



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](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.

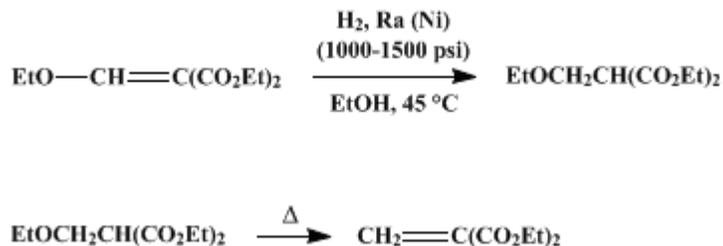
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*These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.*

*Organic Syntheses, Coll. Vol. 4, p.298 (1963); Vol. 38, p.22 (1958).*

## DIETHYL METHYLENEMALONATE

[Malonic acid, methylene-, diethyl ester]



Submitted by Wayne Feely and V. Boekelheide<sup>1</sup>.

Checked by Max Tishler, Barbara P. Birt, and Arthur A. Patchett.

### 1. Procedure

A solution of 108 g. (0.5 mole) of [diethyl ethoxymethylenemalonate](#) ([Note 1](#)) in 100 ml. of commercial absolute alcohol is placed in an apparatus for high-pressure hydrogenation together with 10 g. of [Raney nickel](#) catalyst ([Note 2](#)). The pressure in the bomb is raised to 1000–1500 lb. with [hydrogen](#), and the temperature is adjusted to 45° ([Note 3](#)). The bomb is shaken, and the reaction is allowed to proceed for 12–20 hours, during which time 0.5 mole of [hydrogen](#) is absorbed.

The apparatus is allowed to cool to room temperature, the pressure is released, and the catalyst is removed by filtration. Concentration of the filtrate under reduced pressure at room temperature yields a colorless oil ([Note 4](#)).

The residual oil is transferred to a distillation flask ([Note 5](#)), and the flask is carefully warmed with a small flame ([Note 6](#)). After a fore-run of [ethanol](#) is collected, the variable transformer controlling the heating tape is set at a voltage to give an internal temperature in the distilling head of 80–100° before distillation. The flask is then heated to effect slow distillation at atmospheric pressure. About 10–13 g. of fore-run is collected before the temperature of the distillate vapor reaches 200°. The main fraction (68–71 g., 79–82%) is collected between 200° and 216° as a colorless oil. For most purposes, the fore-run is sufficiently pure that it can be combined with the main fraction to give an over-all yield of 78–81 g. (91–94%) ([Note 7](#)). [Diethyl methylenemalonate](#) polymerizes on standing to a white solid, from which the monomer can be recovered by slow distillation. The [diethyl methylenemalonate](#) should be distilled just prior to use ([Note 8](#)).

### 2. Notes

1. [Diethyl ethoxymethylenemalonate](#) can be prepared by the method of Parham and Reed.<sup>2</sup> The submitters used [diethyl ethoxymethylenemalonate](#) obtained commercially from Kay-Fries Chemicals Inc., 180 Madison Avenue, New York 16, New York.

2. [Raney nickel](#) catalyst can be prepared by the method of Mozingo.<sup>3</sup> The submitters used [Raney nickel](#) catalyst obtained commercially from the Gilman Paint and Varnish Company, Chattanooga, Tennessee.

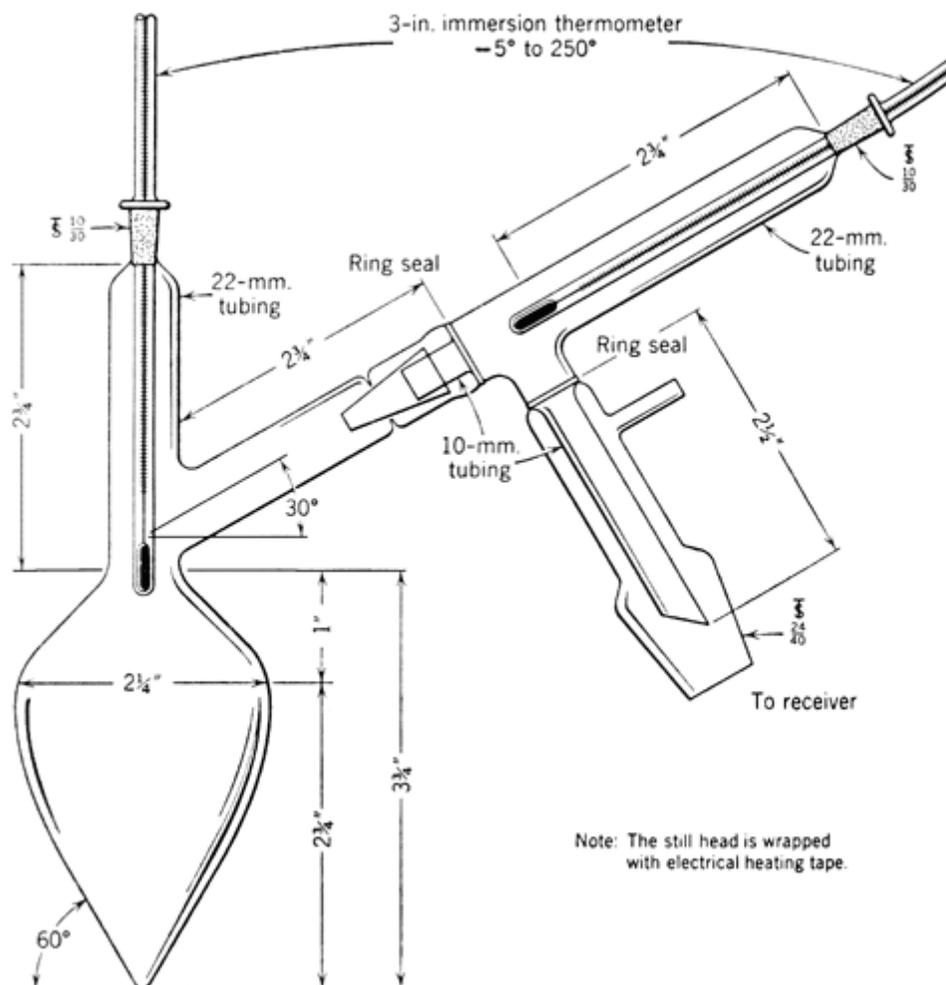
3. At higher temperatures (about 70°) the [diethyl ethoxymethylmalonate](#) formed tends to eliminate [ethanol](#), forming [diethyl methylenemalonate](#) which is hydrogenated to [diethyl methylmalonate](#).

