosphorochloridite (required for the preparation of mixed phosphites) in good yield, an attempt was made to hinder loss of the third chlorine atom by a mass-law effect, by using alcohol saturated with hydrogen chloride for addition either to the trichloride or to the dichloridite, a procedure which had been found very effective in the thionyl chloride system (unpublished work). This, however, failed. The method found most convenient (60% yields) was the addition of an ethereal solution of alcohol (1 mol.) and pyridine (1 mol.) to the dichloridite (1 mol.) in ether.

A complete description of phosphorus trichloride-alcohol systems must include the reactions :



These are slow compared with reactions (1)—(3), of which they are not the reverse.

In the systems described, any reaction between alcohol and hydrogen chloride is likely to be too slow to make an observable contribution to the formation of alkyl chloride. This cannot be stated of alcohols such as *tert.*-butyl alcohol: the hydrogen chloride formed at the beginning of the mixing can react with the alcohol and form water, which, in turn, by

reaction with the trichloride or chloro-esters, can form hydrogen chloride for further attack on the alcohol. This possibility must be kept in mind in considering the behaviour of such alcohols as *tert.*-butyl alcohol in inorganic non-metallic halide systems. In none of these systems have the esters containing the non-metal been isolated by direct interaction of the halide and the alcohol.

All attempts failed to prepare *tert.*-butyl esters containing phosphorus by the interaction of the trichloride and the alcohol; the products isolated were the alkyl chloride and phosphorous acid. The titration procedure was adapted to cope with the more easily hydrolysed *tert.*-butyl chloride, chlorine other than in this compound being precipitated and separated as pyridine hydrochloride. Table 5 shows the yield of alkyl chloride during 1 hour at 0° when the alcohol (1 mol.) was allowed to react with the trichloride (0.33 mol.) in ethereal solutions of different concentrations. At low concentrations a minimum yield of 25% was obtained, and this was not increased by extending the reaction time to 96 hours. In pentane (Table 6) there was no asymptotic approach to a certain minimum at low concentration, and furthermore, for, *e.g.*, 0.25M-solution the yield increased from 36.1% (1 hour) to 77.4% (10 hours). These data are consistent with the rapid formation of the esters and their ready dealkylation by hydrogen chloride, the effect when ether was solvent probably being due to retention of hydrogen chloride as the ether oxonium salt. This view is in accordance with the rapid and complete dealkylation of di-*tert.*-butyl hydrogen phosphite by hydrogen chloride alone, and with the very much slower dealkylation in dilute ethereal solutions.

The general procedure for preparing trialkyl phosphites, *viz.*, addition of the trichloride (1 mol.) to a solution of the alcohol (3 mol.) and tertiary base (3 mol.) in a solvent such as ether or pentane, was not effective with *tert.*-butyl alcohol; for although 93% of the chlorine was rapidly precipitated as salt, even at -78°, it was the hydrogen phosphite and not the tri-ester which was isolated.

Ethyl glycolate,  $\beta$ -hydroxypropionate, and malate were examined to reveal any special influence of the carbethoxy-group. Reaction sequences conform clearly with those for *n*-butyl alcohol and for octan-2-ol. Comparison of rotatory powers leads to the postulation that the final attachment of chlorine entails inversion of configuration without material loss in rotatory power.

#### EXPERIMENTAL

All materials were rigorously purified just before use, and solvents were dried.

*Butyl Phosphorodichloridite and Dibutyl Phosphorochloridite.*—Alcohol (1 mol.) was added to phosphorus trichloride (1 mol.) (Gerrard, *loc. cit.*). *n*-Butyl alcohol (74 g.) gave the dichloridite (70%), b. p. 47°/10 mm.,  $d_4^{20}$  1.166 (Found: Cl, 40.2; P, 17.55. Calc. for  $C_4H_9OCl_2P$ : Cl, 40.5; P, 17.7%), and a residue (52.1 g.). *iso*Butyl alcohol (50.0 g.) gave the dichloridite (67.5%), b. p. 42.5°/12 mm.,  $d_4^{20}$  1.169,  $n_D^{20}$  1.4642 (Found: Cl, 40.3%), and a residue (17.1 g.). *sec.*-Butyl alcohol (40.0 g.) gave the *dichloridite* (46%), b. p. 61—64°/22 mm.,  $d_4^{20}$  1.173,  $n_D^{20}$  1.4655 (Found: Cl, 40.0%), and a residue (11.4 g.). It was not possible to obtain good yields of chloridite by careful addition of alcohol (1 mol.) to the corresponding dichloridite. *n*-Butyl alcohol (12.8 g.) was added dropwise to *n*-butyl phosphorodichloridite (35.0 g.) at -10°; a liquid (6.94 g.), b. p. up to 60°/12 mm., dichloridite (8.57 g.), b. p. 65—70°/20 mm. (Found: Cl, 40.8%), a mixture of chloridite and dibutyl hydrogen phosphite (3.83 g.), b. p. 114—119°/20 mm. (Found: Cl, 11.0%), the hydrogen phosphite (mainly) (9.54 g.), b. p. 122—125°/14 mm. (Found: Cl, 0.75%), and a residue (4.53 g.) were obtained.

