

### 285. Interaction between Phosphorus Halides and Alkoxytrimethylsilanes.

By J. FERTIG, W. GERRARD, and H. HERBST.

Stepwise replacement of halogen in phosphorus trihalides has been effected by alkoxytrimethylsilanes, thus avoiding the presence of hydrogen halides or tertiary base. The 1-phenylethoxysilane afforded the dichloridite, but the *tert.*-butoxy-analogue gave only alkyl chloride. Replacement in the oxychloride proceeded to the dichloridate, and much more slowly to the chloridate, and there was evidence of formation of *n*-butyl phosphorodibromidate from the oxybromide. Fission of the alkoxy-silane occurred differently in the examples of the 1-phenylethyl and diphenylmethyl derivatives, the oxychloride affording alkyl chloride and trimethylsilyl phosphorodichloridate.

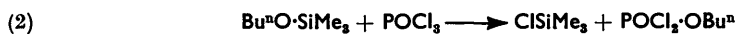
REPLACEMENT of halogen in phosphorus trihalides and oxyhalides by the alkoxy group has been effected by alkoxytrimethylsilane under conditions in which the presence of a tertiary base and a hydrogen halide is avoided. Certain limitations have been observed. Thus stepwise replacement of halogen in the trichloride by alkoxy was effected by *n*-butoxytrimethylsilane, giving the alkyl phosphorodichloridite, the dialkyl phosphorochloridite, and the trialkyl phosphite [scheme (1)]. *n*-, *iso*-, and *sec.*-Butyl phosphorodibromidites, and the corresponding bromidites were prepared from phosphorus tribromide. The halogeno-trimethylsilane formed concurrently was readily separated and used for the preparation of further supplies of the alkoxy-silane.



Even when the 1-carbon atom of the alkyl group is as reactive as that in 1-phenylethyl, the dichloridite is formed, although decomposition into alkyl chloride occurs slowly at 15° and more quickly on attempted distillation. However, *tert.*-butoxytrimethylsilane and phosphorus trichloride gave alkyl chloride without revealing even the transitory formation of a phosphorus ester; and diphenylmethoxytrimethylsilane behaved similarly.

Interaction of the alkoxy-silanes with phosphorus oxychloride presented a novel feature depending on the relative reactivity of the 1-carbon atom in the alkyl group. With *n*-butoxytrimethylsilane, the first alkoxy group was introduced smoothly [scheme (2)], but the second reaction (3) was very slow. The products from the 1-phenylethoxysilane

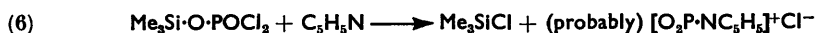
and diphenylmethoxysilane were alkyl chloride and trimethylsilyl phosphorodichloridate [reactions (4) and (5)], showing fission of the O-C rather than the O-Si bond. On the other



hand *tert.*-butoxytrimethylsilane did not react with phosphorus oxychloride even at 110°. Models show that steric hindrance is the likely cause.



An attempt to convert the trimethylsilyl phosphorodichloridate into the diethyl ester,  $\text{Me}_3\text{Si}\cdot\text{O}\cdot\text{PO}(\text{OEt})_2$  by means of pyridine and ethanol was abortive, because the dichloridate reacted more quickly with the base itself (this being reminiscent of the interaction of *n*-butyl phosphorodichloridate and pyridine<sup>1</sup>) and led to formation of ethoxytrimethylsilane (reaction 6).



Phosphorus oxybromide (1 mol.) with *n*-butoxytrimethylsilane (1 mol.) at 0° afforded bromotrimethylsilane and *n*-butyl phosphorodibromidate (apparently the first example of an alkyl phosphorodibromidate). It decomposed steadily at 15° and quickly on attempted distillation, *n*-butyl bromide being a product. With butan-1-ol (2 mols.) and pyridine (2 mols.) it afforded tri-*n*-butyl phosphate. Gerrard and Jeacocke<sup>2</sup> were unable to isolate the dibromidate on interaction of phosphorus oxybromide and tri-*n*-butyl phosphate, although there was indication of its formation by the interaction of the oxybromide and alcohol. The oxybromide (1 mol.) and the silane (3 mols.) gave tri-*n*-butyl phosphate.

