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.

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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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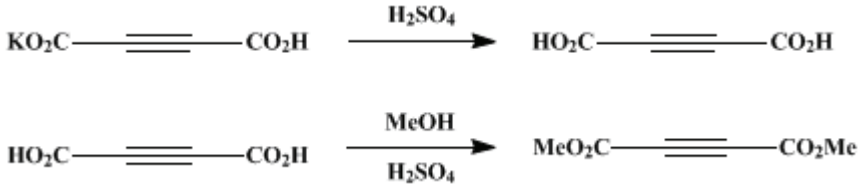
Organic Syntheses, Coll. Vol. 4, p.329 (1963); Vol. 32, p.55 (1952).

DIMETHYL ACETYLENEDICARBOXYLATE

[Acetylenedicarboxylic acid, dimethyl ester]



Submitted by E. H. Huntress, T. E. Lesslie, and J. Bornstein[1].
Checked by T. L. Cairns and M. J. Hogsed.

1. Procedure

To 400 g. (510 ml., 12.5 moles) of methanol (commercial grade) in a 2-l. round-bottomed flask is added in small portions with cooling 200 g. (111 ml., 2.04 moles) of concentrated sulfuric acid. To this cooled solution is added 100 g. (0.66 mole) of the potassium acid salt of acetylenedicarboxylic acid (Note 1). The flask is fitted with a stopper holding a calcium chloride drying tube and allowed to stand with occasional swirling for 4 days at room temperature.

The liquid in the flask is then decanted from the inorganic salt, which is washed with 500 ml. of cold water. The solutions are combined and extracted with five 500-ml. portions of ether. The ether extracts are combined and washed successively with 200 ml. of cold water, 150 ml. of saturated sodium bicarbonate solution (Note 2), and 200 ml. of cold water and then dried over anhydrous calcium chloride. After removal of the ether by distillation from a steam bath, the ester is distilled under reduced pressure from a modified Claisen flask. The yield of ester boiling at 95–98°/19 mm. is 67–82 g. (72–88%) (Note 3) and (Note 4); n_D^{25} 1.4444–1.4452.

2. Notes

1. The potassium acid salt of acetylenedicarboxylic acid is commercially obtainable from the National Aniline Division, Allied Chemical and Dye Corporation, New York, New York. Directions for the preparation of the free acid are given in earlier volumes.[2,3]
2. If the ether extract is not washed with sodium bicarbonate solution, considerable loss occurs during the distillation of the ester because of decomposition in the flask.
3. Dimethyl acetylenedicarboxylate is a powerful lachrymator and vesicant; it should be handled with extreme care. Even traces of ester on the skin should be washed off at once with 95% ethanol followed by washing with soap and water.
4. The same general method has been used by the submitters to prepare diethyl acetylenedicarboxylate. In this case absolute ethanol was used, and the ether extract was dried over anhydrous magnesium sulfate. The yield of diethyl ester from 100 g. of the acid potassium salt of acetylenedicarboxylic acid was 57–59 g. (51–53%); b.p. 96–98°/8 mm.; n_D^{25} 1.4397.

3. Discussion

Dimethyl acetylenedicarboxylate has been prepared by refluxing the acid potassium salt of acetylenedicarboxylic acid with methanol and sulfuric acid.[4,5] The method described here is a substantial improvement over the method of Moureu and Bongrand,[6] who prepared it from acetylenedicarboxylic acid, absolute methanol, and sulfuric acid.

This preparation is referenced from:

- Org. Syn. Coll. Vol. 4, 444

- Org. Syn. Coll. Vol. 5, 985
- Org. Syn. Coll. Vol. 6, 196
- Org. Syn. Coll. Vol. 8, 298

References and Notes

1. Massachusetts Institute of Technology, Cambridge, Massachusetts.
2. *Org. Syntheses Coll. Vol.* **2**, 10 (1943).
3. *Org. Syntheses*, **18**, 3 (1938).
4. Baudrowski, *Ber.*, **15**, 2694 (1882).
5. Curtius and Heynemann, *J. prakt. Chem.*, [2] **91**, 66 (1915).
6. Moureu and Bongrand, *Ann. chim.*, [9] **14**, 11 (1920).

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

potassium acid salt of acetylenedicarboxylic acid

acid potassium salt of acetylenedicarboxylic acid

ethanol (64-17-5)

calcium chloride (10043-52-4)

sulfuric acid (7664-93-9)

methanol (67-56-1)

ether (60-29-7)

sodium bicarbonate (144-55-8)

Acetylenedicarboxylic acid (142-45-0)

magnesium sulfate (7487-88-9)

Dimethyl acetylenedicarboxylate,
Acetylenedicarboxylic acid, dimethyl ester (762-42-5)

diethyl acetylenedicarboxylate (762-21-0)