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.

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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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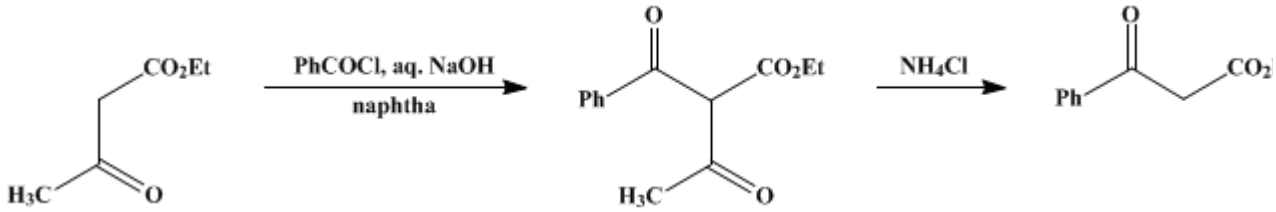
*Organic Syntheses, Coll. Vol. 4, p.415 (1963); Vol. 37, p.32 (1957).*

# ETHYL BENZOYLACETATE

## [Acetic acid, benzoyl-, ethyl ester]




Submitted by J. M. Straley and A. C. Adams[1].
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## 1. Procedure

In an open 3-l. three-necked flask, equipped with an efficient mechanical stirrer (Note 1) and two dropping funnels, are placed 500 ml. of water, 250 ml. of technical naphtha boiling at 95–110°, and 195 g. (1.5 moles) of freshly distilled ethyl acetoacetate. The mixture is cooled to 5° with a water-ice bath, and 65 ml. of 33% sodium hydroxide solution (33 g. sodium hydroxide in 100 g. solution) is added. As the temperature is maintained below 10° (Note 2) and the pH near 11 (Note 3), the mixture is stirred vigorously (Note 1), and there are added simultaneously from the two dropping funnels 230 g. (1.62 moles) of benzoyl chloride and 270 ml. of 33% sodium hydroxide solution. This addition should be made during about 2 hours. After addition is complete, the cooling bath is removed, and the mixture is allowed to come to room temperature. In order to ensure complete reaction, the mixture is finally brought to 35° during about 1 hour. The stirrer is then stopped, and the aqueous layer is separated and placed in a 2-l. Erlenmeyer flask (Note 4).

To the mixture is added 80 g. of technical ammonium chloride; then it is stirred slowly overnight. The specific gravity is brought to 1.13 by the addition of about 90 g. of sodium chloride, after which the mixture is transferred to a separatory funnel. About 10 ml. of benzene is used to rinse the flask and is added to the separatory funnel. The aqueous layer is withdrawn (Note 5), and the oil is washed three times with 100-ml. portions of cold water.

An additional 40 ml. of benzene is added (to accomplish drying on distillation), and the product is distilled under reduced pressure, using a short still head with no fractionating column (Note 6). The yield of ethyl benzoylacetate, b.p. 145–150°/12 mm., is 197–203 g. (68–71%) (Note 4).

## 2. Notes

1. Good stirring is essential. Slow stirring results in low yields.
2. Temperatures above 10° did not result in consistently good yields.
3. Lower pH did not give good yields. The pH was checked by means of filter paper, which had been dipped in an alcoholic solution of alizarin and then dried.
4. The naphtha layer may be used without further treatment for the next run. Yields of 76% have been obtained on such a second run without making allowance for recovered ethyl acetoacetate. Distillation of the naphtha layer together with the fore-run from the final distillation of ethyl benzoylacetate yields 11–14 g. of recovered ethyl acetoacetate and about 235 ml. of naphtha.
5. As high as 62 g. of benzoic acid has been recovered by acidification of the aqueous layer.
6. The chief impurity in the crude ester is a high-boiling material of unknown composition.

## 3. Discussion

The methods of preparation have been listed in two earlier volumes.[2,3] The present method, which is an adaptation of a process found in German documents,[4] is a shorter, more simple procedure which does

not require use of dry solvent or metallic sodium.

## References and Notes


1. Research Laboratories, Tennessee Eastman Company, Kingsport, Tennessee.
2. *Org. Syntheses Coll. Vol.* **2**, 266 (1943).
3. *Org. Syntheses Coll. Vol.* **3**, 381 (1955).
4. B.I.O.S., *Final Rept.* **1149**, 115.


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

naphtha

Benzene (71-43-2)

ammonium chloride (12125-02-9)

sodium hydroxide (1310-73-2)

sodium chloride (7647-14-5)

Benzoic acid (65-85-0)

benzoyl chloride (98-88-4)

sodium (13966-32-0)

Ethyl acetoacetate (141-97-9)

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

alizarin (72-48-0)