270. *The Interaction of* n-*Butyl Alcohol and the Chlorides and Oxychloride of Phosphorus in the Absence and in the Presence of Pyridine.*

By WILLIAM GERRARD.

In continuation of recent work (this vol., p. 218), it is now shown that the production of *n*-butyl chloride by reaction of the alcohol with the chlorides and oxychloride of phosphorus in absence of pyridine is due to the interaction of hydrogen chloride and *n*-butyl-phosphorous or -phosphoric esters produced, and not to spontaneous decomposition of the *n*-butyl chlorophosphites and chlorophosphates. Pyridine inhibits this action of hydrogen chloride and facilitates the formation of the tri-*n*-butyl esters, which by the action of excess of the phosphorus reagent are converted into the corresponding chloro-esters. The chlorophosphites $PCl(OBu)_2$ and $PCl_2{\cdot}OBu$ do not react with pyridine at temperatures up to 100°, whereas *n*-butoxyphosphoryl dichloride reacts below 0° and the monochloride at 100°, giving rise to *n*-butyl chloride and phosphorus–pyridine compounds.

THE formation of optically active α-chloroethylbenzene by the interaction of *l*-phenylmethylcarbinol and phosphorus trichloride in the absence (McKenzie and Clough, J., 1913, **103**, 687) and in the presence of pyridine (Kenyon, Phillips, and Taylor, J., 1931, 382) has been assumed by the latter investigators to take place by the formation and decomposition of an intermediate chlorophosphite, $PCl_2{\cdot}OR$ or $PCl(OR)C_5H_5NCl$. The corresponding chlorophosphates, $POCl_2{\cdot}OR$, $POCl(OR)C_5H_5NCl$, and the chlorophosphites and chlorophosphates of ethyl *l*-mandelate (Kenyon, Lipscomb, and Phillips, J., 1931, 2275) are also assumed to be intermediates in the formation of the chloride, RCl. The only evidence submitted in support of this view is based on analogy.

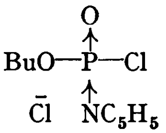
Kenyon, Phillips, and Taylor (*loc. cit.*) found that pyridine used in conjunction with the chlorides and oxychloride of phosphorus gave a greater yield of the desired chloride, RCl, and Wagner-Jauregg (*Helv. Chim. Acta*, 1929, **12**, 61) obtained a similar result with methyl *dl*-mandelate, and Boyd and Ladhams (J., 1928, 215) considered pyridine to be a necessary factor in the formation of the diaryloxy*iso*propyl chlorides by the agency of phosphorus oxychloride. On the other hand, Houssa and Phillips (J., 1932, 108) found that pyridine almost completely inhibited the formation of β-chloro-octane by the agency of the trichloride and the oxychloride of phosphorus. It is therefore desirable to preface experiments on optically active material by an examination of the action of these reagents upon *n*-butyl alcohol.

Milobendzki and Sachnowski (*Chem. Polski*, 1917, **15**, 34) realised the reactions $P(OBu)_3 + HCl \longrightarrow P(OBu)_2{\cdot}OH + BuCl$ and $P(OBu)_2{\cdot}OH + HCl \longrightarrow P(OH)_2{\cdot}OBu + BuCl$, and it is now shown that addition of phosphorus trichloride to *n*-butyl alcohol in the cold, with removal of as much hydrogen chloride as possible by a stream of carbon dioxide, resulted in the formation mainly of di-*n*-butyl hydrogen phosphite and some *n*-butyl chloride, whereas agitation by a current of hydrogen chloride diminished the yield of the former and increased that of the latter. Addition of the alcohol to excess of phosphorus trichloride yielded chiefly *n*-butoxyphosphorus dichloride and other phosphorus compounds, but little butyl chloride. The general effect of increasing the proportion of alcohol was to decrease the total amount of alkyl phosphorus compounds and modify their relative proportions. This result is in accordance with that of Walker and Johnson (J., 1905, **87**, 1592), who found that " when only one mol. of alcohol (Me, Et, Pr) was added to phosphorus trichloride, scarcely any alkyl chloride was produced." They showed that addition of a second mol. of alcohol yielded 1·1, 0·87, and 0·75 mols. respectively of the alkyl chloride, and for 3 mols. of alcohol the respective values were 1·5, 1·0, and 1·6 mols.

