



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.

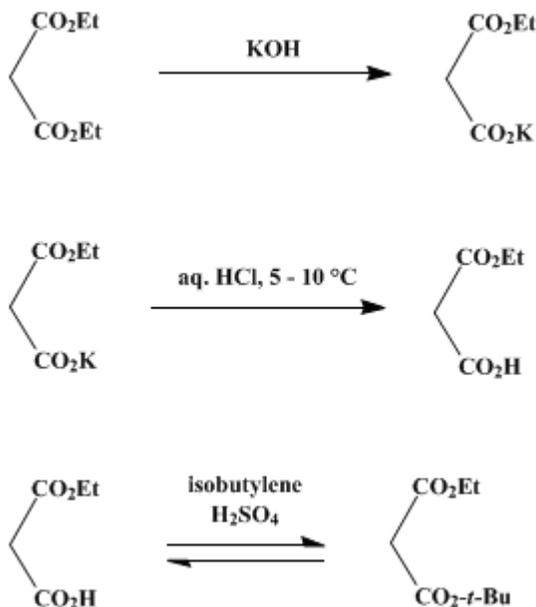
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 4, p.417 (1963); Vol. 37, p.34 (1957).

ETHYL *tert*-BUTYL MALONATE

[Malonic acid, *tert*-butyl ethyl ester]



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Checked by William S. Johnson and Duff S. Allen, Jr..

1. Procedure

A 2-l. three-necked flask, equipped with a sealed stirrer, a dropping funnel and a reflux condenser provided with a calcium chloride drying tube, is charged with 100 g. (0.625 mole) of **diethyl malonate** (Note 1) and 400 ml. of commercial absolute **ethanol**. Stirring is started, and a solution of 35 g. of **potassium hydroxide** pellets (Note 2) in 400 ml. of commercial absolute **ethanol** is added at room temperature during a period of 1 hour. A white crystalline precipitate forms during the addition, and, after all the hydroxide has been added, stirring is continued for an additional 2 hours. After the mixture has stood overnight, it is heated to boiling on the steam bath and filtered while hot with suction (Note 3). Precipitation of the **potassium ethyl malonate** is completed by cooling the filtrate in an ice bath. The salt is collected by suction filtration, washed with a small amount of **ether**, and dried under reduced pressure at room temperature. An additional amount of the potassium salt is obtained by concentrating the mother liquors on the steam bath to about 100–125 ml. The total yield is 80–87 g. (75–82%).

A 250-ml. three-necked flask provided with a stirrer, a dropping funnel, and a thermometer is charged with 80 g. (0.470 mole) of **potassium ethyl malonate** and 50 ml. of water. The mixture is cooled to 5° with an ice bath, and 40 ml. of concentrated **hydrochloric acid** is added over a 30-minute period while the temperature is maintained below 10°. The mixture is filtered with suction, and the precipitate of **potassium chloride** washed with 75 ml. of **ether**. The aqueous layer of the filtrate is separated and washed with three 50-ml. portions of **ether**. The combined **ether** solutions are dried over anhydrous **magnesium sulfate**; then most of the solvent is removed by distillation at atmospheric pressure, and the remainder under reduced pressure. Finally, the liquid residue of **monoethyl malonate** is dried at 50°/1 mm. for 1 hour. The yield is 58–62 g. (93–100%).

A 500-ml. Pyrex heavy-walled, narrow-mouthed pressure bottle is charged with 100 ml. of **ether** and 3.5 ml. of concentrated **sulfuric acid**. The solution is cooled with an ice bath to 5°, and 56 g. (0.42 mole) of **monoethyl malonate** and approximately 60 ml. (about 0.75 mole) of **isobutylene** (Note 4) are added. The bottle is immediately closed with a rubber stopper, which is clamped or wired in place, and

is shaken mechanically at room temperature overnight (Note 5). The bottle is chilled in an ice-salt bath and then opened. The reaction mixture is poured into a 1-l. Erlenmeyer flask containing a cooled solution of 50 g. of sodium hydroxide in 200 ml. of water and 200 g. of ice. The mixture is swirled a few times and then transferred to a separatory funnel (Note 6). The layers are separated, and the aqueous portion is extracted with two 75-ml. portions of ether. The organic layers are combined and dried over anhydrous magnesium sulfate. The solution is concentrated in a 125-ml. round-bottomed flask (Note 7) and distilled at reduced pressure through a 10-cm. Vigreux column. The fraction distilling at 98–100°/22 mm. or 107–109°/24 mm. is collected. The yield is 42–47 g. (53–58%), n_D^{25} 1.4128, n_D^{23} 1.4142.

2. Notes

1. Diethyl malonate as supplied by the Eastman Kodak Company (white label grade) or by Abbott Laboratories may be used without further purification.
2. Potassium hydroxide (85% minimum assay) obtained from the Mallinckrodt Chemical Works is satisfactory.
3. A steam-heated Büchner or a warmed sintered glass funnel is recommended.
4. Technical grade isobutylene supplied by Matheson Company was used. The isobutylene gas is liquefied by passage into a large test tube immersed in a Dry Ice-acetone bath.
5. For convenience, the reaction was carried out overnight. The reaction time may probably be shortened (compare the preparation of di-*tert*-butyl malonate, p. 261).
6. The mixture may be filtered, if necessary, to remove ice.
7. Since traces of acid will decompose the ester during the distillation, it is essential to wash the distillation apparatus carefully with a sodium hydroxide solution before rinsing and drying. The addition of some potassium carbonate or magnesium oxide before distillation is recommended (see Note 5 on p. 262).

3. Discussion

Ethyl *tert*-butyl malonate has been prepared by adding *tert*-butyl acetate and ethyl carbonate to sodium triphenylmethyl,² and from ethyl malonyl chloride and *tert*-butyl alcohol.³ The present procedure is an adaptation of that for the preparation of di-*tert*-butyl malonate (p. 261).

This preparation is referenced from:

- Org. Syn. Coll. Vol. 7, 213

References and Notes

1. The Upjohn Company, Kalamazoo, Michigan.
2. Hauser, Abramovitch, and Adams, *J. Am. Chem. Soc.*, **64**, 2714 (1942).
3. Breslow, Baumgarten, and Hauser, *J. Am. Chem. Soc.*, **66**, 1287 (1944).

Appendix

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

sodium triphenylmethyl

ethanol (64-17-5)

potassium carbonate (584-08-7)

sulfuric acid (7664-93-9)

hydrochloric acid (7647-01-0)

ether (60-29-7)

sodium hydroxide (1310-73-2)

potassium hydroxide (1310-58-3)

diethyl malonate (105-53-3)

monoethyl malonate (1071-46-1)

potassium chloride (7447-40-7)

magnesium sulfate (7487-88-9)

ethyl carbonate

magnesium oxide

isobutylene (9003-27-4)

tert-butyl alcohol (75-65-0)

potassium ethyl malonate (6148-64-7)

ethyl malonyl chloride

tert-Butyl acetate (540-88-5)

Di-tert-butyl malonate (541-16-2)

Ethyl tert-butyl malonate,
Malonic acid, tert-butyl ethyl ester (32864-38-3)