The preparation of alkyl phosphorodibromidites and bromidites in phosphorus tri-bromide-alcohol systems has been described by Gerrard and Herbst.<sup>3</sup>

Although tertiary base is avoided at the alkoxylation stage, it still must be used in the preparation of the alkoxytrimethylsilane, for owing to intervention by hydrogen chloride and the volatility of chlorotrimethylsilane, reaction (7) has not yet been made to proceed to the right to a satisfactory extent.<sup>4</sup>



## EXPERIMENTAL

*Phosphorus Trichloride Systems.*—*n*-Butoxytrimethylsilane (14.6 g., 1 mol.) was added dropwise to phosphorus trichloride (13.75 g., 1 mol.) at -10°, and after the mixture had remained at 15° for 12 hr. chlorotrimethylsilane (97.2%), b. p. 58—60° (Found : Cl, 32.7%). Calc. for  $\text{C}_3\text{H}_9\text{ClSi}$  : Cl, 32.7%), and *n*-butyl phosphorodichloridite (88.6%), b. p. 68—70°/22 mm. (Found : Cl, 40.2; P, 17.6. Calc. for  $\text{C}_4\text{H}_9\text{OCl}_2\text{P}$  : Cl, 40.6; P, 17.7%), were obtained.

Similarly the silane (23.02 g., 2 mols. for 1 mol. of trichloride) afforded chlorotrimethylsilane (91.5%), b. p. 58—60° (Found : Cl, 32.3%) (withdrawn from the mixture at 20 mm. and trapped at -80°), *n*-butyl phosphorodichloridite (19.4%), b. p. 70—72°/22 mm. (Found : Cl, 40.4; P, 17.2%), di-*n*-butyl phosphorochloridite (27.3%), b. p. 96—104°/6 mm. (Found : Cl, 16.5; P, 14.4. Calc. for  $\text{C}_8\text{H}_{18}\text{O}_2\text{ClP}$  : Cl, 16.7; P, 14.6%), and tri-*n*-butyl phosphite (19.0%), b. p. 119—122°/12 mm. (Found : P, 12.6. Calc. for  $\text{C}_{12}\text{H}_{27}\text{O}_3\text{P}$  : P, 12.4%).

With the silane (14.6 g., 3 mols. for 1 mol. of trichloride) it was necessary to heat the mixture at 70° for 3 hr. to obtain a satisfactory replacement of the third chlorine atom. Separation of chloridite and phosphite was protracted. Besides the chlorotrimethylsilane, drawn off at

<sup>1</sup> Gerrard, *J.*, 1940, 1464.

<sup>2</sup> Gerrard and Jeacocke, *J.*, 1954, 3647.

<sup>3</sup> Gerrard and Herbst, *J.*, 1955, 277.

<sup>4</sup> Gerrard and Kilburn, *J.*, 1956, 1536.

15 mm., tri-*n*-butyl phosphite (74.6%), b. p. 78°/0.2 mm.,  $n_D^{20}$  1.4324,  $d_4^{25}$  0.9251 (Found: P, 12.8%), and a mixture of chloridite and phosphite (1.0 g.) were obtained.

After a mixture of tri-*n*-butyl phosphite (4.24 g., 1 mol.) and chlorotrimethylsilane (5.5 g., 3 mols.) had been heated at 90° (reflux) for 5 hr., the phosphite (3.9 g.), b. p. 76°/0.2 mm. (Found: P, 12.2%), and the chlorosilane (4.8 g.), b. p. 57° (Found: Cl, 32.1%), were recovered.

The butoxysilane (16.24 g., 1 mol.) was added to *n*-butyl phosphorodichloridite (19.46 g., 1 mol.) at -10°, and after the mixture had remained at 15° for 12 hr. chlorotrimethylsilane (96%), the dichloridite (3.7 g.) (Found: Cl, 40.2; P, 17.4%), the chloridite (7.45 g.) (Found: Cl, 16.8; P, 14.5%), and the phosphite (10.75 g.), b. p. 116—122°/9 mm. (Found: P, 12.6%), were isolated.

A mixture of the butoxysilane (14.6 g., 1 mol.) and the chloridite (21.3 g., 1 mol.) was heated at 65° for 5 hr. The chlorosilane (90.7%) and unchanged butoxysilane (1.1 g.), b. p. 115—120°, were removed at 20°/10 mm. (trap at -80°), and from the residue (24.85 g.) a mixture of chloridite and phosphite (2.5 g.), b. p. 103—118°/10 mm. (Found: Cl, 8.6%), and tributyl phosphite (20.55 g.), b. p. 120—122°/10 mm. (Found: P, 12.4%), were obtained.

