



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.

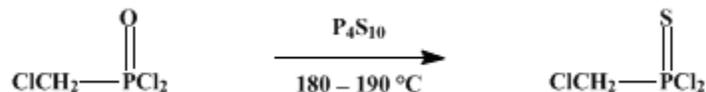
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The procedures described in *Organic Syntheses* are provided as published and are conducted at one's own risk. *Organic Syntheses, Inc.*, its Editors, and its Board of Directors do not warrant or guarantee the safety of individuals using these procedures and hereby disclaim any liability for any injuries or damages claimed to have resulted from or related in any way to the procedures herein.

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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CHLOROMETHYLPHOSPHONOTHIOIC DICHLORIDE



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1. Procedure

A 500-ml. three-necked flask is provided with a mechanical stirrer, thermometer, and reflux condenser equipped with a drying tube. The flask is flushed with dry [nitrogen](#) and charged under [nitrogen](#) with 502 g. (3 moles) of [chloromethylphosphonic dichloride](#) ([Note 1](#)) and 160 g. (0.36 mole) of tetraphosphorus decasulfide ([Note 2](#)). The reaction mixture is heated under reflux with stirring for 6 hours, the liquid temperature being 180–190° ([Note 3](#)). The nearly black reaction mixture is then allowed to cool to room temperature and is distilled under reduced pressure. Material distilling between 70° (40 mm.) and 150° (20 mm.) is collected ([Note 4](#)). The yield is 364–396 g. (66–72%). There is no impurity in the material thus obtained which is detectable by gas chromatography ([Note 5](#)). The product may be redistilled if desired, although in most cases this is superfluous; b.p. 64–65° (10 mm.); n_{D}^{25} 1.5730–1.5741 ([Note 6](#)). The P^{31} n.m.r. spectrum of the product shows a peak at -74.2 p.p.m. relative to external [phosphoric acid](#).

2. Notes

- [Chloromethylphosphonic dichloride](#) is used as obtained from Stauffer Chemical Co. Alternatively it may be prepared from the reaction of [phosphorus trichloride](#) with [paraformaldehyde](#).²
- Technical tetraphosphorus decasulfide (Stauffer Chemical Co.) is employed. The product is weighed under [nitrogen](#) protection.
- In order to prevent contact of the boiling reaction mixture with air, [nitrogen](#) is passed through a T-tube on top of the drying tube on the reflux condenser.
- Toward the end of the distillation a thick residue is formed, and this makes the distillation difficult. After the contents of the distillation flask are cooled to room temperature, this residue may be disposed of by careful continuous rinsing with water under a well-ventilated hood.
- An F&M 500 Program-Temperature Unit (8 ft., 20% [silicon](#) rubber on 60–80 Super Support) was used for the VPC work: program 11°/min., flow 55 ml/min. [Chloromethylphosphonothioic dichloride](#) and [chloromethylphosphonic dichloride](#), a potential impurity, are separated cleanly under these conditions.
- Literature³ values are: b.p. 89° (30 mm.), n_{D}^{25} 1.5741, d_{25}^{25} 1.5891.

3. Discussion

[Chloromethylphosphonothioic dichloride](#) has been prepared by the reaction of [chloromethylphosphonic dichloride](#) with tetraphosphorus decasulfide^{3,4,5} or with [thiophosphoryl chloride](#) under autogenous pressure.^{3,5}

4. Merits of the Preparation

The reaction of [chloromethylphosphonic dichloride](#) with tetraphosphorus decasulfide^{3,4,5} or with [thiophosphoryl chloride](#)³ are the only methods of preparation for this compound reported. The method is applicable more generally, and the syntheses of methyl-, trichloromethyl-, ethyl-, propyl-, cyclohexyl-, phenyl-, and *p*-chlorophenylphosphonothioic dichloride from the corresponding phosphonic dichlorides have been reported.^{4,5} Phosphinic chlorides of varying structures could also be converted to the corresponding thiono compounds by comparable procedures.^{4,5} The present method is preferable to the [thiophosphoryl chloride](#) procedure^{3,5} in that does not require working under pressure.

Chloromethylphosphonothioic dichloride is a reactive and useful intermediate in organophosphorus chemistry.^{3,4,6} Of special interest is its desulfurization by trivalent phosphorus compounds such as phenylphosphonous dichloride leading to the formation of chloromethylphosphonous dichloride.³

References and Notes

1. Explosives Department, E. I. duPont deNemours and Company, Wilmington, Delaware.
 2. R. A. B. Bannard, J. R. Gilpin, G. R. Vavasour, and A. F. McKay, *Can. J. Chem.* **31**, 976 (1953).
 3. E. Uhing, K. Rattenbury, and A. D. F. Toy, *J. Am. Chem. Soc.*, **83**, 2299 (1961).
 4. M. I. Kabachnik and N. N. Godovikov, *Dokl. Akad. Nauk SSSR*, **110**, 217 (1956).
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Appendix Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

tetraphosphorus decasulfide

chloromethylphosphonous dichloride

[nitrogen \(7727-37-9\)](#)

[phosphoric acid \(7664-38-2\)](#)

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

[phenylphosphonous dichloride \(644-97-3\)](#)

[Chloromethylphosphonothioic dichloride \(1983-27-3\)](#)

[chloromethylphosphonic dichloride \(1983-26-2\)](#)

[silicon](#)

[thiophosphoryl chloride \(3982-91-0\)](#)

[p-chlorophenylphosphonothioic dichloride](#)

[paraformaldehyde \(30525-89-4\)](#)