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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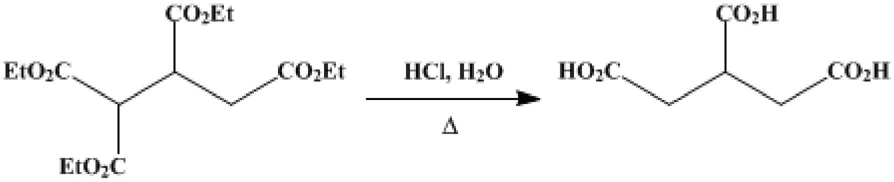
TRICARBALLYLIC ACID



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1. Procedure

In a 3-l. flask, fitted with a stirrer and a fractionating column with condenser for downward distillation, are placed 912 g. (815 cc., 2.75 moles) of ethyl propane-1,1,2,3-tetracarboxylate (p. 272) and 950 cc. of a solution of equal volumes of pure concentrated hydrochloric acid and distilled water. A receiver with a side tube is attached to the condenser; this side tube leads to a water trap. The mixture is boiled, with continual stirring, at such a rate that the alcohol is removed as fast as it is formed, but without undue removal of water from the flask (Note 1). The progress of the reaction can be followed by noting the rate at which carbon dioxide passes through the trap. When the temperature at the head of the column approaches 100°, the flame is turned down so that very little liquid distils over. Heating is continued until evolution of carbon dioxide ceases (Note 2).

The flask is now disconnected from the stirrer and column, and the contents distilled off as completely as possible on the steam bath under reduced pressure. The remaining solid is freed from residual moisture and hydrochloric acid by allowing a slow current of dry air to pass over it, while still heating on the steam bath and maintaining a partial vacuum (Note 3). It is then redissolved in distilled water; the solution is filtered with the use of decolorizing carbon, and again evaporated under reduced pressure.

The residue, when completely dry, is ground up, mixed to a paste with dry ether, filtered by suction, washed with dry ether, and dried. The product so obtained (Note 4) is practically pure and melts at 160–161°. The yield is 474–479 g. (95–96 per cent of the theoretical amount).

2. Notes

1. The temperature at the head of the column will give some idea of the relative amount of water passing over with the alcohol, but allowance must be made for the lowering of the distilling temperature by the carbon dioxide evolved.
2. Twelve hours' heating is necessary to complete the reaction.
3. The dry air is best introduced through a tube leading to the bottom of the flask; it is well not to disconnect the condenser, but to note the point at which no more drops condense. The current of dry air should be quite slow—not more than two bubbles per second in the sulfuric acid wash bottle.
4. Tricarballylic acid is readily soluble in water (requiring about twice its weight at room temperature), but may, if desired, be recrystallized from it. Dry ether may also be employed, about 50 parts by weight being necessary.

3. Discussion

Tricarballylic acid can be prepared by the hydrolysis of the nitrile obtained from glycerol tribromohydrin and potassium cyanide;[1] by reduction of aconitic acid by sodium amalgam[2] or electrolytically;[3] and by the hydrolysis of ethyl propanetetracarboxylate in alkaline solution[4] or more conveniently with hydrochloric acid.[5]

References and Notes

1. Simpson, Proc. Roy. Soc. **12**, 237 (1862); Ann. **128**, 352 (1863); **136**, 272 (1865).
2. Wichelhaus, Ann. **132**, 62 (1864); Emery, Ber. **22**, 2920 (1889); Fittig, Ann. **314**, 15 (1901).
3. Marie, Compt. rend. **136**, 1331 (1903).
4. Emery, Ber. **23**, 3760 (1890); Michael and Schulthess, J. prakt. Chem. (2) **45**, 56 (1892).
5. Auwers, Köbner, and v. Meyenburg, Ber. **24**, 2889 (1891); Staudinger, Ann. **341**, 102 (1905); Gault and Klees, Bull. soc. chim. (4) **39**, 892 (1926).

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

nitrile

glycerol tribromohydrin

alcohol (64-17-5)

hydrochloric acid (7647-01-0)

ether (60-29-7)

potassium cyanide (151-50-8)

carbon dioxide (124-38-9)

decolorizing carbon (7782-42-5)

sodium (13966-32-0)

Ethyl propane-1,1,2,3-tetracarboxylate

Tricarballylic acid (99-14-9)

Aconitic acid (499-12-7)

ethyl propanetetracarboxylate