Further, it is concluded that the production of *n*-butyl chloride by means of phosphorus trichloride is essentially due to the interaction of hydrogen chloride with tri-*n*-butyl phosphite or di-*n*-butyl hydrogen phosphite, at least below 150°, and not to the decomposition of the chlorophosphites $PCl(OBu)_2$ and $PCl_2{\cdot}OBu$. These chloro-esters were obtained by the addition of the correct amounts of phosphorus trichloride to tri-*n*-butyl phosphite. The interaction of the alcohol and phosphorus oxychloride may be similarly explained.

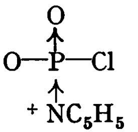
Addition of an ethereal solution of phosphorus trichloride (1 mol.) to an ethereal solution of the alcohol (3 mols.) and pyridine (3 mols.) at − 10° resulted in the immediate precipitation of pyridine hydrochloride and the quantitative occurrence of the reactions $PCl_3 + 3BuOH + 3C_5H_5N \longrightarrow P(OBu)_3 + 3C_5H_5N,HCl$, a similar result being obtained by reversing the order of addition. Further addition of the trichloride to such a reaction mixture most probably produced the chlorophosphites as mentioned above; but no butyl chloride was isolated when the product was heated with or without the addition of more pyridine. Pyridine or its hydrochloride did not produce *n*-butyl chloride from the chlorophosphites at temperatures up to 100°.

With phosphorus oxychloride the reaction $POCl_3 + 3BuOH + 3C_5H_5N \longrightarrow PO(OBu)_3 + 3C_5H_5N,HCl$ occurred; but further addition of the oxychloride, followed by heating in the presence of pyridine or its hydrochloride, gave rise to some *n*-butyl chloride, a result explained by observations on the chlorophosphates themselves. n-*Butoxyphosphoryl dichloride* reacted readily with pyridine at 0°, vigorously above this temperature, forming *n*-butyl chloride and a solid mixture of pyridine–phosphorus compounds possibly of the types (I)—(IV), whereas *di*-n-*butoxyphosphoryl chloride* reacted rapidly with pyridine at



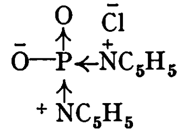
$\mathrm{BuO{-}\overset{\overset{O}{\uparrow}}{\underset{\underset{NC_5H_5}{\uparrow}}{P}}{-}Cl}\quad \bar{\mathrm{Cl}}$

(I.)



$\mathrm{O{-}\overset{\overset{O}{\uparrow}}{\underset{\underset{{}^{+}NC_5H_5}{\uparrow}}{P}}{-}Cl}$

(II.)



$\mathrm{\bar{O}{-}\overset{\overset{O}{\uparrow}}{\underset{\underset{{}^{+}NC_5H_5}{\uparrow}}{P}}{\leftarrow}\overset{+}{N}C_5H_5}\quad \bar{\mathrm{Cl}}$

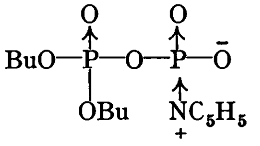
(III.)

$C_5H_5N(Bu){\cdot}OPCl_2$

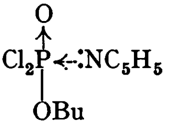
(IV.)

100°, producing a theoretical yield of *n*-butyl chloride and a water-soluble *gum*, possibly (V). This difference in behaviour between the chlorophosphites and chlorophosphates would appear to be due to co-ordinately linked oxygen (VI).

(V.)



