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17. TRIMETHYLPHOSPHINE

$$CH_3Cl + Mg \xrightarrow[\text{cold}]{Me(OCH_2CH_2)_4OMe} CH_3MgCl$$

$$3CH_3MgCl + PCl_3 \xrightarrow{Me(OCH_2CH_2)_4OMe} P(CH_3)_3 + 3MgCl_2$$

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Trimethylphosphine is commonly prepared by the reaction of a phosphorus trihalide with a methyl Grignard reagent CH_3MgX (X = Br, I) in ether solution[1–8] or with dimethylzinc.[4,9,10] The highly reactive product is usually collected and stored as the stable silver iodide complex $[(CH_3)_3P \rightarrow AgI]_4$.[8,11] Exact information concerning the yield of pure product is given in none of the literature references.[1–8,10] Burg and Wagner[12] report a 38% yield of product for the reaction between phosphorus(III) bromide and methylmagnesium iodide in di-*n*-butyl ether solution. Usually, however, preparations of trimethylphosphine by the reaction of phosphorus(III) chloride and methylmagnesium iodide in ether solution result in quite low yields,[4,6] the Grignard reaction being more difficult for trimethylphosphine than for any of the higher trialkylphosphines. The preparation of trimethylphosphine by the phosphorus(III) chloride–dimethylzinc reaction[10] is somewhat hazardous and results in an impure product when the reaction is carried out in a vacuum in the absence of a solvent.

It has been pointed out[13] that the best yields of trialkylphosphines are obtained from phosphorus(III) chloride and a large excess of the chloride–Grignard reagent reacting at as low a temperature as practicable, down to −78°. Further, it is known[14] that methylmagnesium chloride can be

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prepared in good yield, without the precipitation of magnesium salts, if the preparation is carried out in tetraethylene glycol dimethyl ether.

Procedure

Caution. Trimethylphosphine is a toxic gas.

The reaction vessel used in the preparation of methylmagnesium chloride[14] is a 2-l. round-bottomed flask with a 30-cm.-long 20-mm.-o.d. glass column sealed to its bottom. The flask is fitted with a two-hole rubber stopper which bears 6-mm. glass inlet and outlet tubes for the methyl chloride gas. The inlet tube extends to the bottom of the glass column, and the outlet tube is fitted with a silica gel drying tube to prevent moisture from entering the system.

Tetraethylene glycol dimethyl ether is the solvent for the preparation. Practical-grade material is purified before use by allowing approximately 2 kg. to remain overnight in contact with about 20 g. of fresh lithium tetrahydroaluminate in a properly vented vessel at 80°. Then it is distilled from lithium tetrahydroaluminate under reduced pressure (b.p. 110° at 0.75 mm.) and kept dry until used. (The checkers note that the solvent can be dried by heating with sodium as an alternate to the somewhat more hazardous tetrahydroaluminate.)

Iodine-activated magnesium[14,15] is used to initiate the reaction of magnesium and methyl chloride. About 0.5 g. of magnesium turnings and 0.1 g. of iodine are placed in a 10-ml. test tube and covered with about 2 ml. of anhydrous ethyl ether. After the reaction has proceeded for about 5 minutes, the excess liquid is decanted, and the test tube is heated carefully with a free flame to a dull redness. The test tube is allowed to cool somewhat. While it is still warm, about 5 ml. of tetraethylene glycol dimethyl ether, previously saturated with methyl chloride, is added. Additional gentle warming may be required if the reaction does not start immediately.

The iodine-activated magnesium is added immediately to 24 g. of standard Grignard magnesium turnings in approximately 150 ml. of tetraethylene glycol dimethyl ether which has been introduced into the dry reaction vessel described above and saturated with methyl chloride. The magnesium turnings fill the column around the methyl chloride inlet tube and are covered by the solvent. A rapid methyl chloride flow rate is helpful in the initial stage. When the reaction is well started and all the magnesium has become activated, as evidenced by the heat and bubbling produced in the column, an additional 850 ml. of solvent is added quickly. The methyl chloride is slowly and continuously bubbled through the reaction vessel for several hours until the reaction is completed and the column is cold.

The 1 l. of approximately 1 *M* methylmagnesium chloride solution is filtered through dry glass wool into a 2-l. four-necked round-bottomed flask fitted with ground-glass connections for a Tru-bore mechanical stirrer, a pressure-equilibrated 500-ml. dropping funnel, and a dry nitrogen gas inlet and outlet tube. The dry nitrogen gas inlet tube extends well below the surface of the Grignard solution. It is important that all glassware be thoroughly dry before use and that the round-bottomed flask be flushed with dry nitrogen before the Grignard solution is introduced. The outlet tube from the flask delivers into the first of two 250-ml. bottles connected in series, each containing about 200 ml. of saturated potassium iodide solution which is 1.11 *M* in silver iodide. The inlet tube to each of the bottles extends nearly to the bottom, and the outlet tube of the second bottle is open to the atmosphere. The Grignard solution is cooled, while stirring vigorously and with dry nitrogen flowing through the flask, by surrounding it with a Dry Ice–trichloroethylene slush bath. The cooling is continued prior to the addition of the phosphorus(III) chloride for about one half-hour, but solidification of the solvent and consequent clogging of the dry-nitrogen inlet tube should be avoided. Tetraethylene glycol dimethyl ether

(250 ml.) containing 13 ml. of reagent-grade phosphorus(III) chloride is added dropwise over a period of 1½ hours with continued stirring, cooling, and dry nitrogen flow.

When the phosphorus(III) chloride addition is complete, the reaction flask is allowed to warm to room temperature. Then, using an oil bath, the trimethylphosphine is distilled under a stream of dry nitrogen from the reaction flask into the silver iodide–potassium iodide solution. Solid $[(CH_3)_3P \rightarrow AgI]_4$ complex is observed to form steadily. It is helpful to have the ground-glass connections secured with springs, thus preventing loss of product from leakage due to the slight overpressure inside the reaction flask. When the oil bath reaches a final temperature of 100°, an excess of saturated ammonium chloride solution is added dropwise to the reaction flask to ensure complete decomposition of the trimethylphosphine-Grignard complex. This decomposition reaction may be quite vigorous, particularly in the beginning of the addition of the ammonium chloride solution. The $[(CH_3)_3P \rightarrow AgI]_4$ complex is collected by filtration, washed first with saturated potassium iodide solution, then with water, and finally dried in a desiccator over phosphorus(V) oxide.

A total of 20 g. of the complex can be obtained, corresponding to a yield of 43% trimethylphosphine based on the original amount of phosphorus(III) chloride used. (The checkers report a yield of 11%.) Trimethylphosphine is obtained by decomposition of the complex through heating. Decomposition becomes observable at an oil bath temperature of 140°, and heating can be continued to 260°.

Properties

As a test on the purity of the product obtained by decomposition of the complex, the vapor pressure was measured in the manometer section of a vacuum line. The experimental value of 158.5 mm. at 0° agrees with reported values of 158,[7] 159,[10] 161,[12] 154,[4] and 159 mm.[16] The vapor pressure at 20° is 466 mm., and the normal boiling point is 37.8°.[3]

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18. FLUOROPHOSPHORANES

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Fluorophosphoranes are derivatives of phosphorus(V) fluoride of the composition R_nPF_{5-n}, where $n = 1$ to 3 and R may be an aliphatic or aromatic hydrocarbon group. Unlike the formally analogous and long-known chloro compounds, R_nPCl_{5-n}, fluorophosphoranes are typical covalent

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