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.

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.

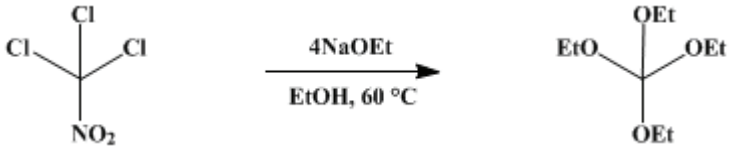
These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

DOI:10.15227/orgsyn.032.0068

Organic Syntheses, Coll. Vol. 4, p.457 (1963); Vol. 32, p.68 (1952).

ETHYL ORTHOCARBONATE

[Orthocarbonic acid, tetraethyl ester]



Submitted by John D. Roberts and Robert E. McMahon[1].
Checked by William S. Johnson and William E. Loeb.

1. Procedure

This preparation should be conducted in a hood to avoid exposure to chloropicrin.

A solution of sodium ethoxide is prepared under nitrogen from 70 g. (3.04 g. atoms) of sodium and 2 l. of absolute ethanol (Note 1) in a 3-l. three-necked flask which is equipped with mechanical stirrer, efficient reflux condenser, dropping funnel, and a thermometer which dips below the level of the liquid in the flask. Chloropicrin (100 g., 0.61 mole) (Note 2) is placed in the dropping funnel, and the stirred solution is heated to 58–60° with a water bath. The chloropicrin is added at a rate of 30–35 drops per minute until the reaction becomes self-sustaining (about 20 minutes), at which point the water bath is removed and the balance of the chloropicrin is added at a rate sufficient to maintain the temperature at 58–60° (Note 3). When the addition, which requires nearly 2 hours, is complete, the stirrer is stopped and the mixture is allowed to stand overnight.

The flask is connected to a 2 by 50 cm. Vigreux column equipped with a total-reflux partial take-off head, and all but about 400 ml. of the ethanol is removed at 200 mm. pressure with a reflux ratio greater than 5:1 (Note 4).

The residue is cooled, diluted with 1.2 l. of water, and transferred to a 2-l. separatory funnel. The organic layer is separated, washed with 200 ml. of saturated salt solution, and dried over anhydrous magnesium sulfate. The aqueous layer is extracted with a total of 800 ml. of ether used in several small portions. The ethereal extracts are combined, washed first with 500 ml. of water then with 500 ml. of saturated salt solution, and finally dried over anhydrous magnesium sulfate. The ether is removed through a 1.8 by 25 cm. glass-helix-packed fractionating column with a total-reflux partial take-off head. The residue is combined with the balance of the crude product and distilled through the fractionating column at atmospheric pressure. The yield of ethyl orthocarbonate is 54–57.5. g. (46–49%); b.p. 158–161°; n_D^{25} 1.3905–1.3908.

2. Notes

1. The absolute ethanol was a good commercial grade and contained less than 0.1% of water according to the paraffin-oil test.[2]
2. Chloropicrin is a skin irritant and a lachrymator. No difficulty was experienced when the preliminary steps were carried out in a good hood.
3. Care should be taken to regulate the temperature and rate of addition of chloropicrin as specified in order to avoid accumulation of unreacted chloropicrin in the reaction mixture during the induction period; otherwise the reaction, which is strongly exothermic, may get out of control.
4. A water bath should be used as a heat source to avoid over-heating, which leads to lowered yields. This distillation should be carried out carefully to prevent loss of product by co-distillation with the ethanol.

3. Discussion

The above procedure is essentially that of Tieckelmann and Post.[3] Ethyl orthocarbonate has been prepared by the reaction of chloropicrin and sodium ethoxide by Bassett[4] and Röse.[5] Thiocarbonyl perchloride has been reported[3,6] to react with sodium ethoxide to give good yields of ethyl orthocarbonate.

References and Notes

1. Massachusetts Institute of Technology, Cambridge, Massachusetts.
2. Robertson, *Laboratory Practice of Organic Chemistry*, p. 177, The Macmillan Company, New York, 1943.
3. Tieckelmann and Post, *J. Org. Chem.*, **13**, 265 (1948).
4. Bassett, *Ann.*, **132**, 54 (1864).
5. Röse, *Ann.*, **205**, 249 (1880).
6. Connolly and Dyson, *J. Chem. Soc.*, **1937**, 827.

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

chloropicrin

Thiocarbonyl Perchloride

ethanol (64-17-5)

ether (60-29-7)

nitrogen (7727-37-9)

sodium (13966-32-0)

sodium ethoxide (141-52-6)

magnesium sulfate (7487-88-9)

Ethyl orthocarbonate

Orthocarbonic acid, tetraethyl ester (78-09-1)