By corresponding procedures *sec.*-butoxytrimethylsilane (14.6 g., 1 mol.) and phosphorus trichloride (13.75 g., 1 mol.) gave chlorosilane (97.2%), *sec.*-butyl phosphorodichloridite (79.4%), b. p. 61°/19 mm. (Found: Cl, 40.4; P, 17.5%), and a mixture (2.2 g.) of dichloridite and chloridite, b. p. 61—90°/19 mm. (Found: Cl, 29.0%).

When 3 mols. of silane (21.9 g.) were used for one of trichloride, chlorotrimethylsilane (66%) and unchanged silane (7 g.) were withdrawn at 20°/10 mm., and the residue afforded mixtures (total, 9.2 g.) of tributyl phosphite and chloridite, b. p. 98—112°/16 mm., which were very slowly separated into the constituents.

A mixture of *tert.*-butoxytrimethylsilane (7.30 g., 1 mol.) and trichloride (6.87 g., 1 mol.) was stored at 15° for 12 hr., and volatile matter was removed at 15°/15 mm. (trap at -80°). When a half of the material had evaporated, the remainder suddenly showed signs of decomposition, and there was a residue (1.5 g.) (Found: P, 36.6%). It was evident that the trap contents (12.61 g.) (Found: Cl, 40.4; P, 7.2%) comprised *tert.*-butyl chloride (4.2 g., 0.92 mol.), chlorosilane, and phosphorus trichloride, which would be extremely tedious to separate. By the addition of sufficient butan-1-ol and pyridine, pyridine hydrochloride (11.7 g., 1.96 mol.), containing the chlorine other than that in *tert.*-butyl chloride, was obtained, and from the filtrate tri-*n*-butyl phosphite (3.4 g.), b. p. 120°/10 mm. (Found: P, 13.0%), was isolated.

A mixture of trimethyl-1-phenylethoxysilane (9.7 g., 1 mol.) and trichloride (6.9 g., 1 mol.) was stored at 15° for 12 hr., and chlorotrimethylsilane (5.2 g., 96%), b. p. 57—61° (Found: Cl, 33.1%), was withdrawn at 25°/18 mm., leaving a residue (*A*) (vigorously shaken) which could not have contained phosphorus trichloride. To 4.0 g. of the residue, 1-phenylethanol (4.38 g.) and pyridine (2.38 g.) in ether were added at -10°, and base hydrochloride (3.9 g.) and a final residue (6.85 g., after being at 65°/0.2 mm. for 3 hr.) (Found: P, 8.0. Calc. for  $C_{24}H_{27}O_3P$ : P, 7.9%),  $n_D^{18}$  1.5450 (identified as tri-1-phenylethyl phosphite), were separated (see Gerrard and Shepherd <sup>5</sup>). This result indicates that residue (*A*) was 1-phenylethyl phosphorodichloridite, but after it (10.2 g.) had been stored for several hours at 18°, phosphorus trichloride (2.2 g.), b. p. 76° (Found: Cl, 76.7; P, 21.8. Calc. for  $Cl_3P$ : Cl, 77.45; P, 22.55%), was withdrawn at 18°/15 mm.; from the residue, 1-chloro-1-phenylethane, b. p. 42°/0.1 mm. (Found: Cl, 25.0. Calc. for  $C_8H_9Cl$ : Cl, 25.3%), was distilled.

A mixture of diphenylmethoxytrimethylsilane (15.9 g., 1 mol.) and trichloride (8.60 g., 1 mol.) afforded chlorotrimethylsilane (88.4%; withdrawn at 18°/12 mm., final pressure being reduced to 0.05 mm.) and a residue (*B*) (16.35 g.) of which 5.85 g. gave chlorodiphenylmethane (1.23 g.), b. p. 104°/0.1 mm. (Found: Cl, 17.7. Calc. for  $C_{13}H_{11}Cl$ : Cl, 17.5%), and a final residue (2.58 g.) (Found: Cl, 6.6; P, 13.1%). Addition of diphenylmethanol (13.56 g.) and pyridine (5.82 g.) (in ether) to the residue (*B*) (10.5 g.) gave no base hydrochloride, thus showing absence of dichloridite and chloridite.

