



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](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.

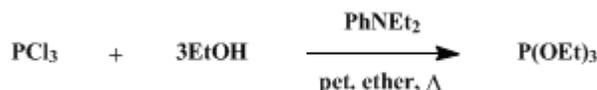
The procedures described in *Organic Syntheses* are provided as published and are conducted at one's own risk. *Organic Syntheses, Inc.*, its Editors, and its Board of Directors do not warrant or guarantee the safety of individuals using these procedures and hereby disclaim any liability for any injuries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

*Organic Syntheses, Coll. Vol. 4, p.955 (1963); Vol. 31, p.111 (1951).*

## TRIETHYL PHOSPHITE

### [Ethyl phosphite]



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Checked by William S. Johnson and James Ackerman.

### 1. Procedure

A solution of 138 g. (175 ml., 3 moles) of absolute ethanol (Note 1) and 447 g. (477 ml., 3 moles) of freshly distilled diethylaniline in 1 l. of dry petroleum ether (b.p. 40–60°) is placed in a 3-l. three-necked flask fitted with a sealed stirrer, an efficient reflux condenser, and a 500-ml. dropping funnel (Note 2) which is charged with a solution of 137.5 g. (87.5 ml., 1 mole) of freshly distilled phosphorus trichloride in 400 ml. of dry petroleum ether (b.p. 40–60°). The flask is cooled in a cold-water bath. With vigorous stirring (Note 3), the phosphorus trichloride solution is introduced at such a rate that the mixture boils gently towards the end of the addition. After the addition, which requires about 30 minutes, the mixture is heated under gentle reflux for about 1 hour with stirring. The suspension, containing a copious precipitate of diethylaniline hydrochloride, is then cooled and filtered with suction through a sintered-glass funnel. The cake of the amine salt is well compressed and washed with five 100-ml. portions of dry petroleum ether (b.p. 40–60°). The filtrate and washings are combined and concentrated by distillation at water-bath temperature through a 75-cm. Vigreux column. The residue is transferred to a pear-shaped flask and distilled under water-pump vacuum through a 75-cm. Vigreux column. After a small fore-run, the product is collected at 57–58°/16 mm. (51–52°/13 mm., 43–44°/10 mm.). The yield of colorless product is 138 g. (83%),  $n_D^{25}$  1.4104–1.4106,  $d_4^{20}$  0.963 (Note 4) and (Note 5).

### 2. Notes

1. It is important that the ethanol be thoroughly anhydrous. The checkers employed ethanol dried over magnesium ethoxide.<sup>2</sup>
2. It is convenient to connect the dropping funnel to the flask by a piece of 20-mm. glass tubing about 10 cm. long which is sleeved into the neck of the flask by a section of rubber tubing. By this means, the rate of introduction of the phosphorus trichloride solution may be readily observed and clogging by the copious precipitate of diethylaniline hydrochloride is obviated.
3. If efficient mixing is not obtained, hydrogen chloride may be liberated locally and one of the ethyl groups eliminated as ethyl chloride with the resulting appearance of diethyl hydrogen phosphite in the final distillate.
4. The recovered petroleum ether and fore-run contain some of the product. By using the recovered petroleum ether in subsequent runs and adding the fore-run before the final distillation, the yield is increased to 86–90%.
5. Triisopropyl phosphite is prepared similarly, using anhydrous isopropyl alcohol in place of ethanol. It has the following properties: b.p. 43.5°/1.0 mm;  $n_D^{25}$  1.4080;  $d_4^{17}$  0.917.

### 3. Discussion

The method described here is essentially that of McCombie, Saunders, and Stacey<sup>3</sup> except that diethylaniline is employed in place of dimethylaniline or pyridine. Diethylaniline has the advantage that the hydrochloride formed in the reaction is very easily filtered and is non-hygroscopic. Triethyl phosphite has been prepared also from phosphorus trichloride and ethanol in the presence of other tertiary amines, such as tributylamine and triamylamine;<sup>4</sup> in the presence of ammonia,<sup>5</sup> aniline,<sup>6</sup> and ammonium carbamate.<sup>7</sup> It also has been obtained from the reaction of magnesium ethoxide with

phosphorus trichloride.<sup>8</sup>

This preparation is referenced from:

- Org. Syn. Coll. Vol. 4, 325
- Org. Syn. Coll. Vol. 6, 448

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## References and Notes

1. Chemical Defence Experimental Station, Porton, Nr. Salisbury, Wilts, England.
  2. Fieser, *Experiments in Organic Chemistry*, 3rd ed., p. 286, D. C. Heath and Company, Boston, Massachusetts, 1955.
  3. McCombie, Saunders, and Stacey, *J. Chem. Soc.*, **1945**, 381.
  4. Marshall (to Monsanto Chemical Co.), U. S. pat. 2,848,474 [*C. A.*, **53**, 1144 (1959)].
  5. Boyer and Mangham (to Virginia-Carolina Chemical Corp.), U. S. pat. 2,678,940 [*C. A.*, **49**, 4704 (1955)].
  6. VEB Farbenfabrik Wolfen (by Maier-Bode and Kötz), Ger. pat. 1,028,554 [*C. A.*, **54**, 10860 (1960)].
  7. Reetz (to Monsanto Chemical Co.), U. S. pat. 2,859,238 [*C. A.*, **54**, 1299 (1960)].
  8. Mel'nikov, Mandel'baum, and Bakanova, *Zhur. Obshchei Khim.*, **28**, 2473 (1958) [*C. A.*, **53**, 3032 (1957)].
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## Appendix Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

petroleum ether

ethanol (64-17-5)

hydrogen chloride (7647-01-0)

ammonia (7664-41-7)

aniline (62-53-3)

pyridine (110-86-1)

isopropyl alcohol (67-63-0)

phosphorus trichloride (7719-12-2)

ammonium carbamate (1111-78-0)

dimethylaniline (121-69-7)

diethylaniline (91-66-7)

magnesium ethoxide (2414-98-4)

ethyl chloride (75-00-3)

triisopropyl phosphite (116-17-6)

Triethyl phosphite (122-52-1)

Ethyl phosphite

diethylaniline hydrochloride

diethyl hydrogen phosphite (762-04-9)

triethylamine (621-77-2)

tributylamine (102-82-9)