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.

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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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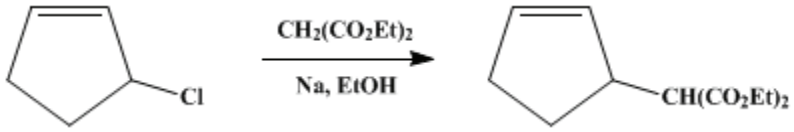
*Organic Syntheses, Coll. Vol. 4, p.291 (1963); Vol. 32, p.52 (1952).*

# DIETHYL Δ²-CYCLOPENTENYLMALONATE

## [2-Cyclopentene-1-malonic acid, diethyl ester]

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## 1. Procedure

Nine hundred and twenty-five milliliters of absolute ethanol (Note 1) is placed in a 2-l. three-necked round-bottomed flask, fitted with a mercury or glycerin-sealed stirrer (Note 2), dropping funnel, and reflux condenser. To this is added 46 g. (2 g. atoms)[2] of freshly cut sodium, a few pieces at a time and at such a rate that the reaction proceeds rapidly but the solvent does not reflux too vigorously. When most of the sodium has dissolved, a calcium chloride drying tube is fitted to the top of the condenser and 320 g. (2 moles) of redistilled diethyl malonate is added from the dropping funnel. Then 205 g. (2 moles) of 3-chlorocyclopentene (p. 42) (Note 3) is added at such a rate that a gentle reflux is maintained. Toward the end of the addition, it is desirable to test the reaction mixture with pH test paper, and the addition should be stopped if the solution becomes acidic.

When the addition is complete, the condenser is set downward for distillation, the stirring is continued, and most of the ethanol is removed by distillation on a steam bath (Note 4). After cooling, the reaction mixture is diluted with sufficient water to dissolve the salt, and the layers are separated. The aqueous layer is extracted with 50 ml. of ether. The ethereal solution is added to the ester, and the resulting solution is washed with saturated salt solution and dried over anhydrous magnesium sulfate. The ethereal solution is transferred to a Claisen flask, the solvent is evaporated, and the product is distilled under reduced pressure. The fraction boiling at about 85–140°/12 mm. is collected and redistilled through an efficient fractionating column (Note 5). The product distils at 130°/12 mm. (Note 6). The yield is about 276.5 g. (61%); $n_D^{20}$ 1.4536.

## 2. Notes

1. The preparation of absolute ethanol has been described earlier.[3]
2. The glycerin-sealed stirrer has been described earlier.[2]
3. It is not necessary to use redistilled 3-chlorocyclopentene; however, if large amounts of impurities are present, difficulty may be encountered in obtaining a pure product.
4. If a glycerin-sealed stirrer is used, the rate of solvent evaporation may be accelerated by means of gentle water-pump suction.
5. Careful fractionation is necessary in order to secure a pure product. The submitter used a 12-in. column packed with 1/8-in. glass helices. The fore-run should be redistilled to separate any ester it may contain.
6. Other boiling points are 140°/18 mm.; 97°/1 mm.

## 3. Discussion

Diethyl Δ²-cyclopentenylmalonate has been prepared by the alkylation of malonic ester with 3-chlorocyclopentene.[4,5,6,7,8]

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## References and Notes

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2. *Org. Syntheses Coll. Vol.* **3**, 368 (1955).
3. *Org. Syntheses Coll. Vol.* **1**, 259 (1941).
4. Noller and Adams, *J. Am. Chem. Soc.*, **48**, 2444 (1926).
5. Perkins and Cruz, *J. Am. Chem. Soc.*, **49**, 518 (1927).
6. Wagner-Jauregg and Arnold, *Ann.*, **529**, 274 (1937).
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## Appendix
## Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

Diethyl $\Delta^2$-cyclopentenylmalonate

ethanol (64-17-5)

ether (60-29-7)

sodium (13966-32-0)

diethyl malonate (105-53-3)

2-Cyclopentene-1-malonic acid, diethyl ester (53608-93-8)

magnesium sulfate (7487-88-9)

3-Chlorocyclopentene (96-40-2)

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