$\mathrm{BuO{-}\overset{\overset{O}{\uparrow}}{\underset{\underset{OBu}{|}}{P}}{-}O{-}\overset{\overset{O}{\uparrow}}{\underset{\underset{\overset{}{N}C_5H_5\,{}^{+}}{\uparrow}}{P}}{-}\bar{O}}$



$\mathrm{Cl_2\overset{\overset{O}{\uparrow}}{\underset{\underset{OBu}{|}}{P}}{\leftarrow}{:}NC_5H_5}$

(VI.)

n-Butoxyphosphoryl dichloride when refluxed with pyridine hydrochloride at 100° yielded *n*-butyl chloride and a crystalline mixture of unchanged pyridine hydrochloride and $C_5H_5N,P(OH)OCl_2$; and di-*n*-butoxyphosphoryl chloride behaved similarly.

Phosphites and phosphates were produced by the addition of the appropriate chloroester to an ethereal solution of alcohol and pyridine :

$$PCl_2{\cdot}OBu + 2BuOH + 2C_5H_5N \longrightarrow P(OBu)_3 + 2C_5H_5N,HCl$$
$$POCl_2{\cdot}OBu + 2EtOH + 2C_5H_5N \longrightarrow PO(OEt)(OBu)_2 + 2C_5H_5N,HCl.$$

EXPERIMENTAL.

The weights of residues (which decomposed when attempts were made to continue the distillation) are given to account for as much of the total mass as possible. In certain experiments the residue represents part of the mass which could not have been *n*-butyl chloride. The composition of some of the less important fractions is given as probable because the production of fractions approaching constant composition was very slow, owing to the nearness of b. p. and/or incipient interaction of the constituents. The probable composition is based on analytical tests.

Interaction of n-*Butyl Alcohol and Phosphorus Trichloride.*—*Expt.* 1. The alcohol (37 g., 1 mol.) was added dropwise to the trichloride (100 g., 1·5 mols.), agitated by a stream of dry carbon dioxide and kept at − 10°. After being at 16° for 1 hour, the mixture was kept under reduced pressure (water-pump) for 2 hours, and then on distillation it yielded *n*-butoxyphosphorus dichloride (63 g., 71%), b. p. 56°/14 mm., $d_{4^\circ}^{16^\circ}$ 1·1801 (Found : Cl, 40·7. Calc. for

$PCl_2 \cdot OC_4H_9$: Cl, 40·6%), impure di-*n*-butoxyphosphorus chloride, b. p. 90—116°/14 mm. (8 g.), and dibutyl hydrogen phosphite (3 g.), b. p. 122—125°/14 mm.

Expt. 2. The alcohol (37 g., 1 mol.), added to the trichloride (44·7 g., 0·65 mol.) as in Expt. 1, gave a colourless product, difficult to fractionate, from which *n*-butoxyphosphorus dichloride (21·4 g.), b. p. 58—61°/15 mm. (Found : Cl, 40·2%), a fraction of b. p. 90—113°/14 mm. (12·3 g.), dibutyl hydrogen phosphite (4·5 g.), b. p. 120—125°/13 mm., and a residue (3·1 g.) were obtained. Fractionation of the middle fraction was unsatisfactory, but half of it distilled between 90° and 110°/13 mm. and was impure *di-*n*-butoxyphosphorus chloride* (Found : Cl, 16·0; P, 15·5. $C_8H_{18}O_2ClP$ requires Cl, 16·7; P, 14·6%) (see below).

Expt. 3. The alcohol (37 g., 1 mol.) added to the trichloride (34·4 g., 0·5 mol.) gave the same products in different proportions, 10 g., 9·2 g., 20 g., and 2·1 g.

Expt. 4. When the trichloride (23 g., 1 mol.) was added to the alcohol (37 g., 3 mols.), agitated by carbon dioxide, *n*-butyl chloride (10 g.), b. p. 77·5°, di-*n*-butyl hydrogen phosphite (28 g.), b. p. 126—127°/18 mm., $d_{4^\circ}^{13^\circ}$ 0·9916, $n_D^{16^\circ}$ 1·4270 (Found : P, 16·1. Calc. for $C_8H_{19}O_3P$: P, 16·0%), and a residue (5 g.) were obtained.

