48. TRIS(TRIMETHYLSILYL)PHOSPHINE AND LITHIUM BIS(TRIMETHYLSILYL)PHOSPHIDE·BIS-(TETRAHYDROFURAN)

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Tris(trimethylsilyl)phosphine¹ and its more reactive derivative lithium bis-(trimethylsilyl)phosphide·2tetrahydrofuran² are very useful reagents for the preparation of compounds with a single or a multiple element phosphorus bond. They react readily with various element halides,³⁻⁵ with carboxylic acid chlorides,⁶ and with carboxylic esters,⁷ as well as with other organic electrophiles⁷ *via* a substitution of lithium and/or a cleavage of the weak polar Si-P bonds.

A. TRIS(TRIMETHYLSILYL)PHOSPHINE

M = Na, K; DME = 1,2-dimethoxyethane

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■ **Caution.** Sodium and particularly potassium react violently with water and may ignite in air. The incrustations of potassium may be explosive; only potassium with little or no incrustation should be cut, and care should be taken to ensure anhydrous conditions. Sodium–potassium alloy as well as malodorous tris(trimethylsilyl)phosphine are pyrophoric and extremely sensitive to moisture. Therefore the entire procedure must be carried out in an atmosphere of dry argon in a well-ventilated fume hood. In case of emergency a sand bath should be available to catch the liquid alloy. 1,2-Dimethoxyethane and tetrahydrofuran (THF) may form explosive peroxides. Only fresh, peroxide-free material should be used.

These solvents must be deoxygenated and freed from traces of water before use by refluxing over sodium wire in the presence of benzophenone in a slight stream of argon. When the color has changed to deep blue, the solvent is distilled off. Pentane is purified in a similar way with lithium tetrahydridoaluminate.

Procedure

The complete equipment used in this procedure must first be evacuated and then filled with argon. All joints are greased with H-grease (Apiezon Products). When stoppers are removed and compounds are transferred from one flask to the other, a slight stream of argon must be maintained.

A 46-g quantity (2.0 mol) of sodium and 59 g (1.5 mol) of potassium are purified by removing their incrustations under petroleum ether. The metals are cut into pieces and placed in a 500-mL two-necked round-bottomed flask provided with a 500-mL pressure equalizing dropping funnel and connected to the argon–vacuum supply *via* a side arm with a stopcock (see Fig. 1). After evaporation of the residual organic solvent *in vacuo*, the sodium–potassium alloy is formed by warming the metals cautiously with a hair

Fig. 1. Apparatus for preparing sodium–potassium alloy.

Fig. 2. Apparatus for preparing sodium-potassium phosphide and reacting it with chlorotrimethylsilane.

dryer, while the flask is shaken occasionally. The alloy is then poured into the dropping funnel.

■ **Caution.** *White phosphorus is extremely toxic and causes severe burns; gloves should be worn when handling the solid or solution.*

A 2-L three-necked flask is equipped with a reflux condenser* and a mechanical stirrer, which is sealed with paraffin oil. The condenser is fitted with a three-way stopcock connecting to an argon-vacuum supply and to two wash bottles filled with paraffin oil (see Fig. 2). Small pieces of white phosphorus (31 g, 1 mol) are placed in the flask and freed from traces of water *in vacuo*.[†] After adding 1 L of DME the dropping funnel with the liquid alloy

*The use of a reflux condenser with a metallic coil is strongly recommended.

[†]The checkers report white phosphorus can also be freed from traces of water by washing with 50 mL of DME.

is mounted on the free neck of the flask, and the stopcock is switched from the argon supply to the wash bottles. The solvent is heated to 50 °C and the alloy is added slowly, in the beginning drop by drop, over a period of 1 h to the vigorously stirred emulsion. To complete the formation of black sodium–potassium phosphide the suspension must be heated at reflux with a heating mantle for 24 h.

A slight excess of freshly distilled chlorotrimethylsilane (353 g, 3.25 mol) is added carefully to the phosphide suspension while stirring and refluxing. These conditions are maintained for another 24 h. During this period, the reaction mixture becomes increasingly viscous,* and its color changes from black to gray. The dropping funnel is exchanged for an argon inlet; the reflux condenser and stirrer are removed in a slight stream of argon. After filtration (see Fig. 3) through sintered glass (porosity 50 μm), the residue is washed several times with a total of 2 L of DME. Finally, the solvent is distilled off at atmospheric pressure, and the remaining tris(trimethylsilyl)phosphine is purified by vacuum distillation (30-cm-Vigreux column). Bp 30–35 °C/10^{−3} mbar. Yield: 188 g (75%).