*Phosphorus Oxychloride Systems.*—The *n*-butoxysilane (21 g., 1 mol.) and oxychloride (11.6 g., 0.5 mol.) gave (12 hr. at 20°) chlorotrimethylsilane and unchanged silane (removed at 20°/15 mm. and trapped at -80°), *n*-butyl phosphorodichloridate (9.0 g.), b. p. 38—42°/0.08 mm. (Found: Cl, 36.5; P, 16.9. Calc. for  $C_4H_9O_2Cl_2P$ : Cl, 37.2; P, 16.2%), and di-*n*-butyl phosphorochloridate (4.1 g.), b. p. 70—72°/0.08 mm. (Found: Cl, 15.7; P, 14.05. Calc. for  $C_8H_{18}O_3ClP$ : Cl, 15.5; P, 13.6%). The chlorosilane (1 mol.) and the chloridate

<sup>5</sup> Gerrard and Shepherd, *J.*, 1953, 2069.

(1 mol.) were mixed, but were quantitatively separated after being at 20° or 60° for several hours.

The *isobutoxysilane* (14.6 g., 1 mol.) and phosphorus oxychloride (0.5 mol.) gave the dichloridate (5.1 g.), b. p. 36°/0.1 mm. (Found: Cl, 36.0%), and the chloridate (2.4 g.), b. p. 74°/0.1 mm. (Found: Cl, 17.0; P, 14.4%). A mixture of the dichloridate (8.1 g., 1 mol.) and the alkoxytrimethylsilane (1 mol.) was heated at 120° for 5 hr., whereafter the dichloridate (5.1 g.) was recovered and the chloridate (3.5 g.), b. p. 74°/0.1 mm., was obtained. The *sec.-butoxysilane* (7.3 g., 1 mol.) and phosphorus oxychloride (7.7 g., 1 mol.) afforded the dichloridate (8.6 g., 90%), b. p. 46°/4 mm. (Found: Cl, 37.0; P, 16.4%), after the mixture had been heated at 75° for 6 hr. Chlorotrimethylsilane (94.5%), b. p. 58—62° (Found: Cl, 32.5%), was withdrawn at 20°/12 mm.

Diphenylmethoxytrimethylsilane (12.8 g., 1 mol.) and the oxychloride (7.7 g., 1 mol.) were mixed and heated at 100° for 4 hr., whereafter *trimethylsilyl phosphorodichloridate* (6.1 g., 59.4%), b. p. 40°/0.1 mm. (Found: Cl, 34.3; P, 14.8.  $C_3H_9O_2Cl_2PSi$  requires Cl, 34.3; P, 14.9%), and chlorodiphenylmethane (8.66 g., 85.3%), b. p. 96°/0.02 mm. (Found: Cl, 17.5%), were obtained.

The silyl phosphorodichloridate decomposes slowly at 15°, and to some extent on distillation. In the attempt to prepare the diethyl trimethylsilyl phosphate, the dichloridate (8.05 g., 1 mol.) was added to ethanol (3.6 g., 2 mols.) and pyridine (6.1 g., 2 mols.) in ether (30 c.c.) at -10°. The white solid (9.8 g.), which was formed immediately, contained phosphorus (Found: Cl, 25.2; P, 9.3;  $C_5H_5N$ , 59.6%); the residue (3.9 g.) from evaporation of the filtrate gave only ethoxytrimethylsilane (3.5 g.), b. p. 73—76°, and an undistillable residue containing phosphorus.

It was then shown that the dichloridate (3.45 g., 1 mol.) reacted immediately with pyridine (1.32 g., 1 mol.) at -15° and afforded chlorotrimethylsilane (1.4 g. 78.2%), b. p. 57—60° (Found: Cl, 32.3), and a solid (2.91 g.) (Found: Cl, 18.4; P, 18.9;  $C_5H_5N$ , 48.1%) containing all the phosphorus and pyridine and half of the chlorine in the system. A solid of similar composition was formed when pyridine (2 mol.) was added to the dichloridate (1 mol.).

Trimethyl-1-phenylethoxysilane also afforded the trimethylsilyl phosphorodichloridate and alkyl chloride.

*Phosphorus Tribromide Systems.*—The silane and tribromide (1 mol.) were mixed slowly at 15°, and after 6 hr. the bromotrimethylsilane (90—97%), b. p. 79—80° (Found: Br, 52.3 ± 0.3. Calc. for  $C_3H_9BrSi$ : Br, 52.3%), was withdrawn at 15°/5 mm. and condensed at -79°. Results are recorded in the Table. The bromidite was accompanied by dibromidite.