Expt. 5. The trichloride (9·2 g., 1 mol.), added to the alcohol (14·8 g., 3 mols.) agitated by dry hydrogen chloride, yielded *n*-butyl chloride (7·8 g.), b. p. 77·5°, $d_{4^\circ}^{18^\circ}$ 0·8874, di-*n*-butyl hydrogen phosphite (7·5 g.), b. p. 122°/13 mm., $d_{4^\circ}^{19^\circ}$ 0·9852 (Found : P, 16·1. Calc. : P, 16·0%), and residue (4·4 g.) having the properties of the dihydrogen phosphite.

Interaction of n-*Butyl Phosphite and Phosphorus Trichloride.—Expt.* 1. The trichloride (13·8 g., 2 mols.) was added to the phosphite (12·5 g., 1 mol.) at room temperature. The colourless product was then heated at 50° for 1 hour and distilled. *n*-Butoxyphosphorus dichloride (21 g., 80%), b. p. 56°/14 mm. (Found : Cl, 40·6%), and a residue (3·5 g.) were obtained.

Expt. 2. Addition of the trichloride (7 g., 1 mol.) to the phosphite (25 g., 2 mols.), followed by standing at room temperature for 48 hrs., gave a colourless product which yielded : F.1 (7·0 g.), b. p. 60—95°/16 mm.; F.2 (14·9 g.), b. p. 95—106°/16 mm.; F.3 (3·3 g.), b. p. 106—112°/16 mm., and a residue (3·1 g.), oil-bath at 170°. F.2 yielded di-*n*-butoxyphosphorus monochloride (14·1 g.), b. p. 99—102°/12 mm. (Found : Cl, 16·7; P, 14·9. Calc. for $C_8H_{18}O_2ClP$: Cl, 16·7; P, 14·6%). F.1 was mainly the dichloride, and F.3 appeared to be a mixture of the monochloride and phosphite. Increasing the proportion of the trichloride resulted in an increase in F.1 and a corresponding decrease in F.2 and F.3.

n-*Butyl Alcohol and Phosphorus Oxychloride.*—The alcohol (20 g., 1 mol.) was added dropwise to the oxychloride (60 g., 1·45 mols.), agitated by dry carbon dioxide at − 5°. The colourless product, after standing overnight at room temperature, yielded n-*butoxyphosphoryl dichloride*, $C_4H_9O \cdot POCl_2$ (41 g., 80%), b. p. 90°/17 mm., 85°/13 mm., $d_{4^\circ}^{11^\circ}$ 1·2711, $d_{4^\circ}^{25^\circ}$ 1·2560, $n_D^{11^\circ}$ 1·4453 (Found : Cl, 36·2. $C_4H_9O_2Cl_2P$ requires Cl, 36·3%), and a residue (8·3 g.).

The product obtained by heating on a steam-bath for 1 hour a mixture of tri-*n*-butyl phosphate (5·32 g., 1 mol.) and phosphorus oxychloride (6·2 g., 2 mols.) gave *n*-butoxyphosphoryl dichloride (2 g.) and a residue (decomp. 150°). The phosphate (5·3 g., 1 mol.) and oxychloride (1·53 g., 1 mol.) gave 2 g. of impure *di-*n*-butoxyphosphoryl chloride*, b. p. 126—135°/16 mm. (Found : Cl, 15·9. $C_8H_{18}O_3ClP$ requires Cl, 15·5%) (see below). The passage for 2 hrs. of dry hydrogen chloride into tri-*n*-butyl phosphate (26·6 g.) at room temperature, followed by distillation, gave a liquid, b. p. 60—90°, from which, by treatment with water, *n*-butyl chloride (8·3 g.), b. p. 77·5°, $d_{4^\circ}^{20^\circ}$ 0·8854, was obtained.

