The reaction between trialkylaluminums and phosphorus trichloride has not been studied previously. Organolithium, organomagnesium, and organozinc compounds alkylate phosphorus trichloride to trialkylphosphines. By the action of organocadmium compounds (prepared via Grignard reagents) on phosphorus trichloride, low yields (26-43%) have been obtained of alkyldichlorophosphines [1]. Kharash [2] heated PCl₃ with tetraethyllead at 110° for 30 hours and obtained a 90% yield of dichloroethylphosphine. The action of dialkylmercurys [3, 4] on phosphorus trichloride gives difficultly separable mixtures of alkyldichloro- and dialkylchloro-phosphines with the original organomercury compound.

We found that, depending on the way in which the reaction was carried out, reaction between a trialkylaluminum and phosphorus trichloride leads to the formation of all three possible alkylated products from PCl₃:

\[ \text{AlR₃} + \text{PCl₃} \rightarrow \text{RPCl₂} + \text{R₂PCl} + \text{R₃Al}. \]

It was characteristic, however, that even in an excess of triethylaluminum, triethylphosphine is formed in a yield of only about 30%, and a considerable proportion of the Al-C bonds are preserved. In the reaction between equimolecular amounts of phosphorus trichloride and triisobutylaluminum, the main product was chlorodiformylphosphine, which was identified in the form of dilsobutylphosphonic acid. By reaction of trialkylaluminums with excess of PCl₃ we succeeded in obtaining satisfactory yields of alkyldichlorophosphines, which may be of definite interest in view of the accessibility of trialkylaluminums [5]. Since trialkyl- and dialkylchlorophosphines give stable complexes with the aluminum halide compounds formed, only alkyldichlorophosphines distill from the reaction mixtures together with excess of PCl₃. Higher yields of alkyldichlorophosphines are attained when the trialkylaluminums are used as their complexes with either ether or pyridine. In this way we prepared alkyldichlorophosphines RPCl₂, in which R = C₂H₅, n-C₃H₇, i-C₃H₇, n-C₄H₉, i-C₄H₉, and n-C₅H₁₁. Under the conditions of the reaction the alkyl groups did not undergo isomerization.

EXPERIMENTAL

Dichloroethylphosphine. A solution of the "etherate" of triethylaluminum (prepared from 20 g of (C₂H₅)₃Al and 25 ml of ether) was added in a stream of pure nitrogen with vigorous stirring to 110 ml of PCl₃ at 50-55° (attained as a result of the heat of reaction). A mixture of PCl₃ and C₂H₅PCl₂ was distilled off under reduced pressure (200 mm) into a cooled receiver. Fractionation through a 15-plate column gave 42.5 g (61.5%) of dichloroethylphosphine; b. p. 112°; n₁₀D 1.4930; d₁₀ 1.2600. The literature gives: b. p. 112°; n₁₀D 1.4930; d₁₀ 1.2952 [3].

Dichloropropylphosphine. This was prepared similarly from 23 g of triethylaluminum etherate and 55 ml of PCl₃: yield 22 g (59.6%); b. p. 157°; n₁₀D 1.4580; d₁₀ 1.1854. The literature gives: b. p. 134.5°; n₁₀D 1.4842; d₁₀ 1.1867 [1]; d₁₀ 1.1771 [3]. Boiling of 10.7 g of n-C₃H₇PCl₂ with 2.4 g of sulfur in presence of 0.05 g of AlCl₃ for two hours gave 10.9 g of propylphosphonothioic dichloride; b. p. 62-63° (9 mm); n₁₀D 1.5290; d₁₀ 1.2832; found MR 42.48; calculated MR 42.43.

Dichloroisopropylphosphine. This was prepared similarly from 23 g of tripropylaluminum etherate and 55 ml of PCl₃: yield 22 g (59.6%); b. p. 157°; n₁₀D 1.4580; d₁₀ 1.1854. The literature gives: b. p. 134.5°; n₁₀D 1.4842; d₁₀ 1.1867 [1]; d₁₀ 1.1771 [3]. Boiling of 10.7 g of n-C₃H₇PCl₂ with 2.4 g of sulfur in presence of 0.05 g of AlCl₃ for two hours gave 10.9 g of propylphosphonothioic dichloride; b. p. 62-63° (9 mm); n₁₀D 1.5290; d₁₀ 1.2832; found MR 42.48; calculated MR 42.43.

Found %: C 20.75, 20.75; H 3.96; P 17.73. n-C₃H₇P(S)Cl₂. Calculated %: C 20.36; H 3.96; P 17.50.

Propylphosphonothioic dianilide had m. p. 133° (from alcohol-water); m. p. of mixture with known sample [6] 132-133°.

Dichloroisopropylphosphine. Triisopropylaluminum (22.5 g) and 63 ml of PCl₃ gave 18.4 g (43.1%) of dichloroisopropylphosphine; b. p. 135°-136° (745 mm); n₁₀D 1.4980; d₁₀ 1.1922. The literature [3] gives: b. p. 135-136°; d₁₀ 1.2181.
Found %: Cl 49.05, 49.36; \( \text{C}_3\text{H}_7\text{PCl}_3 \) Calculated %: Cl 48.93.

