Organic Syntheses

A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

The procedures in *Organic Syntheses* are intended for use only by persons with proper training in experimental organic chemistry. All hazardous materials should be handled using the standard procedures for work with chemicals described in references such as "Prudent Practices in the Laboratory" (The National Academies Press, Washington, D.C., 2011; the full text can be accessed free of charge at http://www.nap.edu/catalog.php?record_id=12654). All chemical waste should be disposed of in accordance with local regulations. For general guidelines for the management of chemical waste, see Chapter 8 of Prudent Practices.

In some articles in *Organic Syntheses*, chemical-specific hazards are highlighted in red "Caution Notes" within a procedure. It is important to recognize that the absence of a caution note does not imply that no significant hazards are associated with the chemicals involved in that procedure. Prior to performing a reaction, a thorough risk assessment should be carried out that includes a review of the potential hazards associated with each chemical and experimental operation on the scale that is planned for the procedure. Guidelines for carrying out a risk assessment and for analyzing the hazards associated with chemicals can be found in Chapter 4 of Prudent Practices.

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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

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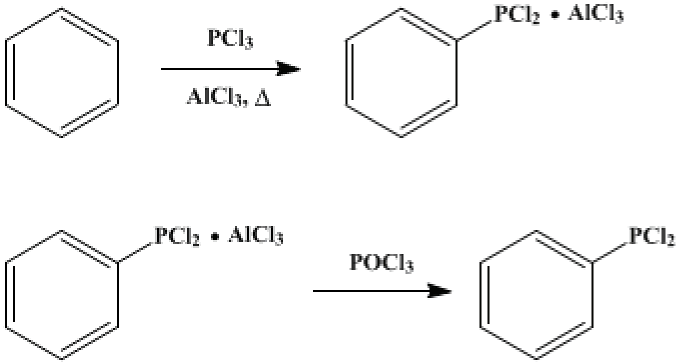
PHENYLDICHLOROPHOSPHINE

[Phosphonous dichloride, phenyl-]



Submitted by B. Buchner and L. B. Lockhart, Jr.[1].
Checked by Cliff S. Hamilton and P. J. Vanderhorst.

1. Procedure

In an all-glass apparatus consisting of a 1-l. three-necked flask equipped with a long-stem thermometer, a rubber-sealed mechanical stirrer, and a suitable condenser (Note 1) are placed 165 g. (1.2 moles) of phosphorus trichloride, 23.4 g. (0.3 mole) of benzene, and 53 g. (0.4 mole) of anhydrous aluminum chloride. The mixture is stirred continuously and heated (Note 2). As the temperature increases, the mixture becomes a homogeneous yellow solution and begins to reflux. After 2 hours, the reaction mixture is heated under reflux as vigorously as possible (Note 3). At the end of the third hour, the evolution of hydrogen chloride has almost ceased. The heat source is removed, and, while the mixture is still hot, 62 g. (0.4 mole) of phosphorus oxychloride is added gradually (Note 4) from a dropping funnel (Note 5). The granular precipitate of aluminum chloride-phosphorus oxychloride complex settles rapidly. After the apparatus is disassembled, 6–8 petroleum ether extractions of 100 ml. each are performed to remove phenyldichlorophosphine and the unreacted starting materials from the reaction flask. The residue is transferred to a Büchner funnel and washed with several small portions of petroleum ether, and the combined extracts and washings are concentrated under reduced pressure. Crude phenyldichlorophosphine is removed by distilling to dryness under reduced pressure and is purified by fractionating through a satisfactory column (Note 6). The product distils at 68–70°/1 mm. (90–92°/10 mm.), n_D^{25} 1.5962 (Note 7), and weighs 38.5–42 g. (72–78%).

2. Notes

1. The submitters and checkers used a Friedrichs condenser. The condenser outlet was connected to a gas absorption trap filled with sodium hydroxide solution to neutralize escaping acid vapors. A tube filled with Drierite was inserted between the condenser and trap to absorb moisture which might diffuse from the trap.
2. Slow heating is desirable to prevent too rapid evolution of hydrogen chloride.
3. Cold water, approximately 0°, is circulated by means of a water pump in order to increase the efficiency of the condenser.
4. The reaction between phosphorus oxychloride and aluminum chloride is exothermic.
5. The thermometer is replaced by a dropping funnel.
6. The submitters and checkers employed a 20-cm. column packed with glass helices.
7. The checkers obtained an average value of n_D^{24} 1.5919.

3. Discussion

Phenyldichlorophosphine has been prepared by the vaporphase reaction of benzene and phosphorus trichloride over pumice in a hot tube[2] and by the action of diphenylmercury[3] or phenylzinc bromide[4] on phosphorus trichloride. The method described here is a Michaelis' modification of a Friedel-Crafts reaction.[5] It has been claimed[6] that pyridine is advantageous for the removal of aluminum chloride from the reaction mixture.

References and Notes

1. Naval Research Laboratory, Washington, D. C.
2. Michaelis, *Ber.*, **6**, 601 (1873).
3. Michaelis, *Ann.*, **181**, 288 (1876).
4. Weil, Prijs, and Erlenmeyer, *Helv. Chim. Acta*, **35**, 1412 (1952).
5. Michaelis, *Ber.*, **12**, 1009 (1879); Buchner and Lockhart, *J. Am. Chem. Soc.*, **73**, 755 (1951).
6. Gefter, *Zhur. Obshchei Khim.*, **28**, 1338 (1958) [*C. A.*, **52**, 19999 (1958)].

Appendix
Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

petroleum ether

Drierite

aluminum chloride-phosphorus oxychloride complex

hydrogen chloride (7647-01-0)

Benzene (71-43-2)

sodium hydroxide (1310-73-2)

Phosphorus Oxychloride (21295-50-1)

aluminum chloride (3495-54-3)

pyridine (110-86-1)

phosphorus trichloride (7719-12-2)

Diphenylmercury (587-85-9)

Phenyldichlorophosphine,
Phosphonous dichloride, phenyl- (644-97-3)

phenylzinc bromide