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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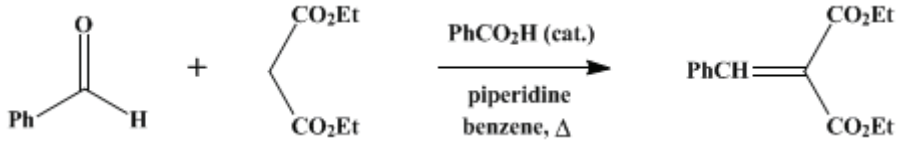
Organic Syntheses, Coll. Vol. 3, p.377 (1955); Vol. 25, p.42 (1945).

ETHYL BENZALMALONATE

[Malonic acid, benzal-, diethyl ester]



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1. Procedure

In a 1-l. round-bottomed flask, which is fitted with a Clarke-Rahrs column[1] with a unit for removing water and surmounted by a reflux condenser, are placed 100 g. (0.63 mole) of ethyl malonate (Note 1), about 72–76 g. of commercial benzaldehyde (Note 2), 2–7 ml. of piperidine (Note 3), and 200 ml. of benzene. The mixture is refluxed vigorously in an oil bath at 130–140° until no more water (total, 12–13 ml.) is collected; this operation requires 11–18 hours. After the mixture has been cooled, 100 ml. of benzene is added and the solution is washed with two 100-ml. portions of water, with two 100-ml. portions of 1 *N* hydrochloric acid, and then with 100 ml. of a saturated solution of sodium bicarbonate. The aqueous wash solutions are shaken with a single 50-ml. portion of benzene, the benzene extract is added to the original organic layer, and the organic solution is dried with 30 g. of anhydrous sodium sulfate. After the benzene has been removed under reduced pressure on a steam bath, the residue is distilled under reduced pressure from a 250-ml. modified Claisen flask well wrapped with asbestos. The yield of colorless ethyl benzalmalonate boiling at 140–142° /4 mm. (Note 4) is 137–142 g. (89–91%) (Note 5).

2. Notes

1. B.p. 94–96° /16mm. The checkers used redistilled ethyl malonate.
2. Commercial benzaldehyde which contains 2–8% of benzoic acid is eminently satisfactory. The acid content is determined (conveniently by titration of a sample in neutral ethanol with standard alkali), and a quantity of aldehyde containing 70 g. (0.66 mole) of benzaldehyde is used. The checkers used 76 g. of commercial benzaldehyde which contained 8% of benzoic acid. If pure benzaldehyde is employed, then 2 g. of benzoic acid should be added. It has been shown[2] that piperidine salts and not the free base act as the catalyst in the Knoevenagel reaction. The checkers obtained only a 71% yield with benzaldehyde containing less than 0.2% of benzoic acid.
3. The amount of piperidine that is employed depends on the benzoic acid content of the aldehyde; it should be slightly in excess of that required to neutralize the benzoic acid. About 1.2 ml. of piperidine per gram of acid is satisfactory.
4. Another boiling point is 179–181° /10 mm. The boiling points reported for ethyl benzalmalonate vary widely. The temperature observed depends on the degree of superheating and the rapidity of distillation.
5. Methyl benzalmalonate (b.p. 143–146° /2 mm., 169–171° /10 mm.) can be prepared in the same manner and in the same apparatus in yields of 90–94%.

3. Discussion

Ethyl benzalmalonate has been prepared by the esterification of benzalmalonic acid in the presence of concentrated sulfuric acid;[3] by the action of benzal chloride on sodiomalonic ester;[4] by the condensation of benzaldehyde and malonic ester in the presence of hydrogen chloride,[5,6] acetic anhydride,[7] alcoholic piperidine or ammonia,[8] or aluminum chloride,[9] and by the action of phenylmagnesium bromide on hydroxymethylene malonic ester.[10]

This preparation is referenced from:

- Org. Syn. Coll. Vol. 4, 80
- Org. Syn. Coll. Vol. 4, 804
- Org. Syn. Coll. Vol. 9, 314

References and Notes

1. Clarke and Rahrs, *Ind. Eng. Chem*., **18**, 1092 (1926).
2. Kuhn, Badstubner, and Grundmann, *Ber*., **69**, 98 (1936).
3. Stuart, *J. Chem. Soc*., **47**, 158 (1885).
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5. Claisen, *Ber*., **14**, 348 (1891).
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8. Ger. pat. 97,734 [*Frdl*., **5**, 906 (1898–1900)].
9. Breslow and Hauser, *J. Am. Chem. Soc*., **62**, 2385 (1940).
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Appendix
Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

sodiomalonic ester

hydroxymethylene malonic ester

ethanol (64-17-5)

sulfuric acid (7664-93-9)

hydrogen chloride,
hydrochloric acid (7647-01-0)

ammonia (7664-41-7)

Benzene (71-43-2)

acetic anhydride (108-24-7)

sodium bicarbonate (144-55-8)

sodium sulfate (7757-82-6)

Benzoic acid (65-85-0)

benzaldehyde (100-52-7)

aluminum chloride (3495-54-3)

piperidine (110-89-4)

Phenylmagnesium bromide (100-58-3)

ethyl malonate (1071-46-1)

Ethyl benzalmalonate

benzal chloride (98-87-3)

Malonic acid, benzal-, diethyl ester (5292-53-5)

Methyl benzalmalonate

benzalmalonic acid (584-45-2)