



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.

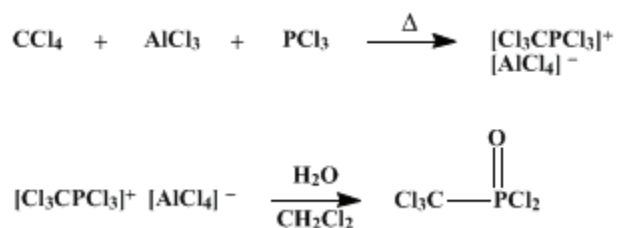
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 4, p.950 (1963); Vol. 37, p.82 (1957).

TRICHLOROMETHYLPHOSPHONYL DICHLORIDE

[Phosphonic dichloride, (trichloromethyl)-]



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Checked by John C. Sheehan and J. L. Yeh.

1. Procedure

Caution! This preparation should be conducted in a hood.

In a 2-l. round-bottomed three-necked flask, fitted with an efficient reflux condenser, mechanical stirrer, and dropping funnel (Note 1), are placed 133.3 g. (1 mole) of anhydrous powdered aluminum chloride, 137.4 g. (1 mole) of phosphorus trichloride, and 184.6 g. (1.2 moles) of carbon tetrachloride (Note 2). The reactants are stirred slowly until they are thoroughly mixed, and then heat is applied carefully until the reaction begins. At this point the liquid boils vigorously, and the reaction mixture becomes thicker so that faster stirring is necessary. Finally, the stirrer is stopped when the mixture becomes solid. After the reaction has cooled for 30 minutes, 1 l. of methylene chloride is run into the flask (Note 3), and the solvent is stirred vigorously until the solid is finely suspended (Note 4). The reflux condenser is replaced by a low-temperature thermometer which dips into the reaction mixture, the suspension is cooled in a Dry Ice-acetone bath, and the temperature is kept at -10° to -20° as distilled water (180 g., 10 moles) is added dropwise with vigorous stirring over a period of about 25 minutes (Note 5). After the water addition is complete, stirring is continued for 15 minutes without the cold bath.

The apparatus is dismantled, and the reaction mixture is filtered quickly by suction through a 1.5-cm. layer of filter aid on an 11-cm. Büchner funnel placed on a 2-l. filter flask. The filter cake is pressed down well and washed with three 50-ml. portions of methylene chloride. The filtrate is immediately protected from moisture by calcium chloride tubes, and the solvent is removed by distillation from a 2-l. flask. After the solution has been concentrated to about 225 ml., the hot liquid is poured into a suitable container (Note 6), and the remaining solvent is removed under reduced pressure (Note 7). The yield is 192–199 g. (81–84%) of a white, crystalline solid which melts at $155\text{--}156^\circ$.

2. Notes

1. The equipment is dried and protected from atmospheric moisture by calcium chloride tubes.
2. It is important that the reactants are pure; otherwise the complex is colored. If the containers are freshly opened, C.P. reagents are satisfactory.
3. The methylene chloride must be redistilled from aluminum chloride to prevent coloration of the product.
4. If the solid adheres to the flask, the flask is heated lightly with a free flame to loosen it.
5. Vigorous stirring is necessary to prevent caking of the aluminum chloride hydrate and to prevent localized hydrolysis. The checkers found that exactly 7 moles of water gave a somewhat improved yield, but handling was more difficult.
6. The submitters used a 500-ml. round-bottomed wide-mouthed flask.
7. The product may be warmed to aid solvent removal, but it is decomposed by prolonged heating above 60° .

3. Discussion

The [aluminum chloride](#) process^{2,3} is a general method for the preparation of alkylphosphonyl dichlorides. Trichloromethylphosphonyl dichloride has been made also by the chlorination of chloromethyldichlorophosphonic dichloride in the presence of light or other catalysts⁴ and by the reaction of [tetrachloro\(trichloromethyl\)phosphorane](#) with [sulfur dioxide](#).⁵ The procedure described here is essentially that of Kennard and Hamilton⁶ and is based on the procedure of Kinnear and Perren.²

References and Notes

1. University of Nebraska, Lincoln, Nebraska.
2. Kinnear and Perren, *J. Chem. Soc.*, **1952**, 3437.
3. Clay, *J. Org. Chem.*, **16**, 892 (1951).
4. Traise and Walsh (to Victor Chemical Works), U. S. pat. 2,924,560 [*C. A.*, **54**, 11994 (1960)].
5. Yakubovich and Ginsburg, *Zhur. Obshchei Khim.*, **24**, 1465 (1954) [*C. A.*, **49**, 10834 (1955)].
6. Kennard and Hamilton, *J. Am. Chem. Soc.*, **77**, 1156 (1955).

Appendix

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

Trichloromethylphosphonyl dichloride

chloromethyldichlorophosphonic dichloride

[calcium chloride](#) (10043-52-4)

[sulfur dioxide](#) (7446-09-5)

[carbon tetrachloride](#) (56-23-5)

[aluminum chloride](#) (3495-54-3)

[phosphorus trichloride](#) (7719-12-2)

[methylene chloride](#) (75-09-2)

[Phosphonic dichloride, \(trichloromethyl\)-](#) (21510-59-8)

[aluminum chloride hydrate](#)

[tetrachloro\(trichloromethyl\)phosphorane](#)