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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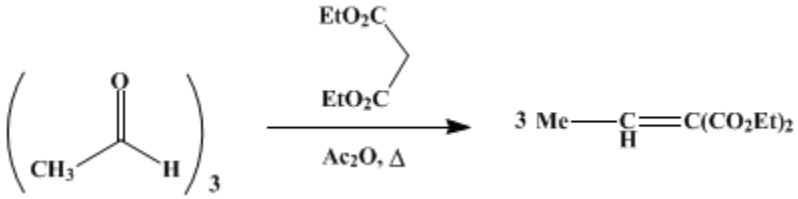
DIETHYL ETHYLIDENEMALONATE

[Malonic acid, ethylidene-, diethyl ester]



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1. Procedure

In a 1-l. three-necked flask, equipped with a thermometer and a reflux condenser, are placed 60 g. of paraldehyde (0.45 mole, equivalent to 1.35 moles of acetaldehyde) and 100 ml. (1.06 moles) of acetic anhydride. Ice water is circulated through the condenser, and the reaction mixture is protected from atmospheric moisture by a drying tube containing Drierite. The temperature of the mixture is raised slowly by heating with an electric mantle to 125°, at which point gentle refluxing begins. Then 100 g. (0.62 mole) of diethyl malonate is added in 15-ml. portions at a rate of 1 portion every 30 minutes. During the addition of diethyl malonate, the temperature gradually drops to about 100°, and the mixture is heated so as to maintain a reflux rate of 30–60 drops per minute. After the addition is complete, the reaction mixture is heated under reflux for 4 hours at the specified rate.

The reflux condenser is replaced by a Claisen distillation head, and the reaction mixture is distilled until the temperature of the vapor reaches 140°. The residue is transferred to a smaller flask and fractionated through a 30-cm. column packed with glass helices. A low-boiling fraction containing ethylidene diacetate and diethyl malonate is collected first, followed by 79–89.5 g. (68–77%) of diethyl ethylidenemalonate; b.p. 102–106°/10 mm.; n_D^{25} 1.4394 (Note 1) and (Note 2).

2. Notes

1. The submitter obtained a yield of 70% when three times the above quantities were used, in which case the diethyl malonate was added at a rate of 90 ml. per hour.
2. Horton[2] has reported that a higher yield of diethyl ethylidenemalonate has been obtained by the following procedure. A mixture of 50 g. of redistilled malonic ester, 50 g. of acetic anhydride and 28.5 g. of acetaldehyde, enclosed in a hydrogenation bomb, was mixed and heated at 100° for 24 hours without shaking. The bomb contents were transferred with the aid of benzene, and three pooled runs were distilled through a 15-in. Vigreux column at 18–20 mm. A fore-run of diethyl malonate was removed, and then 149.8 g. (86.2%) of diethyl ethylidenemalonate was collected at 106–109°/13 mm. The product was stored at 5°.

3. Discussion

Diethyl ethylidenemalonate has been prepared by heating acetaldehyde, diethyl malonate, and acetic anhydride;[3,4] by heating the same reagents plus zinc chloride;[5] by treating acetaldehyde and diethyl malonate with sodium ethoxide or piperidine;[6] and by heating diethyl malonate, ethylidene bromide, and ethanolic sodium ethoxide.[7]

References and Notes

1. National Institutes of Health, Bethesda, Maryland.

2. Horton, Private communication.
3. Komnenos, *Ann.*, **218**, 157 (1883).
4. Goss, Ingold, and Thorp, *J. Chem. Soc.*, **123**, 3353 (1923).
5. von Auwers and Eisenlohr, *J. prakt. Chem.*, [2] **84**, 101 (1911).
6. Higginbotham and Lapworth, *J. Chem. Soc.*, **123**, 1622 (1923).
7. Loevenich, Losen, and Dierichs, *Ber.*, **60**, 957 (1927).

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

acetaldehyde (75-07-0)

Benzene (71-43-2)

acetic anhydride (108-24-7)

piperidine (110-89-4)

sodium ethoxide (141-52-6)

zinc chloride (7646-85-7)

diethyl malonate (105-53-3)

Diethyl ethylidenemalonate,
Malonic acid, ethylidene-, diethyl ester (1462-12-0)

ethylidene diacetate (542-10-9)

ethylidene bromide (557-91-5)

paraldehyde (123-53-7)