



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.

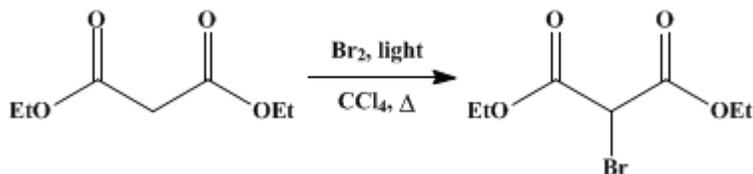
The procedures described in *Organic Syntheses* are provided as published and are conducted at one's own risk. *Organic Syntheses, Inc.*, its Editors, and its Board of Directors do not warrant or guarantee the safety of individuals using these procedures and hereby disclaim any liability for any injuries or damages claimed to have resulted from or related in any way to the procedures herein.

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. 1, p.245 (1941); Vol. 7, p.34 (1927).

ETHYL BROMOMALONATE

[Malonic acid, bromo-, ethyl ester]



Submitted by C. S. Palmer and P. W. McWherter.
Checked by Roger Adams and M. M. Brubaker.

1. Procedure

A 1-l. three-necked flask is fitted with a stirrer, a reflux condenser with a tube leading to a flask of water for absorption of [hydrogen bromide](#), and a separatory funnel with a stem drawn to a fine tip which reaches almost to the blades of the stirrer. In the flask are placed 160 g. (1 mole) of [diethyl malonate](#) ([Note 1](#)) and 150 cc. of [carbon tetrachloride](#). In the separatory funnel is placed 165 g. (53 cc., 1.03 moles) of dry [bromine](#) ([Note 2](#)). The stirrer is started, and a few cubic centimeters of [bromine](#) are run into the solution. A large electric bulb is held under the flask until the reaction starts. Then the rest of the [bromine](#) is added gradually at such a rate as to keep the liquid boiling gently. It is then refluxed until no more [hydrogen bromide](#) is evolved (about one hour).

The mixture is cooled and washed five times with 50-cc. portions of 5 per cent [sodium carbonate](#) solution. It is then distilled under reduced pressure, fractions being taken up to 130°/40 mm. and at 130–150°/40 mm. The residue amounts to about 20 g. ([Note 3](#)). The lower-boiling fraction is redistilled. The combined fractions boiling at 130–150°/40 mm. are redistilled under reduced pressure. The product boiling at 132–136°/33 mm. (121–125°/16 mm.) amounts to 175–180 g. (73–75 per cent of the theoretical amount). Redistillation of the low fractions gives about 15 g. more of the product.

2. Notes

- Commercial [diethyl malonate](#) distilled under reduced pressure and collected over a 3° range was used.
- Commercial [bromine](#) was dried by shaking with an equal volume of concentrated [sulfuric acid](#). A slight excess of [bromine](#) is used to insure complete bromination.
- A part of the higher-boiling fractions consists of [ethyl dibromomalonate](#) (W. W. Hartman, private communication).

3. Discussion

[Ethyl bromomalonate](#) can be prepared by the bromination of [diethyl malonate](#) either without a solvent¹ or in [carbon tetrachloride](#) as described in the procedure.

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 1, 271](#)
- [Org. Syn. Coll. Vol. 2, 273](#)

References and Notes

1. Knoevenagel, *Ber.* **21**, 1356 (1888).

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

sulfuric acid (7664-93-9)

hydrogen bromide (10035-10-6)

sodium carbonate (497-19-8)

bromine (7726-95-6)

carbon tetrachloride (56-23-5)

Ethyl bromomalonate,
Malonic acid, bromo-, ethyl ester

diethyl malonate (105-53-3)

ethyl dibromomalonate