A mixture of *n*-butyl alcohol (42.2 g., 1 mol.) and pyridine (1 mol.) in ether (100 c.c.) was added dropwise to the dichloridite (99.8 g., 1 mol.) in ether (100 c.c.) at -10°. Base hydrochloride (100%) and a filtrate, which gave a liquid (10 g.), b. p. 80—100°/13 mm., crude chloridite (80.1 g., 65.9%), b. p. 100—102°/13 mm., a liquid (18.7 g.), b. p. 102—112°/13 mm., and a residue (12.5 g.), were obtained. From the crude material the chloridite (60.5%), b. p. 100—103°/12—14 mm., 55—58°/0.05 mm.,  $d_4^{16}$  1.009,  $n_D^{20}$  1.4455 (Found: Cl, 16.45; P, 14.55. Calc. for  $C_8H_{18}O_2ClP$ : Cl, 16.7; P, 14.6%), was obtained.

Addition of *isobutyl* alcohol (3.38 g., 1 mol.) to the dichloridite (8.0 g., 1 mol.) at -10°, in a stream of carbon dioxide, afforded the dichloridite (1.72 g.), b. p. 47—49°/10 mm., *diisobutyl phosphorochloridite* (3.8 g., 40%), b. p. 83—85°/9 mm. (Found: Cl, 16.45.  $C_8H_{18}O_2PCl$  requires

Cl, 16.7%), and the hydrogen phosphite (2.4 g.), b. p. 100—106°/14 mm. In the presence of pyridine (1 mol.) in pentane (300 c.c.), the alcohol (25.4 g., 1 mol.) and dichloridite (60 g., 1 mol.) at  $-10^\circ$  immediately gave the base hydrochloride (100%), the chloridite (42.1 g., 56%), b. p. 102—105°/20 mm.,  $d_4^{19}$  1.007,  $n_D^{20}$  1.4405 (Found: C, 45.8; H, 8.5; Cl, 16.3. Calc.: C, 45.2; H, 8.5; Cl, 16.7%), and a mixture (17.4 g.) of chloridite and phosphite, b. p. 106—117°/19 mm. Addition of the alcohol (2 mol.) and base (2 mol.) to the trichloride (1 mol.) in ether gave the same materials; but distillation was troublesome. Addition of the alcohol (7.4 g., 1 mol.) and base (1 mol.) to the trichloride (1 mol.) in ether afforded base hydrochloride (99.5%), the dichloridite (6.0 g., 40%), b. p. 40—42°/9 mm. (Found: Cl, 39.2%), and chloridite (4.0 g.), b. p. 80—85°/9 mm. (Found: Cl, 17.1%).

From alcohol (8.5 g., 1 mol.), pyridine (1 mol.), and the dichloridite (1 mol.) in pentane (200 c.c.) at  $-10^\circ$ , *di-sec.-butyl phosphorochloridite* (12.0 g., 50%), b. p. 102—104°/23 mm.,  $d_4^{20}$  1.024,  $n_D^{20}$  1.475 (Found: Cl, 16.4; P, 14.8%), was obtained.