*Di-*n*-butoxyphosphoryl Chloride.*—A slow stream of dry chlorine was passed into tri-*n*-butyl phosphite (17·8 g.) at − 10° until the correct increase in weight had occurred for the reaction $P(OBu)_3 + Cl_2 \longrightarrow BuCl + POCl(OBu)_2$. The chloride (14·1 g., 86%), b. p. 132—133°/15 mm., $d_{4^\circ}^{14^\circ}$ 1·0822, $d_{4^\circ}^{30^\circ}$ 1·0680, $n_D^{15^\circ}$ 1·4335 (Found : Cl, 15·6. Calc. : Cl, 15·5%), and a residue (1·8 g.) were obtained. By distilling the primary product first at ordinary pressure, *n*-butyl chloride (4·8 g.), b. p. 77—78°, $d_{4^\circ}^{23^\circ}$ 0·8829, was also obtained.

Use of Pyridine in the Preparation of Phosphites and Phosphates.—Procedure. An ethereal solution of the appropriate chloride was added slowly to an ethereal solution of the alcohol and pyridine at − 10°, the mixture being well shaken. (Dry ether was used throughout.) Precipitation of pyridine hydrochloride commenced immediately. The final mixture was rapidly filtered off, and the hydrochloride washed with ether, put in a vacuum for 2 hrs., weighed, and analysed without further treatment. Yields were practically theoretical, the chlorine content varied from 29·9 to 30·5% (Calc. : Cl, 30·7%), and steam-distillation yielded the appropriate amount of pyridine (Found, for one specimen : C_5H_5N, 68·2. Calc. : 68·4%).

*Tri-*n*-butyl phosphite.* Phosphorus trichloride (45·8 g., 1 mol.), *n*-butyl alcohol (74 g., 3 mols.), and pyridine (79 g., 3 mols.) produced this phosphite (75·5 g., 91%), b. p. 122°/12 mm.,

$d_{4°}^{20°}$ 0·9259 (Found: P, 12·6. Calc. for $C_{12}H_{27}O_3P$: P, 12·4%), and a residue (6 g.). Addition of the alcohol and pyridine to the trichloride gave a similar result.

*Tri-*n*-butyl phosphate.* Phosphorus oxychloride (51·2 g., 1 mol.) and the foregoing quantities of alcohol and pyridine afforded the phosphate (68 g., 79%), b. p. 154°/10 mm., $d_{4°}^{13°}$ 0·9824, $d_{4°}^{21°}$ 0·9761, $n_D^{11°}$ 1·4294 (Found: P, 11·63. Calc. for $C_{12}H_{27}O_4P$: P, 11·65%), and a residue (12 g.). The rate of precipitation of pyridine hydrochloride was slower than in the preceding experiment. The same phosphate (6·5 g., 90%) was produced when di-*n*-butoxyphosphoryl chloride (6·2 g., 1 mol.) was added to *n*-butyl alcohol (2·0 g., 1 mol.) and pyridine (2·15 g., 1 mol.) as described; precipitation of the hydrochloride (2·8 g.; Cl, 30·4%) was again slow.

Diethyl n*-butyl phosphate.* *n*-Butoxyphosphoryl dichloride (9·5 g., 1 mol.), added to ethyl alcohol (4·6 g., 2 mols.) and pyridine (7·9 g., 2 mols.), gave this *compound* (6·8 g.), b. p. 123°/15 mm., $d_{4°}^{13°}$ 1·0340 (Found: P, 15·0. $C_8H_{19}O_4P$ requires P, 14·8%), and a residue (2·1 g.).

