



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.

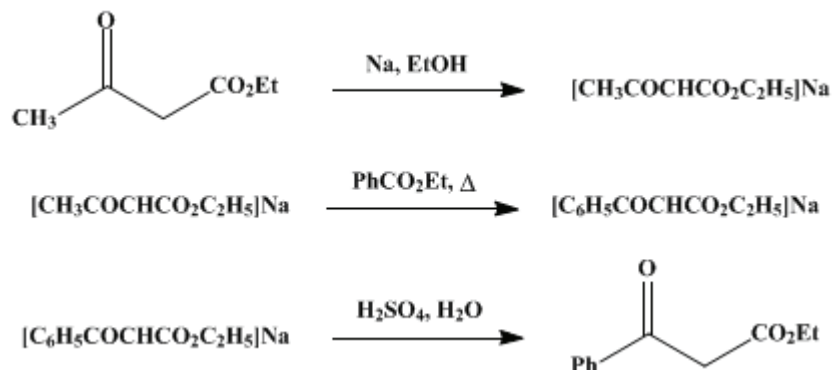
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 3, p.379 (1955); Vol. 23, p.35 (1943).

ETHYL BENZOYLACETATE

[Acetic acid, benzoyl-, ethyl ester]



Submitted by S. M. McElvain and K. H. Weber.

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1. Procedure

A 2-l. three-necked flask is mounted on a steam bath and fitted with a reflux condenser, a separatory funnel, and an efficient sealed stirrer. In the flask is placed 600 ml. of absolute **ethanol**, and to this is added gradually 46 g. (2 gram atoms) of clean **sodium** cut into small pieces. The **sodium ethoxide** solution is stirred and cooled to room temperature, after which 267 g. (260 ml., 2.05 moles) of **ethyl acetoacetate** (Note 1) is added slowly through the separatory funnel. The reflux condenser is then replaced by a short still head, and the **ethanol** is removed by distillation at approximately room temperature and under the pressure of a water pump. When approximately half the **ethanol** has been removed, sufficient sodium enolate precipitates so that stirring has to be discontinued. When the residue appears dry (after about 2 hours) the last traces of **ethanol** are removed by heating for an hour on the steam bath under a pressure of 2 mm. The flask is allowed to cool to room temperature under reduced pressure.

To the cooled residue of sodium enolate is added 600 g. (570 ml., 4 moles) of **ethyl benzoate**. The steam bath is replaced by an oil bath, and the temperature of the bath is raised to 140–150° and maintained there for 6 hours. Then, over a period of another hour, the temperature of the bath is gradually raised to 180° (Note 2). The distillate that is collected during this period of heating amounts to 200–210 g. and consists chiefly of **ethyl acetate** and **ethanol**.

The reaction mixture is cooled, 250 ml. of water is added, and the mixture is made acid to litmus by addition of a cooled solution of 100 g. of concentrated **sulfuric acid** in 200 ml. of water. Chipped ice is added if necessary to keep the mixture cool. The upper ester layer is separated, and the aqueous layer is extracted with 200 ml. of **ether**. The combined **ether** and ester layers are shaken with 350 ml. of a saturated **sodium bicarbonate** solution until no more **carbon dioxide** is evolved, and then the organic layer is washed with 200 ml. of water. The water layer is combined with the **sodium bicarbonate** solution and extracted with 400 ml. of **ether**. The combined **ether** and ester layers are dried over **sodium sulfate**. The **ether** is removed by distillation on the steam bath, and the excess **ethyl benzoate** and acetoacetic ester (Note 3) are then removed by distillation under reduced pressure through a 15-cm. fractionating column. Finally, the ethyl benzoylacetate is distilled (Note 3) at 101–106° /1 mm. (130–135° /3 mm.). The yield of ester boiling over a 5° range is 190–210 g. (50–55% based on the **ethyl acetoacetate**).

2. Notes

1. Commercial **ethyl acetoacetate** was distilled, and the fraction boiling at 68–69° /11 mm. was used.

2. During the last hour of heating about 20 g. of the [ethyl acetate-ethanol](#) mixture distilled.
3. A mixture of [ethyl acetoacetate](#) and [ethyl benzoate](#) (100–150 g.) was collected at 75–90° /12 mm., after which 250–300 g. of pure [ethyl benzoate](#), b.p. 90–93° /12 mm., was recovered. These products were removed through a 15-cm. fractionating column. The remaining [ethyl benzoylacetate](#) was distilled through a short still head without a fractionating column.

3. Discussion

Methods of preparation are listed in an earlier volume.¹ In addition [ethyl benzoylacetate](#) has been prepared by the reaction of [benzoyl chloride](#) with the magnesium enolate of malonic ester² and subsequent decomposition with [β-naphthalenesulfonic acid](#),³ and by the condensation of [acetophenone](#) with [ethyl carbonate](#) in the presence of [sodium hydride](#).⁴

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 4, 415](#)

References and Notes

1. [Org. Syntheses Coll. Vol.2, 266 \(1943\)](#).
2. [Org. Syntheses Coll. Vol.2, 594 \(1943\)](#).
3. Riegel and Lilienfeld, *J. Am. Chem. Soc.*, **67**, 1273 (1945).
4. Swamer and Hauser, *J. Am. Chem. Soc.*, **72**, 1352 (1950).

Appendix

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

[ethyl benzoylacetate](#)

[ethanol](#) (64-17-5)

[sulfuric acid](#) (7664-93-9)

[ethyl acetate](#) (141-78-6)

[ether](#) (60-29-7)

[sodium bicarbonate](#) (144-55-8)

[sodium sulfate](#) (7757-82-6)

[carbon dioxide](#) (124-38-9)

[β-naphthalenesulfonic acid](#) (120-18-3)

[Acetophenone](#) (98-86-2)

[benzoyl chloride](#) (98-88-4)

sodium (13966-32-0)

sodium ethoxide (141-52-6)

ethyl benzoate (93-89-0)

Ethyl acetoacetate (141-97-9)

Ethyl benzoylacetate,
Acetic acid, benzoyl-, ethyl ester (94-02-0)

ethyl carbonate

sodium hydride (7646-69-7)