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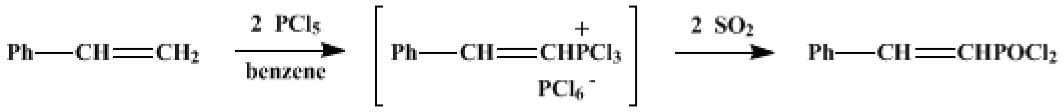
These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

DOI:10.15227/orgsyn.045.0099

Organic Syntheses, Coll. Vol. 5, p.1005 (1973); Vol. 45, p.99 (1965).

STYRYLPHOSPHONIC DICHLORIDE

[Phosphonic dichloride, styryl-]



$$\mathrm{Ph{-}CH{=}CH_2} \xrightarrow[\text{benzene}]{2\ \mathrm{PCl_5}} \left[\mathrm{Ph{-}CH{=}\overset{+}{C}HPCl_3}\ \ \mathrm{PCl_6^-}\right] \xrightarrow{2\ \mathrm{SO_2}} \mathrm{Ph{-}CH{=}CHPOCl_2}$$

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Checked by William G. Dauben and David A. Cox.

1. Procedure

The reaction is conducted in a 500-ml. three-necked flask equipped with a sealed mechanical stirrer, a dropping funnel, and a reflux condenser carrying a drying tube. The flask is flushed with dry nitrogen, and 104 g. (0.50 mole) of phosphorous pentachloride in 150 ml. of dry benzene is added. The mixture is cooled in an ice bath (Note 1) and stirred while a solution of 26 g. (0.25 mole) of styrene in 50 ml. of dry benzene is added through the dropping funnel during a period of 30 minutes. A dense crystalline solid begins to form immediately, and after the addition is completed the mixture is stirred for 30 minutes at room temperature. The dropping funnel is replaced by a gas-inlet tube which is connected to a cylinder of sulfur dioxide through a wash bottle containing concentrated sulfuric acid. Sulfur dioxide is bubbled through the stirred mixture until all the precipitate is dissolved. The mildly exothermic reaction is controlled by occasionally cooling the reactants with an ice bath. The benzene solvent is removed from the clear solution under reduced pressure, and the residue is distilled at reduced pressure from a Claisen flask with Vigreux indentations. The yield of styrylphosphonic dichloride is 49–52 g. (89–94%), b.p. 107–110° (0.2 mm.). The distillate solidifies during or after the distillation, m.p. 71–72°.

2. Notes

1. Care must be taken not to freeze the benzene before the styrene is added.

3. Discussion

Styrylphosphonic dichloride has been prepared by the addition of phosphorus pentachloride to styrene with subsequent reaction of the adduct with phosphorus pentoxide[2] or sulfur dioxide.[3,4]

4. Merits of the Preparation

The addition reaction of phosphorus pentachloride to styrene and its derivatives provides a convenient route to styrylphosphonic acids and their derivatives.[2,3,4,5,6,7] The styrene phosphorus pentachloride adduct also can be reduced with phosphorus to give the corresponding dichlorophosphine.[4,8]

The behavior of phosphorus pentachloride toward carbon-carbon multiple bonds has received considerable attention, and the procedure described represents but one example of a wide variety of derivatives of unsaturated phosphonic acids which are accessible. Indene was the first olefinic compound to be reacted with phosphorus pentachloride,[9] and the reaction of phosphorus pentachloride with other unsaturated compounds has been described.[2,3,4,5,6,10,11,12,13] More recent examples include the reaction of phosphorus pentachloride with vinyl ethers[14,15,16] and vinyl thioethers,[17] providing access to β-alkoxy- and β-alkylmercaptovinylphosphonic and phosphonothioic acid derivatives.

References and Notes

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

sulfuric acid (7664-93-9)

Benzene (71-43-2)

phosphorus pentachloride,
phosphorous pentachloride (10026-13-8)

sulfur dioxide (7446-09-5)

PHOSPHORUS (7723-14-0)

nitrogen (7727-37-9)

styrene (100-42-5)

indene (95-13-6)

vinyl (2669-89-8)

Styrylphosphonic dichloride,
Phosphonic dichloride, styryl- (4708-07-0)

styrene phosphorus pentachloride

dichlorophosphine

phosphorus pentoxide (1314-56-3)