*Dealkylation of Dichloridites and Chloridites by Hydrogen Chloride.*—The dry gas was passed into the ester, a U-tube at  $-80^\circ$  being attached to the apparatus to retain alkyl chloride. The reaction vessel and U-tube were weighed after different intervals of time. At  $25^\circ$  the dichloridites reacted only slowly. After 14 hr. (dichloridite, 10 g.) there was only a slight wetting of the tube, and the dichloridite was distilled almost unchanged in amount. With *n*-butyl phosphorodichloridite (14.13 g.) after 11 hr. at  $65^\circ$  the decrease in weight of the reaction system was 1.36 g., and the increase in weight of the U-tube was 1.52 g. From the condensate, *n*-butyl chloride (1.0 g.), b. p. 78.5°,  $n_D^{20}$  1.4005, was obtained.

Hydrogen chloride was passed into *di-n*-butyl phosphorochloridite (22.0 g.) at  $65^\circ$  for 48 hr. The reaction vessel first gained and then continuously lost weight, and the residue (7.97 g.) after being kept at 15 mm. weighed 7.87 g. (Found: Cl, nil; P, 38.2. Calc. for  $\text{HO}_2\text{P}$ : P, 48.4%. Calc. for  $\text{H}_3\text{O}_3\text{P}$ : P, 37.8%). The U-tube condensate gave *n*-butyl chloride (17.65 g. Calc. for  $2\text{RCl}$ : 19.2 g.), b. p. 78.5° (Found: Cl, 37.8. Calc. for  $\text{C}_4\text{H}_9\text{Cl}$ : Cl, 38.4%). Similarly, *diisobutyl phosphorochloridite* (25.4 g.) gave *isobutyl chloride* (4.0 g.), b. p. 68.5°, after 6 hr. at  $65^\circ$ , whereas the chloridite (19.0 g.) gave the chloride (2.1 g.), b. p. 68.5°, after 27 hr. at  $17^\circ$ .

*Sealed-tube Technique.*—Pipettes made to effect quick delivery of definite molar ratios of reagents on a semimicro-scale were calibrated to deliver amounts of the order of 0.250 g. The phosphorus compound was run into a previously constricted tube, solvent, when used, was added (to give a 5% solution of alcohol in solvent, w/w), and alcohol was added to the contents at  $-78^\circ$  before sealing. The tubes were opened under dilute aqueous ammonia inside a large flask in such a way as to avoid loss of hydrogen chloride. Chloride ion was then determined by Volhard's method. The loss in readily hydrolysable chlorine is expressed as the % formation of alkyl chloride, the chloro-esters giving chloride ion quickly with water. Results are recorded in Tables 1, 2, and 3. The time intervals were 24 and 72 hr.

TABLE 1. ( $18^\circ$ )

Mol. ratio, <i>n</i> -BuOH : $\text{PCl}_3$	Yield of RCl (% , based on R·OH) in 24 hr.				Yield of RCl (% , based on R·OH) in 72 hr.			
	No solvent	$\text{C}_5\text{H}_{12}$	$\text{C}_6\text{H}_6$	$\text{Et}_2\text{O}$	No solvent	$\text{C}_5\text{H}_{12}$	$\text{C}_6\text{H}_6$	$\text{Et}_2\text{O}$
3 : 1	44.7	32.4	28.3	26.3	52.3	31.9	33.9	29.7
3 : 2	34.5	25.7	27.5	18.2	35.8	28.4	28.1	23.0
3 : 3	21.6	21.0	21.8	8.0	22.8	23.4	22.8	6.6

TABLE 2. ( $18^\circ$ )

Mol. ratio, $\text{Bu}^n\text{OH} : \text{PCl}_2 \cdot \text{OBu}^n$	Yield of RCl (% , based on Cl) in 24 hr.				Yield of RCl (% , based on Cl) in 72 hr.			
	No solvent	$\text{C}_5\text{H}_{12}$	$\text{C}_6\text{H}_6$	$\text{Et}_2\text{O}$	No solvent	$\text{C}_5\text{H}_{12}$	$\text{C}_6\text{H}_6$	$\text{Et}_2\text{O}$
6 : 1	48.5	44.8	44.5	42.6	52.8	45.6	44.5	43.5
3 : 1	51.1	47.8	47.8	43.7	55.3	48.9	46.7	43.5
3 : 2	49.3	35.2	36.6	29.2	52.9	36.2	38.0	31.1
3 : 3	31.0	20.4	25.0	19.4	35.4	21.8	25.0	19.5
$\text{Bu}^n\text{OH} : \text{PCl}_2 \cdot \text{OBu}$								
6 : 1	42.8	38.6	36.7	33.5	44.0	40.3	32.7	34.8
3 : 1	42.0	45.1	41.5	39.4	42.6	40.3	42.4	38.7
3 : 2	36.0	27.9	30.5	21.9	36.9	31.0	31.8	21.5
3 : 3	18.7	20.5	20.2	9.5	18.8	20.5	21.8	10.4

