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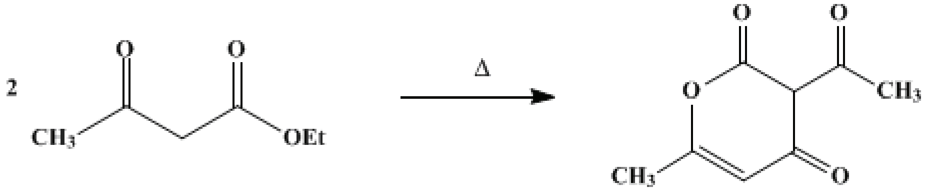
These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

DOI:10.15227/orgsyn.020.0026

Organic Syntheses, Coll. Vol. 3, p.231 (1955); Vol. 20, p.26 (1940).

DEHYDROACETIC ACID



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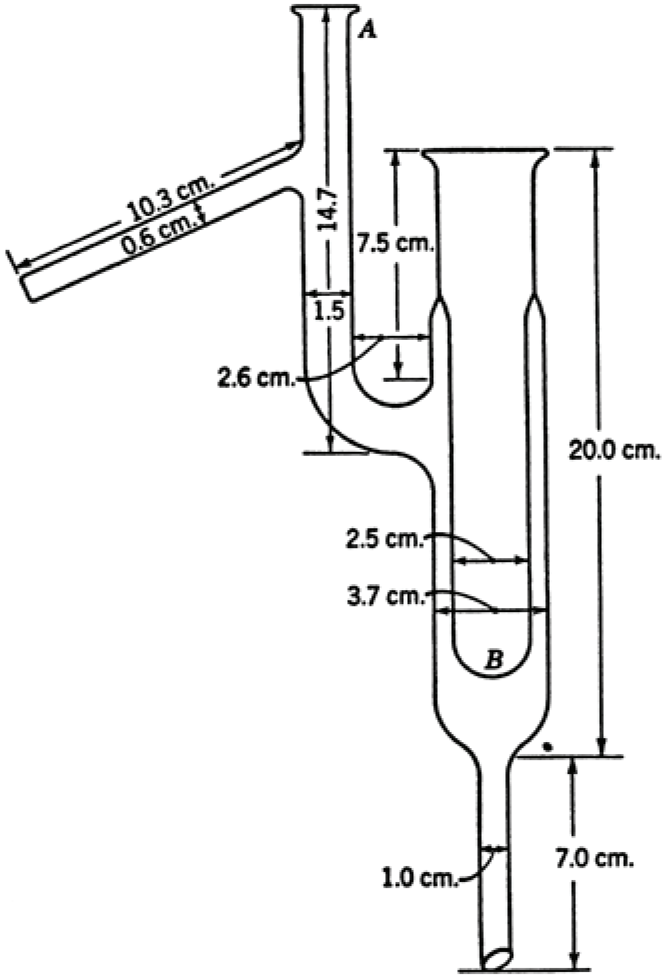
1. Procedure

A 250-ml. round-bottomed flask is fitted with a thermometer reaching nearly to the bottom (Note 1) and a three- or four-bulb fractionating column without a side arm, at the upper end of which is attached a partial condenser (Fig. 11) (Note 2). The side arm (*A*) of the partial condenser carries a 110° thermometer and is connected to a condenser set for downward distillation. The inside container (*B*) of the partial condenser is filled halfway with toluene, a chip of porous plate is added, and the top is attached to a reflux condenser.

Fig. 11.



In the 250-ml. flask 100 g. (0.78 mole) of freshly vacuum-distilled ethyl acetoacetate and 0.05 g. of sodium bicarbonate (Note 3) are placed and heated so that the toluene is kept just boiling until the liquid in the flask has reached 200–210° (Note 4). The time for heating is usually 7–8 hours, during which period 27 g. of distillate boiling at 72° (mostly ethanol) is collected, and the color of the reaction mixture becomes dark brown. The dehydroacetic acid, while still hot (Note 5), is transferred to a 200-ml. distilling flask (Note 6) and distilled under reduced pressure. After a fore-run boiling up to 128° at 12 mm., consisting of ethyl acetoacetate, has been collected, the receiver is changed and dehydroacetic acid is collected up to 140°/12 mm. The yield of dehydroacetic acid melting at 104–110° is 34 g. (53%) (Note 7). A purer product, m.p. 108°, may be secured in 80% yield by recrystallization from ethanol, using 2 ml. per gram of material (Note 8).

2. Notes

1. The bulb of the thermometer must be immersed in the liquid.
2. This partial condenser, which is a modification of one described by Hahn,[1] is very effective in reducing the time required for fractional distillation of many mixtures. It is best constructed of Pyrex. The dimensions given are approximate and may be varied to suit individual needs. The inside container is a 30 by 140 mm. Pyrex test tube sealed at the top to standard Pyrex tubing. It is very effective in the purification of cyclohexene [*Org. Syntheses* Coll. Vol. **1**, 183 (1941)].[2] The crude hydrocarbon mixture is first put into the flask with ethanol in the partial condenser, and the whole heated as long as a distillate is obtained. The ethanol is then replaced by ethylene chloride and the cyclohexene is collected.
3. It is essential to use sodium bicarbonate to secure consistent results.
4. Above this temperature extensive decomposition sets in. The time required varies with the size of the run, being less with smaller quantities.
5. The residue solidifies on cooling. The dehydroacetic acid may be filtered and washed at this stage, but the yield is lower, owing to its solubility in the reaction mixture.
6. An ordinary 200-ml. distilling flask with a large-diameter side arm placed well down on the neck gave the best results. There was no foaming, frothing, or spattering.
7. The yield falls off with larger amounts; e.g., 500 g. of ester gave only 35% of the calculated quantity of acid.
8. The acid may be isolated through the sodium salt, but the quality is poorer and the yield less.

3. Discussion

Dehydroacetic acid has been prepared by the action of acetic anhydride on acetonedicarboxylic acid,[3] as a by-product in the pyrolysis of acetone to give ketene,[4] by treatment of ketene dimer with pyridine[5] or sodium phenoxide,[6] and by removal of ethanol from acetoacetic ester.[7]

This preparation is referenced from:

- Org. Syn. Coll. Vol. 4, 238

References and Notes

1. Hahn, *Ber.*, **43**, 419 (1910).
2. A. W. Hutchison, private communication.
3. von Pechmann, *Ber.*, **24**, 3600 (1891); von Pechmann and Neger, *Ann.*, **273**, 194 (1893).
4. Hurd, Sweet, and Thomas, *J. Am. Chem. Soc.*, **55**, 336 (1933).
5. Chick and Wilsmore, *J. Chem. Soc.*, **93**, 946 (1908); **97**, 1987 (1910).
6. Steele, Boese, and Dull, *J. Org. Chem.*, **14**, 460 (1949).
7. Arndt and Nachtwey, *Ber.*, **57**, 1489 (1924); Arndt, Eistert, Scholz, and Aron, *Ber.*, **69**, 2373 (1936).

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

acetoacetic ester

ethanol (64-17-5)

acetic anhydride (108-24-7)

Acetonedicarboxylic acid

sodium bicarbonate (144-55-8)

Cyclohexene (110-83-8)

ethylene chloride (107-06-2)

acetone (67-64-1)

pyridine (110-86-1)

toluene (108-88-3)

Ethyl acetoacetate (141-97-9)

sodium phenoxide

Ketene (463-51-4)

Dehydroacetic acid (520-45-6)