Interaction of Pyridine and the Chloro-esters of Phosphoric and Phosphorous Acids.—Expt. 1. n*-Butoxyphosphorus dichloride.* Pyridine (4 g., 1 mol.) was added to the chloride (8·8 g., 1 mol.) at − 10°; there was no evolution of heat, and the liquid could be removed immediately from the cooling bath without becoming warm. A small amount of white solid separated. Addition of a further portion of pyridine (4 g.) at room temperature, followed by heating at 100° for 0·5 hr., produced no signs of reaction. The colourless supernatant liquid was then decanted from the solid (1·8 g.) and poured on ice, which was rapidly melted. Ether was added. The water contained 2·55 g. of chloride ion; but from the ethereal solution, no butyl chloride could be isolated. The solid (1·8 g.) dissolved rapidly in water with much heat evolution, gave 0·42 g. of chloride ion, and 2·0 g. of *n*-butylpyridinium ferrocyanide (Found: Fe, 10·9. Calc.: Fe, 10·7%). Hence of the 3·55 g. of chlorine in the system, 2·97 g. were estimated as the ion.

Expt. 2. The chloride (8·8 g.) and pyridine (4 g.), mixed as described, after 4 days at room temperature deposited about 2 g. of white solid. Ether was added, and the colourless ethereal solution was poured into an ethereal solution of *n*-butyl alcohol (7·4 g., 2 mols.) and pyridine (4 g., 1 mol.) at − 5°. Pyridine hydrochloride (9·8 g.; calc. from pyridine used, 12·4 g.) was precipitated, and from the ethereal filtrate, tri-*n*-butyl phosphite (9·8 g.), b. p. 125°/16 mm., $d_{4°}^{14°}$ 0·9324, $d_{4°}^{23°}$ 0·9247, $n_D^{16°}$ 1·4339, was obtained.

Expt. 3. *Di-*n*-butoxyphosphorus chloride.* The chloride (2·13 g., 1 mol.) was added to pyridine (1·58 g., 2 mols.) at − 5°; a slight precipitate (0·033 g. of Cl) was formed, and but little heat was developed. After 1·5 hrs. at room temperature, the liquid was decanted, and heated at 100—102° for 0·5 hr. The colourless liquid was added to *n*-butyl alcohol (0·74 g., 1 mol.) in ether at − 10°; pyridine hydrochloride (0·9 g.) was precipitated. Hence, no butyl chloride could have been formed.

Expt. 4. n*-Butoxyphosphoryl dichloride.* This chloride (19·1 g., 1 mol.) was added rapidly to pyridine (15·8 g., 2 mols.) at − 10°; no precipitate was formed, but when, 30 mins. later, the temperature had risen to 0°, a white crystalline solid began to form rapidly. At 3°, 5 mins. later, the mass was nearly solid. It was crushed under dry ether (50 c.c.), and the liquid filtered and placed in a vacuum for 1 hr.; the resulting pasty solid weighed 21·0 g. The aqueous extract of the ethereal solution contained no chloride ion, but yielded on steam-distillation 4·55 g. of pyridine. From the ethereal solution, *n*-butyl chloride (2·9 g.), b. p. 77°, $d_{4°}^{20°}$ 0·8840, was obtained. The solid dissolved completely in water, evolving much heat and giving a colourless solution. Steam-distillation from sodium hydroxide solution gave pyridine (Found: C_5H_5N, 40·0%), and left a black oil, which solidified on cooling. Estimation of phosphorus in the primary aqueous solution gave P, 10·9%; after refluxing with concentrated hydrochloric acid, P, 14·2%.

Expt. 5. The reaction mixture produced at 0° as in Expt. 4 was heated at 100° for 45 mins. There were two liquid layers, a colourless upper one which refluxed, and a yellow lower one which contained a white solid. The liquid layers were decanted from the solid (S.1); the lower layer became solid (S.2) on being cooled. Ether was added to both, decanted, and extracted with water; this extract contained no chloride ion, but yielded 2·56 g. of pyridine, and from the ethereal solution *n*-butyl chloride (2·5 g.), b. p. 77°, $d_{4°}^{20°}$ 0·8847, was obtained. After being in a vacuum for 1 hour, the solids weighed (S.1) 5·9 g. (Found: C_5H_5N, 41·6; Cl, 18·8; P, 14·8%, after hydrolysis with hydrochloric acid); (S.2) 18·0 g. (Found: C_5H_5N, 38·0; Cl, 18·7; P, 12·7%). The primary solid (S.1 + S.2) softened at 75°, was completely molten at 110°, showed no sign of decomposition at 130°, and on cooling dissolved completely in water.