TABLE 3. (18°)

Mol. ratios	Yield of RCl (% , based on Cl) in 24 hr.				Yield of RCl (% , based on Cl) in 72 hr.			
	No solvent	C <sub>5</sub> H <sub>12</sub>	C <sub>6</sub> H <sub>6</sub>	Et <sub>2</sub> O	No solvent	C <sub>5</sub> H <sub>12</sub>	C <sub>6</sub> H <sub>6</sub>	Et <sub>2</sub> O
Bu <sup>n</sup> OH : PCl(OBu <sup>n</sup> ) <sub>2</sub>								
6 : 1	84.5	79.0	79.9	74.4	87.2	82.6	75.3	76.3
3 : 1	87.7	79.9	—	72.6	91.3	84.5	79.0	76.3
3 : 2	89.0	82.2	88.1	81.8	91.1	87.2	89.5	81.8
3 : 3	90.5	85.4	89.3	83.4	92.4	89.6	91.8	83.8
Bu <sup>n</sup> OH : PCl(OBu <sup>n</sup> ) <sub>2</sub>								
6 : 1	78.0	—	56.2	50.1	82.0	—	69.0	54.1
3 : 1	78.0	—	74.2	49.1	77.0	—	79.0	56.1
3 : 2	84.0	—	81.7	68.3	85.5	—	84.0	70.5
3 : 3	86.3	—	85.5	74.5	84.4	—	85.7	76.4
3 : 6	99.8 *	—	95.4	82.1	—	—	—	—

\* Based on R·OH.

In another series, vessels fitted with taps were used, and the contents were analysed at shorter time intervals. Weights of dichloridite were of the order 0.500 g., and of the chloridite, 1.000 g. Data are recorded in Table 4.

TABLE 4. (25°)

Mol. ratio	No solvent		C <sub>6</sub> H <sub>6</sub>		Et <sub>2</sub> O	
	RCl, %	Time, min.	RCl, %	Time, min.	RCl, %	Time, min.
Bu <sup>n</sup> OH : PCl <sub>2</sub> ·OBu <sup>n</sup>						
1 : 1	19.0	15	18.2	15	13	15
2 : 1	49.8	30	44.7	20	34.2	30
	—	—	49.2	30	42.0	60
Bu <sup>n</sup> OH : PCl(OBu <sup>n</sup> ) <sub>2</sub>						
1 : 1	89.8	1	63.2	1	35.4	5
	90.5	15	82.4	5	53.0	30
	92.0	120	88.0	30	71.8	60
2 : 1	89.8	1	63.7	1	34.8	5
	91.5	2	77.3	10	48.9	30
	93.4	180	89.1	30	57.8	60

As a check on the titration method, *n*-butyl alcohol (3.7 g., 1 mol.) was added to the chloridite (10.6 g., 1 mol.) at -10°. Volatile matter was removed immediately at -10°; *n*-butyl chloride (3.54 g., 78%), b. p. 77.4° (Found : Cl, 37.9%), and dibutyl hydrogen phosphite (9.0 g., 92%), b. p. 120—125°/10 mm. (Found : P, 15.7%), were obtained. Similarly, the dichloridite (4.37 g., 0.5 mol.) and the alcohol (3.7 g., 1 mol.) at -10° gave alkyl chloride (1.56 g., 42%, based on Cl), b. p. 77.5° (Found : Cl, 37.8%), and hydrogen phosphite (4.5 g., 90%), b. p. 120—125°/10 mm. When only 1 mol. of alcohol to 1 mol. of dichloridite was used, the yield of alkyl chloride was 24%, based on the chlorine.

