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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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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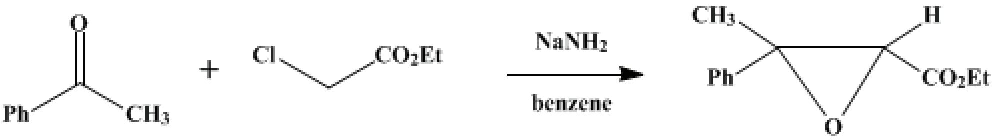
PHENYLMETHYLGLYCIDIC ESTER

[Hydrocinnamic acid, α,β-epoxy-β-methyl-, ethyl ester]



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1. Procedure

To a mixture of 120 g. (118.5 ml., 1 mole) of acetophenone (Note 1), 123 g. (109 ml., 1 mole) of ethyl chloroacetate, and 200 ml. of dry benzene in a 1-l. three-necked round-bottomed flask, fitted with a stirrer and low-temperature thermometer, is added, over a period of 2 hours, 47.2 g. (1.2 moles) of finely pulverized sodium amide. The temperature is kept at 15–20° by external cooling (Note 2). After the addition has been completed, the mixture is stirred for 2 hours at room temperature, and the reddish mixture is poured upon 700 g. of cracked ice, with hand stirring. The organic layer is separated and the aqueous layer extracted once with 200 ml. of benzene. The combined benzene solutions are washed with three 300-ml. portions of water, the last one containing 10 ml. of acetic acid. The benzene solution is dried over 25 g. of anhydrous sodium sulfate, filtered, the drying agent rinsed with a little dry benzene, and, after removal of the solvent, the residue is fractionated under reduced pressure, using a modified Claisen flask. The fraction boiling at 107–113°/3 mm. is collected separately and used for the preparation of hydratropaldehyde (p. 733). Redistillation yields a product which boils at 111–114°/3 mm. (Note 3). The yield is 128–132 g. (62–64%) (Note 4).

2. Notes

1. The practical grades of ketone and ester were used.
2. The reaction is strongly exothermic, and much ammonia is evolved.
3. Other boiling points are 272–275°/760 mm. with decomposition; 153–159°/20 mm.; and 147–149°/12 mm.
4. There are several side reactions which reduce the yield. There are always unchanged ketone and ester in the low-boiling fraction, and also some chlorocinnamic ester.

3. Discussion

This is an example of a general reaction by which haloesters are condensed with ketones by means of sodium,[1] sodium ethoxide,[2,3] or sodium amide.[4,5,6]

This preparation is referenced from:

- Org. Syn. Coll. Vol. 3, 733

References and Notes

1. Erlenmeyer, *Ann.*, **271**, 161 (1892).
2. Darzens, *Compt. rend.*, **139**, 1215 (1904).
3. Dutta, *J. Indian Chem. Soc.*, **18**, 235 (1941) [*C. A.*, **36**, 761 (1942)].
4. Claisen and Feyerabend, *Ber.*, **38**, 702 (1905).
5. I. G. Farbenind. A.-G., Ger. pat. 591,452 [*Frdl.*, **19**, 288 (1934)] [*C. A.*, **28**, 2367 (1934)].

6. I. G. Farbenind. A.-G., Ger. pat. 602,816 [*Frdl.*, **20**, 217 (1935)] [*C. A.*, **29**, 1438 (1935)].

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

Phenylmethylglycidic ester

acetic acid (64-19-7)

ammonia (7664-41-7)

Benzene (71-43-2)

sodium sulfate (7757-82-6)

Acetophenone (98-86-2)

sodium (13966-32-0)

sodium ethoxide (141-52-6)

Ethyl chloroacetate (105-39-5)

sodium amide (7782-92-5)

hydratropaldehyde (93-53-8)

Hydrocinnamic acid, α,β-epoxy-β-methyl-, ethyl ester (77-83-8)