Expt. 6. Repetition of Expt. 4, but with addition of water to the primary product, led to isolation of *n*-butyl chloride (2·6 g.), b. p. 77°, $d_{4°}^{30°}$ 0·8845.

Expt. 7. The mixing was effected as in Expt. 4, but the clear reaction mixture was immediately removed from the cooling bath, whereupon in 3 mins. heat began to develop rapidly, and a vigorous reaction occurred lasting for 1 min. A colourless liquid refluxed, and a white solid separated. The results were essentially the same as for Expt. 4.

Expt. 8. *Di-*n*-butoxyphosphoryl chloride.* The chloride (11·5 g., 1 mol.), and pyridine (7·9 g., 2 mols.) at − 10° afforded a mixture which showed no sign of reaction even after 45 mins. at room temperature. On being slowly heated, the liquid remained clear and colourless until, at 100° (30 mins.), two layers were rapidly formed. After being at 100—105° for 10 mins., the mixture was cooled. The aqueous extract of the colourless supernatant liquid, decanted from the thick gum, contained no chloride ion, 5·1 g. of pyridine, and 0·28 g. of phosphorus as phosphate. *n*-Butyl chloride (4·1 g.), b. p. 76—77°, $d_{4°}^{20°}$ 0·8845, and a residue (2 g.) were obtained from the extracted liquid. The *gum* (4·4 g.) [Found: Cl, a trace; P, after hydrolysis, 17·7; C_5H_5N, 23·3. $C_5H_5N,P_2O_4(OC_4H_9)_2$ requires P, 17·7; C_5H_5N, 22·6%] dissolved slowly in water with but little heat effect. During the steam-distillation of the pyridine, a black non-volatile oil was formed. The aqueous solution gave only a slight precipitate with magnesia mixture, but gave a copious one after being refluxed with concentrated hydrochloric acid.

Pyridine Hydrochloride and the Chloro-esters.—*n*-Butoxyphosphorus dichloride (8·8 g., 1 mol.) and pyridine hydrochloride (5·3 g., 1 mol.) did not react at room temperature, but after 1·5 hrs. on a steam-bath the hydrochloride formed a paste (with an orange tint owing to the usual trace of impurity), which set to a hard mass on being cooled. The product was crushed under ether, and the ethereal solution decanted from the solid (S) into an ethereal solution of *n*-butyl alcohol (7·4 g., 2 mols.) and pyridine (7·9 g., 2 mols.) at − 5°; there were isolated pyridine hydrochloride (10·2 g.) and tri-*n*-butyl phosphite (10·9 g.), b. p. 127—128°/18 mm., $d_{4°}^{20°}$ 0·9266, $n_D^{19°}$ 1·4321. The solid (S) weighed 5·5 g. (Found: Cl, 30·4%).

n-Butoxyphosphoryl dichloride (11·0 g.) and pyridine hydrochloride (9·5 g.) gave two liquid layers at 100°, and butyl chloride refluxed. After 2 hrs. at this temperature, and cooling, the product consisted of a hard white crystalline mass and a colourless liquid. The latter was decanted, and the solid was crushed under ether which was then decanted and added to the liquid. The solid, after being in a vacuum for 2 hrs., weighed 14·4 g. (Found: Cl, 29·4; P, 10·6; C_5H_5N, 43·0%) and appeared to be a mixture of $C_5H_5N,POCl_2(OH)$ (73·6%) and pyridine hydrochloride (26·4%). An aqueous extract of the ethereal solution contained 0·0469 g. of chloride ion; whereas from the ether, *n*-butyl chloride (2·3 g.), b. p. 77°, was obtained.

