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.

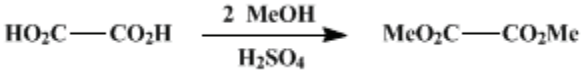
These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

DOI:10.15227/orgsyn.010.0078

Organic Syntheses, Coll. Vol. 2, p.414 (1943); Vol. 10, p.78 (1930).

METHYL OXALATE

[Oxalic acid, dimethyl ester]



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1. Procedure

In a 500-cc. Pyrex flask, fitted with a cork which loosely carries a glass mechanical stirrer and a separatory funnel, are placed 90 g. (1 mole) of anhydrous oxalic acid (Org. Syn. Coll. Vol. I, **1941**, 421) and 100 cc. (79 g., 2.5 moles) of methanol (Note 1). Then, while the mixture is rapidly stirred, 35 cc. of pure concentrated sulfuric acid (Note 2) is slowly added through the separatory funnel. The mixture is heated, if necessary (Note 3), nearly to boiling, then filtered as rapidly as possible through a 15-cm. filter paper placed in a slightly heated glass funnel, the filtrate being collected in a 500-cc. wide-mouthed Erlenmeyer flask. The first flask is rinsed with 40 cc. of hot methanol, which is poured through the filter paper. After twenty-four hours at 15° (Note 4) the crystals are filtered with suction, sucked as dry as possible, pressed between filter paper, and air-dried for a few minutes. The filtrate, after cooling to about −10°, is filtered rapidly and the product dried as before. A total of 100–115 g. of material, slightly moist with sulfuric acid and melting at 50–52°, is obtained.

For purification, the crude product is dissolved in 100 cc. of redistilled methanol, filtered through a warm funnel, and allowed to crystallize. After several hours the crystals are filtered, and the filtrate is chilled and filtered as before. A total of 80–90 g. (68–76 per cent of the theoretical amount) of methyl oxalate, melting at 52.5–53.5° (Note 5), is obtained.

2. Notes

1. The methanol used is the commercial (almost acetone-free) grade known as Columbian Spirits. This material is redistilled for recrystallizing the methyl oxalate.
2. Less sulfuric acid than that employed gives a smaller yield; larger quantities sometimes result in a product that causes difficulty in filtration. It is essential that the acid be added slowly and with vigorous stirring to prevent local superheating and darkening of the solution and product. Some commercial grades of methanol become quite dark in contact with sulfuric acid. The grade of methanol used here does not discolor, the filtrates being only light yellow.
3. Solution of the oxalic acid causes a sharp drop in temperature whereas solution of the sulfuric acid raises the temperature.
4. The major portion of the reaction is complete within a few minutes, but several hours are necessary for complete crystallization.
5. Larger batches give the same percentage yield as the one described. When several batches are to be run, the alcohol from the first recrystallization becomes the starting alcohol for the second batch, etc. This increases the yield somewhat.

3. Discussion

Methyl oxalate has been prepared by distilling a mixture of oxalic acid, methyl alcohol, and sulfuric acid;[1] by dissolving anhydrous oxalic acid in hot methyl alcohol;[2] by esterifying oxalic acid with methyl alcohol, using anhydrous hydrogen chloride as a catalyst;[3] by methanolysis of ethyl oxalate;[4] by passing vapors of dry methanol through hydrated oxalic acid until the water has been removed;[5] and by a process in which the methyl alcohol-water mixture evolved from hydrated oxalic acid and methanol is dried over potassium carbonate and returned to the reaction flask.[6] The method described in the procedure is simpler than any of these and gives very satisfactory yields.

References and Notes

1. Dumas and Peligot, Ann. chim. phys. (2) **58**, 44 (1835); Ann. **15**, 32 (1835); Wöhler, ibid. **81**, 376 (1852).
2. Erlenmeyer, Jahresb. **1874**, 572.
3. Rising and Stieglitz, J. Am. Chem. Soc. **40**, 726 (1918).
4. Pfannl, Monatsh. **31**, 316 (1910); Reimer and Downes, J. Am. Chem. Soc. **43**, 950 (1921).
5. Dutt, J. Chem. Soc. **123**, 2714 (1923).
6. Kenyon, Org. Syn. Coll. Vol. I, **1941**, 264.

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

potassium carbonate (584-08-7)

sulfuric acid (7664-93-9)

hydrogen chloride (7647-01-0)

methyl alcohol,
methanol (67-56-1)

Oxalic acid (144-62-7)

Ethyl oxalate

Methyl oxalate

Oxalic acid, dimethyl ester (553-90-2)