*Reactions with tert.-Butyl Alcohol.*—The alcohol (3.7 g., 1 mol.) was added (molten, dropwise) to the trichloride (13.74 g., 2 mol.) at -10°. After 1 hr. volatile matter was removed at 20°/20 mm., and the nature of the residue (1.863 g.) (Found : Cl, 0.7; P, 37.7. Calc. for H<sub>3</sub>PO<sub>3</sub> : P, 37.8%) showed the absence of esters containing phosphorus. The volatile matter had b. p. 51—75°. Similar results were obtained with the reagents 1 mol. : 1 mol., and after the addition of water, *tert.*-butyl chloride (57%), b. p. 52—53° (Found : Cl, 37.8. Calc. for C<sub>4</sub>H<sub>9</sub>Cl : Cl, 38.4%), was obtained. The ratio being 3 mol. (12.9 g.) of alcohol to 1 mol. of trichloride (7.8 g.), *tert.*-butyl chloride (14.2 g., 88%), b. p. 51° (Found : Cl, 37.9%), and phosphorous acid (Found : P, 37.0%) were immediately obtained. To decrease the rate of reactions solvents were used, and the amount of alkyl chloride formed was estimated by separating the remaining chlorine as pyridine salt. Standard solutions of alcohol and trichloride were mixed at -10° in a specially designed apparatus fitted with a dropping-funnel and a sintered-glass disc, moisture being excluded. After the stated time at 0°, pyridine was added at -10°, and the chlorine content of the precipitate determined. The yield of alkyl chloride was computed by difference. In no case did the filtered solution give a precipitate with ethanol, so conditions were always satisfactory.

Table 5 shows results for a series in which the ratio was 3ROH : PCl<sub>3</sub>, the reactants being mixed in ethereal solution so as to give an initial concentration of alcohol as stated. After the reaction mixture had been at 0° for 1 hr., pyridine was added as described. The yield of 25% persisted in more dilute solutions, and for times up to 96 hr. Corresponding results for pentane

are given in Table 6. For, *e.g.*, 0.25M-solution, the yield of 36.1% did not persist with time, but increased to 49.2% (2 hr.), 65.8% (6 hr.), and 77.4% (10 hr.).

TABLE 5. (Ether)

Initial concn. of ROH, g.-mol./l. ...	7.14	6.25	5.0	4.5	4.0	3.5	2.5	0.25
Yield of Bu <sup>t</sup> Cl, % .....	86.5	77.6	64.5	51.4	46.2	40.1	25.0	25.0

TABLE 6. (Pentane)

Initial concn. of ROH, g.-mol./l.	7.14	6.25	5.55	5.0	4.16	3.57	1.0	0.5	0.25
Yield of Bu <sup>t</sup> Cl, % .....	91.4	89.2	87.2	85.0	83.0	75.6	65.3	56.3	36.1

Despite the utmost efforts, tri-*tert.*-butyl phosphite could not be isolated. Phosphorus trichloride (9.16 g., 0.33 mol.) in ether was added to the alcohol (14.8 g., 1 mol.) and pyridine (15.8 g., 1 mol.) in ether at  $-10^{\circ}$ . From the filtrate *di-tert.*-butyl hydrogen phosphite (10.0 g., 53.6%), b. p. 48–50°/0.4 mm. (oil-bath never over 65°, otherwise vigorous decomposition) (Found: P, 16.1. C<sub>8</sub>H<sub>19</sub>O<sub>3</sub>P requires P, 16.0%), was obtained. Although at  $-78^{\circ}$ , 93% of the chlorine was precipitated as salt, the only ester obtained was the hydrogen phosphite (11.5 g., from ROH, 14.8 g.), b. p. 45°/0.1 mm. (Found: P, 15.9%), the residue weighing 0.40 g.

Hydrogen chloride was passed into the hydrogen phosphite (4.73 g.) at 0°. Volatile matter equivalent to 2.7 g. of alkyl chloride was carried away in 30 min. *tert.*-Butyl chloride actually distilled (1.48 g.) had b. p. 50–51° (Found: Cl, 36.6%), and there was a residue (2.11 g. Calc. for H<sub>3</sub>PO<sub>3</sub>: 2.00 g.) (Found: P, 37.8%).

By the pyridine-titration method it was shown that the hydrogen phosphite gave only a 4% formation of alkyl chloride after 41 hr. at 25° when the reagent was an ethereal solution of hydrogen chloride (0.1 molar), whereas for a 2M-solution at 0° the yield was 14% after 1 hr.