Anal. Calcd. for C₉H₂₇Si₃P: C, 43.1; H, 10.9; Si, 33.6; P, 12.4. Found: C, 43.3; H, 11.0; Si, 33.5; P, 12.0.

■ **Caution.** *On cooling, the pure distillation product may crystallize rapidly and block the apparatus. The residues from the filtration and distillation may contain either pyrophoric sodium–potassium alloy or tris(trimethylsilyl)phosphine and trimethylsilyl-substituted cyclic polyphosphines.⁸ For safety reasons all residues must be treated very cautiously with a mixture of ethanol and petroleum ether (1:10) under an inert atmosphere in a well-ventilated fume hood.*

Properties

Tris(trimethylsilyl)phosphine is a colorless compound with a melting point near room temperature. Characteristic NMR data for a DME solution are $\delta_{(1\text{H})}$ 0.30; $^3J_{\text{P-H}} = 4.4$ cps; $\delta_{(1\text{P})}$ -251. In reactions with alcohols and water bis(trimethylsilyl) and (trimethylsilyl)phosphine can be synthesized;⁹ acetyl chloride in a molar ratio of 1:3 gives triacetylphosphine.¹⁰ For the important reaction with 2,2-dimethylpropionyl chloride see Section 49.

*In case of insufficient stirring, incrustation and subsequent decomposition of tris(trimethylsilyl)phosphine may occur. Therefore, the whole process should be continually supervised.

Fig. 3. Filtration of the reaction mixture after formation of tris(trimethylsilyl)-phosphine.

B. LITHIUM BIS(TRIMETHYLSILYL)PHOSPHIDE·BIS(TETRAHYDROFURAN)²

■ **Caution.** *Methyl lithium and lithium bis(trimethylsilyl)phosphide·bis(tetrahydrofuran) are very sensitive to moisture, and even in solution they are flammable in air. Therefore the entire procedure must be carried out in an atmosphere of dry argon in a well-ventilated fume hood. Solvents should be dried and deoxygenated as described previously.*

Procedure

In a single-necked 1-L flask connected to the argon–vacuum supply *via* a side arm with a stopcock and equipped with a pressure equalizing dropping funnel and a magnetic stirring bar, 62.6 g (0.25 mol) of tris(trimethylsilyl)phosphine is dissolved in 300 mL of THF and cooled to 0 °C. An ~1 M solution of methyl lithium* in diethyl ether (0.245 mol[†]), the molarity of which has been determined by titration,[‡] is added over a period of 1 h. After allowing the reaction mixture to warm to 20 °C and stirring if for another 8 h, all volatile compounds are distilled off under reduced pressure at room temperature. The brown residue is covered with 400 mL of pentane. While stirring the suspension, THF (~20 mL) is slowly added until complete dissolution has been achieved. At –30 °C colorless to pale yellow crystals of lithium bis(trimethylsilyl)phosphide·bis(tetrahydrofuran) precipitate. The liquid phase is carefully removed from the cold solution with a pipette. The precipitate is ground under argon with a flattened glass rod, and the remaining solvent is removed *in vacuo* (minimum pressure 0.3 mbar). The mother liquor is worked-up as above to get another crop of crystals. The exact THF content must be determined by ¹H NMR spectroscopy. Yield: 64 g (80%).

*Solutions of methyl lithium are prepared before use from methyl chloride and pieces of lithium in diethyl ether.¹¹

With solutions of methyl lithium in diethyl ether, either commercially available or prepared from lithium and methyl chloride, the checkers obtained lithium bis(trimethylsilyl)phosphide·bis(tetrahydrofuran) in only 40 or 50% yield. Therefore they advise preparing the compound with *n*-butyllithium as described in the literature.² The submitters report reproducible yields of 80%.

[†]Since excess tris(trimethylsilyl)phosphine can easily be removed by recrystallization of the product, a slight deficiency of methyl lithium is recommended.

[‡]A 10-mL quantity of the solution is cautiously hydrolized in 25-mL of 1 M HCl. Excess acid is determined by back titration with a 1 M solution of sodium hydroxide.

Properties

Lithium bis(trimethylsilyl)phosphide·bis(tetrahydrofuran) is a colorless crystalline compound that has been used by several research groups for introducing the bis(trimethylsilyl)phosphinyl group.³⁻⁶ Characteristic NMR data of the THF solution are $\delta_{(1H)}$ 0.53, $^3J_{P-H} = 4.0$ cps; $\delta_{(13P)} - 298$.

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