4. This oil,  $n_D^{20}$  1.4254, is presumably [diethyl ethoxymethylmalonate](#), as evidenced by its infrared and ultraviolet absorption spectra. It is relatively stable and can be stored at room temperature without change. If the concentration of the filtrate under vacuum is carried out by heating on a steam bath instead of by keeping it at room temperature, the [diethyl ethoxymethylmalonate](#) undergoes elimination of [ethanol](#) to some extent, giving [diethyl methylenemalonate](#) directly. The yield of [diethyl methylenemalonate](#) obtained eventually is not altered by this procedure.

5. The distillation apparatus is shown in [Fig. 7](#). The upper part of the flask and the short column are

wrapped in electrical heater tape, which is operated during distillation of the product.

Fig. 7.



6. The elimination of ethanol is slightly exothermic. It is advisable to heat the flask cautiously with a small flame until the reaction starts and then to remove the flame until the reaction subsides.

7. The fore-run has a refractive index (usually about  $n_D^{22}$  1.4154) lower than that of the main fraction (about  $n_D^{22}$  1.4250). The combined fractions show refractive indices in the range  $n_D^{22}$  1.4210–1.4259.

8. When the solid polymer from the above preparation was slowly distilled to recover diethyl methylenemalonate, there was obtained 57 g. of colorless oil, b.p. 210–216° /730 mm.,  $n_D^{20}$  1.4220.

### 3. Discussion

Diethyl methylenemalonate was prepared first by Perkin<sup>4</sup> from formaldehyde and malonic ester, and more recently a study has been made of the effect of various catalysts on this system.<sup>5</sup> An alternative procedure involving the reaction of methylene chloride or iodide with sodiomalonic ester has been developed by Tanatar.<sup>6</sup> Diethyl methylenemalonate also is formed when hexaethyl pentane-1,1,3,3,5,5-hexacarboxylate is treated with methylene iodide and sodium ethoxide,<sup>7</sup> or when methyl chloromethyl ether is caused to react with sodiomalonic ester.<sup>8</sup> Diethyl methylenemalonate has been obtained from paraformaldehyde<sup>9</sup> and vapor and liquid reactions of formaldehyde with diethyl malonate in the presence of various catalysts.<sup>10</sup>

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### References and Notes

1. University of Rochester, Rochester, New York.

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3. *Org. Syntheses Coll. Vol. 3*, 181 (1955).
4. Perkin, *Ber.*, **19**, 1053 (1886).
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8. Vasiliu and Barbulescu, *Analele univ. C. I. Parhon Bucuresti, Ser. stiint. nat.*, No. **16**, 99 (1957) [*C. A.*, **53**, 1238 (1959)].
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**Appendix Chemical Abstracts Nomenclature  
 (Collective Index Number);  
 (Registry Number)**

methylene chloride or iodide

ethanol (64-17-5)

hydrogen (1333-74-0)

formaldehyde (50-00-0)

Raney nickel (7440-02-0)

sodium ethoxide (141-52-6)

diethyl malonate (105-53-3)

Methylene iodide (75-11-6)

methyl chloromethyl ether (107-30-2)

diethyl methylmalonate (609-08-5)

diethyl ethoxymethylenemalonate (87-13-8)

Diethyl methylenemalonate,  
 Malonic acid, methylene-, diethyl ester (3377-20-6)

diethyl ethoxymethylmalonate

hexaethyl pentane-1,1,3,3,5,5-hexacarboxylate

paraformaldehyde (30525-89-4)