#### Reactions with Hydroxy-esters.

*The Phosphites.*—These were prepared by addition of phosphorus trichloride (1 mol.) to pyridine (3 mol.) and hydroxy-ester (3 mol.) in ether at  $-10^{\circ}$  (Gerrard, *loc. cit.*). Precipitation of base hydrochloride was rapid, even at  $-78^{\circ}$ . *Triscarbethoxymethyl phosphite* (81% yield) had b. p. 125–126°/0.03 mm.,  $n_D^{20}$  1.4508,  $d_4^{20}$  1.214 (Found: C, 41.8; H, 6.1; P, 9.3. C<sub>12</sub>H<sub>21</sub>O<sub>9</sub>P requires C, 42.4; H, 6.2; P, 9.1%). *Tris-2-carbethoxyethyl phosphite* (78%) had b. p. 143–144°/0.02 mm.,  $n_D^{20}$  1.4506,  $d_4^{20}$  1.151 (Found: C, 46.7; H, 6.8; P, 8.5. C<sub>15</sub>H<sub>27</sub>O<sub>9</sub>P requires C, 47.1; H, 7.1; P, 8.1%). *Tris-1:2-dicarbethoxyethyl phosphite* (from ethylmalate) could not be distilled in pure condition owing to decomposition to ethyl fumarate, b. p. 97–98°/13 mm.,  $n_D^{20}$  1.4411, and hydrogen phosphite. The best distilled specimen had b. p. 170–180°/0.01 mm.,  $[\alpha]_D^{20}$   $-60.17^{\circ}$  (from R·OH,  $[\alpha]_D^{21}$   $-10.55^{\circ}$ ),  $d_4^{20}$  1.199 (Found: C, 47.2; H, 6.3; P, 6.05. C<sub>24</sub>H<sub>39</sub>O<sub>15</sub>P requires C, 48.2; H, 6.6; P, 5.2%).

*The Hydrogen Phosphites.*—Trichloride (1 mol.) was added dropwise to the hydroxy-ester (3 mol.) at  $-10^{\circ}$ , in a stream of nitrogen. At 18°/12 mm. (0.5 hr.) and then at 0.2 mm. (2 hr.), the temperature being gradually raised to 50°, volatile matter was removed and collected in a trap at  $-78^{\circ}$ . From the residue *biscarbethoxymethyl hydrogen phosphite* (11.3 g.), b. p. 112°/0.03 mm.,  $n_D^{20}$  1.4430,  $d_4^{20}$  1.255 (Found: C, 38.4; H, 6.0. C<sub>8</sub>H<sub>15</sub>O<sub>7</sub>P requires C, 37.8; H, 6.0%), and from the condensate ethyl chloroacetate (4.75 g.), b. p. 44–45°/14 mm.,  $n_D^{20}$  1.4213, were obtained from the glycollate (15.6 g.).

Similarly, ethyl  $\beta$ -hydroxypropionate (17.7 g.) afforded ethyl  $\beta$ -chloropropionate (5.55 g.), b. p. 64.5°/20 mm. (Found: Cl, 26.0. Calc. for C<sub>5</sub>H<sub>9</sub>O<sub>2</sub>Cl: Cl, 26.0%), and *bis-2-carbethoxyethyl hydrogen phosphite* (12.5 g.), b. p. 132–133°/0.05 mm.,  $n_D^{20}$  1.4456,  $d_4^{20}$  1.192 (Found: C, 42.7; H, 7.0. C<sub>10</sub>H<sub>19</sub>O<sub>7</sub>P requires C, 42.6; H, 6.8%). By the same procedure of isolation, the chloroacetate (1.7 g.) (Found: Cl, 29.0. Calc. for C<sub>4</sub>H<sub>7</sub>O<sub>2</sub>Cl: Cl, 28.9%) and the hydrogen phosphite (3.8 g.) (Found: P, 12.3. Calc. for C<sub>8</sub>H<sub>15</sub>O<sub>7</sub>P: P, 12.2%) were obtained after hydrogen chloride had been passed into the phosphite (5.8 g.) for 3.5 hr. at  $-10^{\circ}$ . The phosphite (6.5 g.) and hydrogen chloride (2 hr. at  $-10^{\circ}$ ) gave the  $\beta$ -chloropropionate (2.1 g.) and the hydrogen phosphite (4.55 g.) (Found: P, 11.1. Calc. for C<sub>10</sub>H<sub>19</sub>O<sub>7</sub>P: P, 11.0%).