*Tri-*n*-butyl Phosphate and Phosphorus Oxychloride.*—The oxychloride (7·7 g., 1 mol.) was added to the phosphate (26·6 g., 2 mols.) at 16°, and the mixture kept at 16° for 48 hrs. 11·4 G. of the product [1 mol. calc. as $POCl(OBu)_2$] were added to an ethereal solution of ethyl alcohol (2·3 g., 1 mol.) and pyridine (3·95 g., 1 mol.); there resulted pyridine hydrochloride (4·9 g.) and chiefly a mixture of ethyl dibutyl and diethyl butyl phosphates, b. p. 130—145° (Found: P, 14·0%).

A second portion of 11·4 g. was added to pyridine (7·9 g., 2 mols.) at − 5°, and the clear supernatant liquid, decanted from the primary white precipitate, separated into two layers precisely at 100—101°. The upper layer gave, on treatment with water, only a trace of chloride ion, but 2·1 g. of *n*-butyl chloride. The lower layer, a gum, dissolved slowly but completely in water and gave only a trace of chloride ion.

A third portion of 11·4 g., heated with pyridine hydrochloride (5·8 g.) for 2 hrs. at 100—105°, yielded 3·5 g. of *n*-butyl chloride, b. p. 77°.

A mixture of the phosphate (26·6 g., 1 mol.) and the oxychloride (30·7 g., 2 mols.) was kept for 48 hrs. at 16°, and two portions, each of 19·1 g. (1 mol. calc. as $POCl_2{\cdot}OBu$), were treated as follows. One was added to an ethereal solution of ethyl alcohol (9·2 g., 2 mols.) and pyridine (15·8 g., 2 mols.), yielding pyridine hydrochloride (22·5 g.) and chiefly a mixture of diethyl butyl and triethyl phosphates (Found: P, 16·2%). The second, mixed with pyridine (15·8 g.) at − 5°, behaved as did *n*-butoxyphosphoryl dichloride. These mixed phosphates were not purified further because fractionation was extremely slow. These experiments serve to show that the oxychloride and tri-*n*-butyl phosphate do not yield butyl chloride at room temperature, but give a mixture of unchanged reagents and a proportion of chloro-esters depending upon the ratio of the amounts of reagents.

Action of Heat on the Chloro-esters.—*n*-Butoxyphosphorus dichloride (14·0 g.) was heated at 180—200° for 1 hr. (cf. Menschutkin, *Annalen*, **1866**, **139**, 343), and the colourless product dissolved in ether and added to an ethereal solution of ethyl alcohol (7·4 g., 2 mols.) and pyridine (12·6 g., 2 mols.), whereupon pyridine hydrochloride (17·6 g. Calc.: 18·4 g.) was precipitated.

n-Butoxyphosphoryl dichloride (9 g.) decomposed vigorously at about 150°, giving 1·8 g. of a colourless distillate which was strongly acid and dissolved for the most part in water, giving chloride and phosphate ions. No butyl chloride could be isolated from the small amount of insoluble liquid. The residue in the distillation flask dissolved in water.

n-*Butyl Alcohol and Phosphorus Pentachloride in Presence of Pyridine.*—The finely powdered pentachloride (10·4 g., 1 mol.) was added slowly at 0° to *n*-butyl alcohol (15 g., 4 mols.) and pyridine (15·8 g., 4 mols.) in ether (20 c.c.). Reaction was very slow, so the mixture was boiled for 1 hr. and then filtered. The white precipitate (16 g.) was contaminated with pale yellow particles of the pentachloride (Found: Cl, 39·6; C_5H_5N, 50·0%, indicating PCl_5,30; C_5H_5N,HCl, 70%); from the ether, unchanged *n*-butyl alcohol (6 g.), *n*-butyl chloride (2 g.), pyridine, and *n*-butyl phosphate were obtained.

THE NORTHERN POLYTECHNIC, LONDON, N. 7.

[*Received, April 22nd,* 1940.]