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.

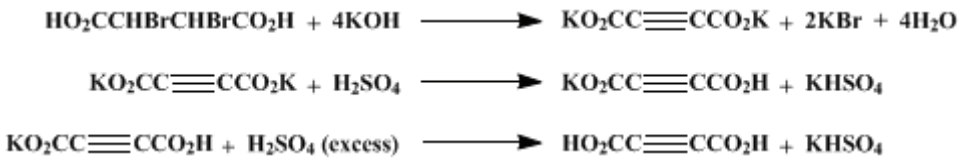
The procedures described in *Organic Syntheses* are provided as published and are conducted at one's own risk. *Organic Syntheses, Inc.*, its Editors, and its Board of Directors do not warrant or guarantee the safety of individuals using these procedures and hereby disclaim any liability for any injuries or damages claimed to have resulted from or related in any way to the procedures herein.

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.018.0003

Organic Syntheses, Coll. Vol. 2, p.10 (1943); Vol. 18, p.3 (1938).

ACETYLENEDICARBOXYLIC ACID



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1. Procedure

A solution of potassium hydroxide is prepared by dissolving 122 g. (2.2 moles; 1.5 times the theoretical amount) of potassium hydroxide in 700 cc. of 95 per cent methyl alcohol (Note 1) contained in a 2-l. round-bottomed flask provided with a reflux condenser. To this alkaline solution is added 100 g. (0.36 mole) of α,β-dibromosuccinic acid (p. 177), and the mixture is refluxed for one hour and fifteen minutes on a steam bath. The reaction mixture is cooled and filtered with suction. The mixed salts are washed with 200 cc. of methyl alcohol (Note 2) and dried by pressing between filter papers; when dry the product weighs 144–150 g.

This salt mixture is dissolved in 270 cc. of water, and the acid potassium salt is precipitated by adding 8 cc. of concentrated sulfuric acid in 30 cc. of water. After standing for three hours, or overnight, the mixture is filtered with suction (Note 3). The acid salt is then dissolved in 240 cc. of water to which 60 cc. of concentrated sulfuric acid has been added, and the solution is extracted with five 100-cc. portions of ether. The combined ether solutions are evaporated to dryness on a steam bath, leaving pure hydrated crystals of acetylenedicarboxylic acid. After drying for two days over concentrated sulfuric acid in a vacuum desiccator the crystals decompose sharply at 175–176°. The yield is 30–36 g. (73–88 per cent of the theoretical amount).

2. Notes

1. The yield is slightly lower when 95 per cent ethyl alcohol is used.
2. This salt mixture is composed of potassium bromide and potassium acetylenedicarboxylate.
3. This acid salt is practically bromine-free and does not require additional washing.

3. Discussion

The procedure described is essentially that of Bandrowski[1] and Baeyer[2] as modified by Ruggli.[3] The same general method has also been used by Backer and van der Zanden,[4] and by Moureu and Bongrand.[5]

This preparation is referenced from:

- Org. Syn. Coll. Vol. 4, 329

References and Notes

1. Bandrowski, Ber. **10**, 838 (1877).
2. Baeyer, ibid. **18**, 677 (1885).
3. Ruggli, Helv. Chim. Acta **3**, 564 (1920).
4. Backer and van der Zanden, Rec. trav. chim. **47**, 776 (1928).
5. Moureu and Bongrand, Ann. chim. (9) **14**, 9 (1920).

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

ethyl alcohol (64-17-5)

sulfuric acid (7664-93-9)

methyl alcohol (67-56-1)

ether (60-29-7)

potassium hydroxide (1310-58-3)

potassium bromide (7758-02-3)

Acetylenedicarboxylic acid (142-45-0)

α,β-Dibromosuccinic acid (526-78-3)

potassium acetylenedicarboxylate