$Me_3Si \cdot OR$ R	Mols.	Yield (%)	B. p. (mm.)	$n_D^{20}$	Found: Br (%)	Calc.: Br (%)
Dibromidites $PBr_2 \cdot OR$						
Bu <sup>a</sup> .....	1	79	38° (0.01)	1.5445	60.3	60.6
Bu <sup>b</sup> .....	1	77	38 (0.1)	1.5410	60.7	—
Bu <sup>c</sup> .....	1	81	37 (0.01)	1.5389	63.3	—
$C_6H_{13} \cdot CHMe$ .....	1	51	76 (0.05)	1.5115	49.2	50.0
Bromidites $PBr(OR)_2$						
Bu <sup>a</sup> .....	2	68	54 (0.06)	1.4689	30.9	31.1
Bu <sup>b</sup> .....	2	66	44 (0.1)	1.4590	31.6	—
Bu <sup>c</sup> .....	2	69	41 (0.04)	1.4536	31.4	—

*n-Butoxytrimethylsilane and Phosphorus Oxybromide.*—The silane (6.6 g., 1 mol.) was added to the oxybromide<sup>a</sup> (13.0 g., 1 mol.) at -10°. Bromotrimethylsilane (5.9 g., 85.5%) was withdrawn at 15°/15 mm. and condensed at -80°, giving a residue (12.7 g.) of *n-butyl phosphorodibromidate* (Found: Br, 53.4; P, 10.9.  $C_4H_9O_2Br_2P$  requires Br, 57.2; P, 11.1%), which afforded *n*-butyl bromide on attempted distillation; this gave tri-*n*-butyl phosphate (5.7 g., 71.3%), b. p. 98°/0.1 mm. (Found: P, 11.4. Calc. for  $C_{12}H_{27}O_4P$ : P, 11.65%), and pyridine hydrobromide (9.0 g., 96.8%) when it (8.34 g., 1 mol.) in ether (50 c.c.) was added to butan-1-ol (4.3 g., 2 mols.) and pyridine (4.7 g., 2 mols.) in ether (25 c.c.) at -10°. After the dibromidate (3.6 g.) had been stored at 15° for 7 days, *n*-butyl bromide (1.5 g., 80%), b. p. 101° (Found: Br, 58.1. Calc. for  $C_4H_9Br$ : Br, 58.3%), was withdrawn at 15°/0.2 mm., leaving a solid (1.8 g.) (Found: Br, easily hydrolysed, 30.8; P, 18.5%).

The oxybromide (8.3 g., 1 mol.) in ether (20 c.c.) was added to the silane (12.7 g., 3 mols.)

<sup>a</sup> Gerrard, Nechvatal, and Wyvill, *Chem. and Ind.*, 1947, 437.

in ether (20 c.c.). After 16 hr. at 15°, bromotrimethylsilane (9.1 g., 69%), b. p. 76—78° (Found : Br, 51.5. Calc. for  $C_3H_9BrSi$ : Br, 52.4%), and tri-*n*-butyl phosphate (5.4 g., 70%), b. p. 90°/0.01 mm. (Found : P, 11.5%), were obtained. The low yield of the purified bromosilane is due to the difficulty in separating it from the solvent.

*Preparation of the Silanes.*—These were prepared by the addition of chlorotrimethylsilane (1 mol.) to a solution of the alcohol (1 mol.) and pyridine (1 mol.) in pentane. A number of alkoxytrimethylsilanes containing phenyl-substituted alkyl groups were thus made by Gerrard and Kilburn; <sup>4</sup> others are : *n*-butoxytrimethylsilane, b. p. 124°,  $n_D^{20}$  1.3927, *sec*-butoxytrimethylsilane, b. p. 112.3°,  $n_D^{20}$  1.3898,  $d_4^{25}$  0.772 (Found : C, 58.0; H, 12.35.  $C_7H_{18}OSi$  requires C, 57.5. H, 12.3%), *isobutoxy*trimethylsilane, b. p. 112.7°,  $n_D^{20}$  1.3880,  $d_4^{25}$  0.770 (Found : C, 58.2; H, 12.6%), *trimethyl-2-methylheptyloxysilane*, b. p. 91°/22 mm.,  $n_D^{20}$  1.4124,  $d_4^{20}$  0.7937 (Found : C, 65.4; H, 12.5; Si, 13.65.  $C_{11}H_{26}OSi$  requires C, 65.3; H, 12.9; Si, 13.85%).

THE NORTHERN POLYTECHNIC,  
HOLLOWAY ROAD, LONDON, N.7.

[Received, November 7th, 1956.]