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.

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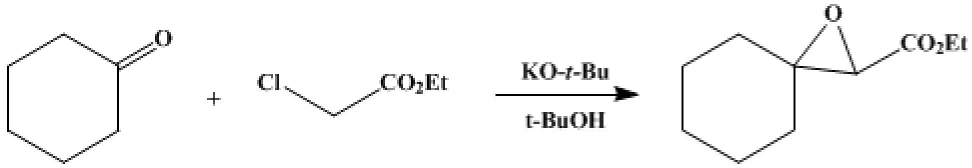
ETHYL β,β-PENTAMETHYLENEGLYCIDATE

[1-Oxaspiro[2.5]octane-2-carboxylic acid, ethyl ester]



Submitted by Richard H. Hunt, Leland J. Chinn, and William S. Johnson[1].
Checked by N. J. Leonard and F. P. Hauck, Jr..

1. Procedure

The reaction is conducted in a 500-ml. round-bottomed three-necked flask to which are attached (ground-glass joints) a rubber slip-sleeve-sealed wire stirrer, a thermometer, and a pressure-equalized dropping funnel. The top of the dropping funnel is connected to a system for exhausting and filling with nitrogen (p. 133). The apparatus is flame-dried at reduced pressure, and the flask is charged with 14.50 g. (0.148 mole) of freshly distilled cyclohexanone and 18.15 g. (0.148 mole) of freshly distilled ethyl chloroacetate. A solution of 6.0 g. (0.153 g. atom) of potassium in 125 ml. of dry *tert*-butyl alcohol (Note 1) and (Note 2) is introduced into the dropping funnel, and the system is exhausted and filled with nitrogen. The flask is cooled with an ice bath, stirring is commenced, and the solution of potassium *tert*-butoxide is added from the dropping funnel over a period of about 1.5 hours, the temperature of the reaction mixture being maintained at 10–15°. After the addition is complete, the mixture is stirred for an additional 1–1.5 hours at about 10°. Most of the *tert*-butyl alcohol is removed by distillation from the reaction flask at reduced pressure (water aspirator) and a bath temperature of 100°. The oily residue is taken up in ether. The ether solution is washed with water, then with saturated aqueous sodium chloride solution, and is finally dried over anhydrous sodium sulfate. The residue obtained on evaporation of the ether is distilled through a 6-in. Vigreux column to give 22.5–26.0 g. (83–95% yield) of colorless glycidic ester, b.p. 134–137°/21 mm., 147–152°/30 mm., n_D^{25} 1.4568–1.4577 (Note 3).

2. Notes

1. The preparation of potassium *tert*-butoxide is carried out according to a procedure already described (p.132). Particular attention should be paid to the precautions in handling potassium.
2. The *tert*-butyl alcohol may be dried over sodium (p.134). Scrupulously dry *tert*-butyl alcohol may be prepared by distilling alcohol thus treated from calcium hydride (about 1 g./4 l.), obtainable from Metal Hydrides, Inc.
3. This material is of satisfactory quality, as shown by its conversion to solid derivatives in good yield.[2]

3. Discussion

Ethyl β,β-pentamethyleneglycidate has been prepared in 65% yield by the condensation of cyclohexanone with ethyl chloroacetate in the presence of sodium ethoxide,[3,4] and in 50% yield in the presence of sodium in xylene.[4,5] The present procedure employs potassium *tert*-butoxide as the condensing agent.[2]

References and Notes

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

ether (60-29-7)

Cyclohexanone (108-94-1)

sodium chloride (7647-14-5)

sodium sulfate (7757-82-6)

nitrogen (7727-37-9)

sodium (13966-32-0)

sodium ethoxide (141-52-6)

Ethyl chloroacetate (105-39-5)

potassium (7440-09-7)

xylene (106-42-3)

tert-butyl alcohol (75-65-0)

Ethyl β,β-pentamethyleneglycidate,
1-Oxaspiro[2.5]octane-2-carboxylic acid, ethyl ester (6975-17-3)

calcium hydride (7789-78-8)

potassium tert-butoxide (865-47-4)