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.

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.

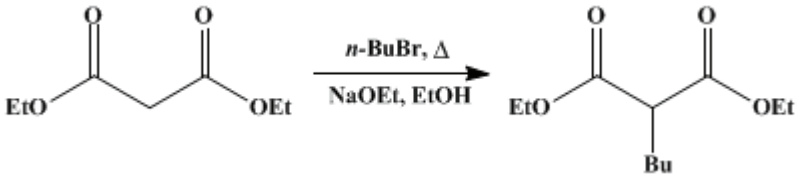
*These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.*

DOI:10.15227/orgsyn.004.0011

*Organic Syntheses, Coll. Vol. 1, p.250 (1941); Vol. 4, p.11 (1925).*

# ETHYL *n*-BUTYLMALONATE

## [Malonic acid, butyl-, ethyl ester]

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## 1. Procedure

A 5-l. round-bottomed flask, fitted with a rubber stopper holding a reflux condenser, a separatory funnel, and a mechanical stirrer, is clamped over a steam or water bath. In the flask is placed 2.5 l. of absolute alcohol (Note 1) and then there is added gradually, through the condenser, 115 g. (5 atoms) of clean sodium cut into pieces of suitable size. If the action becomes too violent, the mixture may be cooled by water poured over the outside of the flask. The sodium ethoxide solution is stirred, and cooled to about 50°, after which 825 g. (780 cc., 5.15 moles) of diethyl malonate (Note 2) is added slowly through the separatory funnel. To the clear solution is added gradually 685 g. (535 cc., 5.0 moles) of *n*-butyl bromide (Note 3). The reaction commences almost immediately and considerable heat is generated. If the addition is too rapid, the reaction may become violent enough to require cooling of the flask by pouring water over it. Up to this point, the time required is about two hours.

The reaction mixture is refluxed until neutral to moist litmus; this requires about two hours. The flask is then connected with a condenser set for distillation. As much alcohol as possible is distilled off by means of the steam or water bath. A period of about six hours is required for this distillation, and about 2 l. of alcohol is recovered.

The residue from which no more alcohol can be distilled is treated with about 2 l. of water and shaken thoroughly. The upper layer of *n*-butylmalonic ester is separated (Note 4) and distilled under diminished pressure from a 2- or a 3-l. Claisen flask. First a low-boiling portion is collected, consisting of alcohol, water, and butyl bromide; then a small intermediate fraction of unchanged malonic ester comes over; and finally *n*-butylmalonic ester boiling at 140–145°/40 mm., 130–135°/20 mm., and 235–240°/760 mm. The first fractions amount to less than 100 cc., while the main fraction weighs 860–970 g. (80–90 per cent of the theoretical amount).

## 2. Notes

1. The quality of the absolute alcohol used has a very marked effect upon the yield. It is desirable to reflux ordinary "absolute" alcohol with about one-twentieth of its weight of sodium and then to distil it directly into the flask in which it is to be used. See Note 2 on p. 249.
A trial run with alcohol of 98.4 per cent purity gave only a 66 per cent yield.
2. The malonic ester used should be redistilled, preferably under diminished pressure, and a 2° fraction used in the preparation. Ordinary commercial malonic ester contains up to 15 per cent of low-boiling impurities.
3. Redistilled *n*-butyl bromide (p. 28) boiling over a 1° range should be used.
4. It is not practical to filter off the sodium bromide either before or after the distillation of the alcohol, as the separation of the ester from the water layer is then very difficult.

## 3. Discussion

Ethyl *n*-butylmalonate can be prepared by the action of *n*-butyl halides on sodium malonic ester,[1]

and by the catalytic reduction of a mixture of butyraldehyde, malonic ester, and piperidine in the presence of Raney nickel.[2]

This preparation is referenced from:

- Org. Syn. Coll. Vol. 1, 258
- Org. Syn. Coll. Vol. 2, 93
- Org. Syn. Coll. Vol. 2, 194
- Org. Syn. Coll. Vol. 2, 284
- Org. Syn. Coll. Vol. 2, 416
- Org. Syn. Coll. Vol. 2, 487

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## References and Notes


1. Bischoff, Ber. **28**, 2622 (1895); Adams and Marvel, J. Am. Chem. Soc. **42**, 316 (1920); Levene and Taylor, J. Biol. Chem. **54**, 351 (1922); Bhide and Sudborough, J. Indian Inst. Sci. A, **8**, 89 (1925) [Chem. Zentr. I, 81 (1926)]; Dolique, Ann. chim. **15**, 439 (1931).
2. Wojcik and Adkins, J. Am. Chem. Soc. **56**, 2424 (1934).


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

alcohol (64-17-5)

n-butyl bromide (109-65-9)

sodium bromide (7647-15-6)

Raney nickel (7440-02-0)

sodium (13966-32-0)

piperidine (110-89-4)

sodium ethoxide (141-52-6)

butyraldehyde (123-72-8)

diethyl malonate (105-53-3)

Malonic acid, butyl-, ethyl ester,
ETHYL n-BUTYLMALONATE