Into the undistilled phosphite of ethyl malate (8.6 g.,  $\alpha_D^{23}$   $-86.12^{\circ}$ ,  $l = 1$ ) and ether (2 c.c.), hydrogen chloride was passed for 8 hr. at  $-10^{\circ}$ . Volatile matter was removed as before, and ethyl chlorosuccinate (2.0 g.), b. p. 59–60°/0.1 mm.,  $[\alpha]_D^{23}$   $+32.41^{\circ}$  (Found: Cl, 16.8. Calc. for C<sub>9</sub>H<sub>13</sub>O<sub>4</sub>Cl: Cl, 17.0%), and a residue (6.8 g. Calc.: 6.6 g.) (Found: P, 7.0. Calc. for C<sub>16</sub>H<sub>27</sub>O<sub>11</sub>P: P, 7.3%), were obtained.

*Addition of Hydroxy-ester to Phosphorus Trichloride.*—Ethyl glycollate (15.6 g., 1 mol.) was added dropwise to the trichloride (2 mol.) at  $-10^{\circ}$  in a stream of nitrogen. Volatile matter being removed at  $20^{\circ}/12$  mm., *carbethoxymethyl phosphorodichloridite* (19.1 g.), b. p.  $91-92^{\circ}/13$  mm.,  $n_D^{20}$  1.4750,  $d_4^{20}$  1.347 (Found: Cl, 34.3; P, 15.2.  $C_4H_7O_3Cl_2P$  requires Cl, 34.6; P, 15.1%), *biscarbethoxymethyl phosphorochloridite* (3.5 g.), b. p.  $117^{\circ}/0.2$  mm.,  $n_D^{20}$  1.4615,  $d_4^{20}$  1.262 (Found: Cl, 13.0; P, 11.7.  $C_8H_{14}O_6ClP$  requires Cl, 13.0; P, 11.4%), and residue (2.3 g.) (undistilled at  $180^{\circ}/0.05$  mm.) were obtained.

Similarly, ethyl  $\beta$ -hydroxypropionate (17.7 g.) gave *2-carbethoxyethyl phosphorodichloridite* (22.05 g.), b. p.  $58-59^{\circ}/0.2$  mm.,  $n_D^{20}$  1.4740,  $d_4^{20}$  1.294 (Found: Cl, 32.4; P, 14.3.  $C_5H_9O_3Cl_2P$  requires Cl, 32.4; P, 14.2%), a fraction (3.45 g., mainly hydrogen phosphite), b. p.  $132-133^{\circ}/0.1$  mm. (Found: Cl, 1.9%), and a residue (2.1 g.).

Ethyl malate ( $[\alpha]_D^{20} + 10.45^{\circ}$ , 24.6 g.) gave *1:2-dicarbethoxyethyl phosphorodichloridite* (22.6 g.), b. p.  $92-93^{\circ}/0.2$  mm.,  $[\alpha]_D^{20} + 84.61^{\circ}$ ,  $n_D^{20}$  1.4719,  $d_4^{20}$  1.286 (Found: Cl, 24.3; P, 10.7.  $C_8H_{13}O_5Cl_2P$  requires Cl, 24.4; P, 10.6%), and a residue (9.9 g.) which decomposed at  $160^{\circ}$ .

*Other Reactions.*—In the proportion required for the reaction  $2P(OR)_3 + PCl_3 = 3PCl(OR)_2$ , the trichloride (2.34 g., 1 mol.) and triscarbethoxymethyl phosphite (11.55 g., 2 mol.) were heated at  $90-100^{\circ}$  for 2.5 hr. The dichloridite (1.9 g.), b. p.  $72-73^{\circ}/3$  mm., the chloridite (7.2 g.), b. p.  $112-113^{\circ}/0.15$  mm. (Found: Cl, 12.7. Calc. for  $C_8H_{14}O_6ClP$ : Cl, 13.0%), the phosphite (1.6 g.), b. p.  $146^{\circ}/0.15$  mm.,  $n_D^{20}$  1.4511, and a residue (2.4 g.) which decomposed at  $205^{\circ}$  were obtained. With the reagents in the proportion trichloride (2 mol.) and phosphite (18.7 g., 1 mol.), the mixture being at  $55-60^{\circ}$  for 3 hr., the dichloridite (10.65 g.), b. p.  $73-74^{\circ}/3$  mm. (Found: Cl, 34.4%), the chloridite (9.65 g.), b. p.  $101-103^{\circ}/0.07$  mm. (Found: Cl, 13.0%), unchanged phosphite (1.4 g.), b. p.  $141^{\circ}/0.1$  mm., and a residue (2.05 g.) were obtained. The dichloridite (3.76 g., 1 mol.) and the phosphite (6.25 g., 1 mol.) were heated at  $90-100^{\circ}$  for 3 hr.; the dichloridite (1.8 g.), the chloridite (4.35 g.), b. p.  $102-103^{\circ}/0.07$  mm., and a third fraction (2.7 g.), b. p.  $114-122^{\circ}/0.05$  mm., were obtained.

