



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.

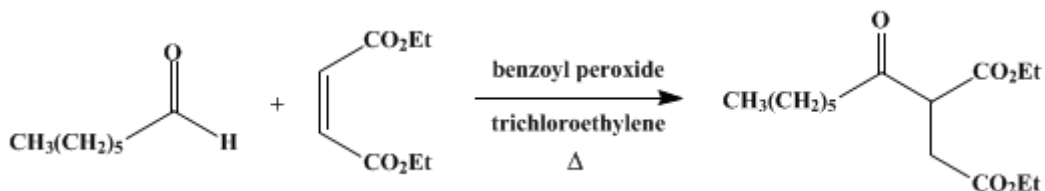
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*These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.*

*Organic Syntheses, Coll. Vol. 4, p.430 (1963); Vol. 34, p.51 (1954).*

## ETHYL ENANTHYLSUCCINATE

[Succinic acid, heptanoyl-, diethyl ester]



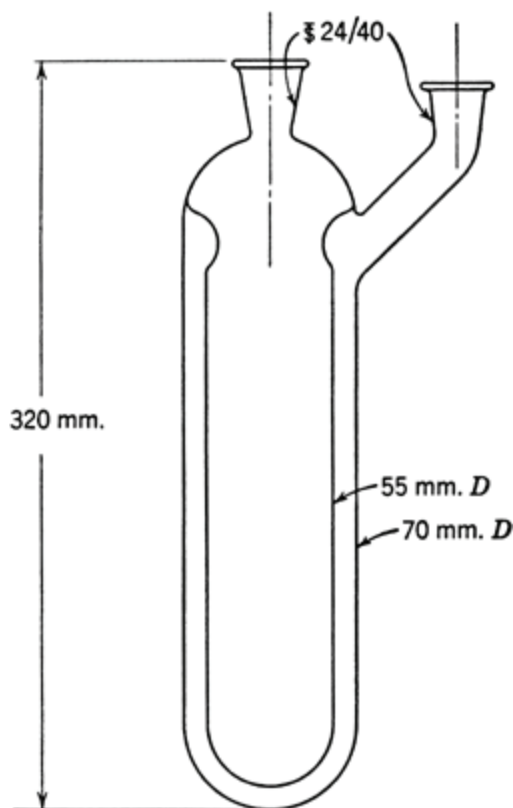
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Checked by T. L. Cairns and R. D. Cramer.

### 1. Procedure

A mixture of 228 g. (2.0 moles) of [enanthaldehyde](#) ([Note 1](#)) and 172 g. (1.0 mole) of [ethyl maleate](#) ([Note 2](#)) is placed in a jacketed flask ([Fig. 9](#)) ([Note 3](#)) with condensers attached to the flask and the jacket openings. The jacket is charged with [trichloroethylene](#) ([Note 4](#)), which is heated to reflux, and, when the reaction mixture reaches 84–85°, 0.5 g. of [benzoyl peroxide](#) is added to the mixture through the condenser. After 3–8 hours an additional 0.5-g. portion of [benzoyl peroxide](#) is added, and heating is continued for a total of 18–24 hours ([Note 5](#)).

**Fig. 9.**



The reaction mixture is distilled through a short (8- to 12-in.) Vigreux column to give 108–111 g. of recovered [enanthaldehyde](#), b.p. 64–65°/38 mm.; 6–16 g. of an intermediate fraction, b.p. 82–128°/1 mm.; and 202–216 g. (71–76% yield) of [ethyl enanthylsuccinate](#), b.p. 119–122°/0.7 mm.,  $n_D^{25}$  1.4392–1.4398 ([Note 6](#)), ([Note 7](#)), and ([Note 8](#)).

## 2. Notes

1. Good-quality [enanthaldehyde](#) such as the white label grade supplied by Eastman Kodak Company was distilled before use. It is best stored in a brown bottle under [nitrogen](#) for protection against oxidation.
  2. [Ethyl maleate](#) from Commercial Solvents Corporation, Terre Haute, Indiana, was distilled before use. [Ethyl fumarate](#) can be used also, but the yield of product is lower since a much greater proportion of high-boiling compounds is obtained. Aldehydes do not undergo free-radical addition to [maleic anhydride](#) under these conditions.
  3. Although this piece of apparatus is not essential, it provides a convenient means of controlling the temperature for a mildly exothermic reaction which must be carried out overnight without close supervision. The submitters carried out one experiment in an ordinary apparatus heated by a mantle. The poorer temperature control (70–91°) resulted in a yield of only 44%.
  4. Any other stable liquid having a boiling point in the neighborhood of 80–90° could be substituted for [trichloroethylene](#).
  5. The reaction time is not critical. For the sake of convenience the reaction can be started early in the day, the second portion of peroxide added before leaving in the evening, and heating discontinued upon arrival the following morning.
  6. The submitters collected material boiling in the range 128–150°/1 mm. and found this product to be satisfactory for the preparation of [γ-oxocaproic acid](#) (Note 7).
  7. The submitters state that [ethyl enanthylsuccinate](#) can be hydrolyzed and decarboxylated to [γ-oxocaproic acid](#). The reaction is carried out by heating 57 g. of the keto ester with a solution of 140 ml. of concentrated [sulfuric acid](#) in 250 ml. of water. The mixture is stirred while the [ethanol](#) is removed gradually by distillation over a period of 3 hours. The acid is taken up in [benzene](#), extracted from the [benzene](#) with aqueous alkali, and liberated from the alkaline solution by acidification with concentrated [hydrochloric acid](#). After recrystallization from 50% [ethanol](#) about 29 g. (78% yield) of [γ-oxocaproic acid](#) is obtained as colorless crystals, m.p. 69–70°.
- The submitters also state that [γ-caprilactone](#) can be prepared by hydrogenation of 50 g. of [γ-oxocaproic acid](#) in 150 ml. of [ethanol](#) over 5 g. of [Raney nickel](#) at 135° and 1000 p.s.i. Filtration and distillation gives about 38 g. (83% yield) of [γ-caprilactone](#), b.p. 109–110°/2.5 mm.,  $n_D^{25}$  1.4470.
8. A number of other acylsuccinic esters can be prepared in a similar fashion from the appropriate saturated aliphatic aldehydes and maleic esters.<sup>2,3</sup> The procedure is equally adaptable to the preparation of  $\alpha$ -acyltricarballic esters from aldehydes and aconitates<sup>2</sup>. Good temperature control (80–90°) is most important for success in these reactions.

## 3. Discussion

[Ethyl enanthylsuccinate](#) has been prepared by the free-radical addition of [enanthaldehyde](#) to [ethyl maleate](#).<sup>2</sup>

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## References and Notes

1. Monsanto Chemical Company, Dayton, Ohio.
2. Patrick, *J. Org. Chem.*, **17**, 1009 (1952).
3. Ladd, U. S. pat. 2,577,133 [*C. A.*, **46**, 6147 (1952)].

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## Appendix

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

[γ-caprilactone](#)

ethanol (64-17-5)

sulfuric acid (7664-93-9)

hydrochloric acid (7647-01-0)

Benzene (71-43-2)

nitrogen (7727-37-9)

Raney nickel (7440-02-0)

ethyl fumarate (2459-05-4)

benzoyl peroxide (94-36-0)

maleic anhydride (108-31-6)

trichloroethylene (79-01-6)

Ethyl enanthylsuccinate

Succinic acid, heptanoyl-, diethyl ester (41117-78-6)

enanthaldehyde (111-71-7)

ethyl maleate (3990-03-2)

$\gamma$ -oxocaproic acid