From 7.2 g of dichloroisopropylphosphine and 1.8 g of sulfur we obtained 6.9 g of isopropylphosphonothioic dichloride; b. p. 63-64° (10 mm); \( n^D_2 1.5322; d^2_4 1.2566; \) found MR 42.36; calculated MR 42.43.

Found %: C 20.52, 20.52; H 3.96, 3.93; P 17.89, 17.40; \( \text{C}_3\text{H}_7\text{P(S)}\text{Cl}_2 \) Calculated %: C 20.36; H 3.96; P 17.50.

The diaminide had m. p. 114° (from benzene-heptane) and showed depression of melting point in admixture with \( \text{n-C}_7\text{H}_7\text{TP(S)} \)(\( \text{HNC}_6\text{H}_5 \))2.

Found %: C 62.10, 61.92; H 6.65, 6.43; S 11.30, 11.17; N 9.59, 9.80; \( \text{i-C}_4\text{H}_9\text{TP(S)(HNC}_6\text{H}_5 \))2 Calculated %: C 62.04; H 6.60; S 11.04; N 9.65.

Dichloroisobutylphosphine. a) Triisobutylaluminum (32.5 g) was added to 120 ml of \( \text{PCl}_3 \) at 60-70°; in the vacuum distillation the excess of \( \text{PCl}_3 \) was followed by 11.5 g (17.6%) of dichloroisobutylphosphine; b. p. 59-60° (50 mm); 35-36° (9 mm); 148-149° (740 mm); \( n^D 1.4818; d^2_4 1.1288 \). The literature [3] gives:

b. p. 155-157°; \( d^2 1.1268 \) [7]; b. p. 48.5-49.5° (12 mm); \( n^D 1.4719; d^2 1.172 \).

Found %: C 30.55, 30.67; H 5.75, 5.88; Cl 44.27, 44.72. \( \text{i-C}_4\text{H}_9\text{PCl}_3 \) Calculated %: C 30.21; H 5.64; Cl 44.60.

b) Triisobutylaluminum (94 g) in 50 ml of ether was added with vigorous stirring to 300 g of \( \text{PCl}_3 \) at 65-70°. By the procedure of the previous experiment we obtained 78.5 g (33%) of dichloroisobutylphosphine, b. p. 35-36° (9 mm); \( n^D 1.4822 \).

Butyldichlorophosphine was prepared similarly to \( \text{n-C}_7\text{H}_7\text{PCl}_2 \) from 27.2 g of tributylaluminum etherate and 82.5 g of \( \text{PCl}_3 \); yield 27.4 g (53%) of dichlorobutylphosphine, b. p. 153-155°, 38.5-39° (9 mm); \( n^D 1.4868; d^4 1.1416; d^4 1.1342 \). The literature [1] gives:

b. p. 160°; \( n^D 1.4838; d^4 1.1341 \).

Dichlorohexylphosphine. Reaction between 38 g of trihexylaluminum and 80 ml of \( \text{PCl}_3 \) gave 32 g (42.5%) of dichlorophosphine; b. p. 83-84° (9 mm); \( n^D 1.4820; d^4 1.0670 \). The literature [1] gives:

b. p. 208°; \( n^D 1.4800; d^4 1.0653 \).

Triethylphosphine. Phosphorus trichloride (33.2 g) was added to 28.5 g of triethylaluminum; the mixture was heated (80°) with stirring for three hours. A viscous complex (35.3 g) was formed. Some of the complex (35.3 g) was decomposed with excess of aqueous sodium hydroxide, and triethylphosphine was extracted with ether. Fractionation in a stream of nitrogen gave 5.4 g (50%) of triethylphosphine; b. p. 129-130° and \( n^D 1.4575 \); the carbon disulfide adduct formed red needles, m. p. 121° (from alcohol). The literature [8] gives:

b. p. 127.5°; \( n^D 1.45799; (\text{C}_2\text{H}_5)_3\text{PCl}_2 \text{PCl}_2 \), m. p. 121°.

Diisobutylphosphinic Acid. A solution of 23 g of phosphorus trichloride in an equal volume of heptane was added to 45 g of triisobutylaluminum in 50 ml of heptane (the temperature rose to 60-70° as a result of the heat of reaction). Heptane was vacuum-distilled from the complex formed, which was then decomposed with sodium hydroxide solution. The mixture of neutral and acid products was treated, with cooling, with 30% hydrogen peroxide, and diisobutylphosphinic acid was extracted with 20% sodium hydroxide solution; the alkaline solution was filtered from resins impurities, washed with benzene, and acidified with hydrochloric acid. Benzene extracted 13.2 g of diisobutylphosphinic acid, b. p. 140-141° (0.4 mm) and m. p. 43-45° (from pentane).

The literature [9] gives m. p. 41-44°.

SUMMARY

1. The reaction of trialkylaluminums with phosphorus trichloride was studied.

2. The conditions were worked out for the synthesis of alkyldichlorophosphines from phosphorus trichloride and the corresponding trialkylaluminums.