Tris-2-carbethoxyethyl phosphite (14.4 g., 2 mol.) and trichloride (2.6 g., 1 mol.) after being at  $70^{\circ}$  for 3 hr. gave the phosphorodichloridite (3.5 g.), b. p.  $58-59^{\circ}/0.2$  mm., the *phosphorochloridite* (3.75 g.), b. p.  $107-108^{\circ}/0.04$  mm.,  $n_D^{20}$  1.4601,  $d_4^{20}$  1.198 (Found: Cl, 11.7; P, 10.7.  $C_{10}H_{18}O_8ClP$  requires Cl, 11.8; P, 10.3%), a third fraction (1.15 g.), b. p.  $114-137^{\circ}/0.07$  mm., a mixture of phosphite and hydrogen phosphite (2.45 g.), b. p.  $138-145^{\circ}/0.1$  mm.,  $n_D^{20}$  1.4472, and a residue (4 g.) which decomposed at  $205^{\circ}$ . Reaction between the phosphite and dichloridite occurred; but apart from recovery (50%) of the latter, material of a wide distillation range was obtained.

Crude tris-1:2-dicarbethoxyethyl phosphite ( $\alpha_D^{25} - 86.12^{\circ}$ ,  $l = 1$ ) (9.3 g., 1 mol.) and trichloride (2 mol.), after being at  $55-60^{\circ}$  for 3.5 hr., gave the dichloridite (4.1 g.), b. p.  $92-93^{\circ}/0.2$  mm.,  $[\alpha]_D^{20} - 82.81^{\circ}$  (Found: Cl, 24.0%), and a residue (6.4 g.) (Found: Cl, 5.9%).

To prepare the chloridite, a mixture of ethyl glycollate (3.47 g., 1 mol.) and pyridine (1 mol.) in ether (20 c.c.) was added dropwise with vigorous shaking to the dichloridite (6.83 g., 1 mol.) in ether (20 c.c.) at  $-10^{\circ}$ . The base hydrochloride (100%) was precipitated, and from the filtrate dichloridite (0.95 g.), chloridite (5.05 g., 55%) (Found: Cl, 12.7%), the phosphite (1.5 g.), b. p.  $143^{\circ}/0.1$  mm.,  $n_D^{20}$  1.4510, and a residue (1.2 g.) were obtained. The chloridite (8.88 g., 1 mol.) with ethyl glycollate (1 mol.) and pyridine (1 mol.) in ether gave immediately at  $-10^{\circ}$  the base hydrochloride (100%) and the phosphite (90%), b. p.  $125-126^{\circ}/0.03$  mm.,  $n_D^{20}$  1.4512.

Similarly, ethyl  $\beta$ -hydroxypropionate (6.35 g., 1 mol.), pyridine (1 mol.), and the dichloridite (1 mol.) gave base hydrochloride (98%), dichloridite (2.75 g.), the chloridite (3.95 g.), b. p.  $103-104^{\circ}/0.03$  mm (Found: Cl, 11.8%), a mixture of phosphite and hydrogen phosphite (2.8 g.), b. p.  $137-149^{\circ}/0.05$  mm., and a residue (2.1 g.).

Similarly, ethyl malate (7.1 g., 1 mol.), base (1 mol.), and dichloridite (1 mol.) gave hydrochloride (100%), the dichloridite (2.7 g.), b. p.  $72-74^{\circ}/0.05$  mm., and a residue (12.15 g.) which decomposed at  $160^{\circ}$ , but which with ethyl malate (2.49 g.) and base (1.04 g.) gave the hydrochloride (98%) and a mixture (12.6 g.) of phosphite and hydrogen phosphite, b. p.  $170-180^{\circ}/0.01$  mm.

Messrs. C. Baggally and B. K. Howe carried out exploratory and check experiments.