



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.

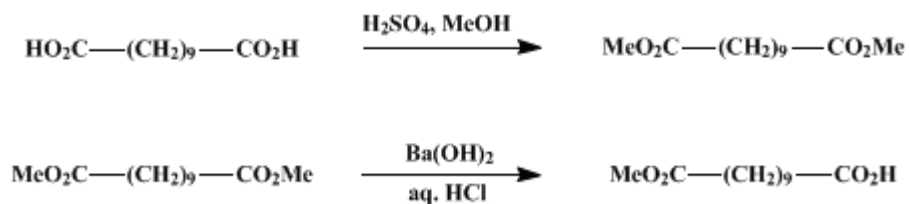
The procedures described in *Organic Syntheses* are provided as published and are conducted at one's own risk. *Organic Syntheses, Inc.*, its Editors, and its Board of Directors do not warrant or guarantee the safety of individuals using these procedures and hereby disclaim any liability for any injuries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

Organic Syntheses, Coll. Vol. 4, p.635 (1963); Vol. 38, p.55 (1958).

METHYL HYDROGEN HENDECANEDIOATE

[Undecanedioic acid, methyl ester]



Submitted by Lois J. Durham, Donald J. McLeod, and James Cason¹.

Checked by N. J. Leonard, D. H. Dybvig, and K. L. Rinehart, Jr..

1. Procedure

Dimethyl hendecanedioate is prepared by heating 23 g. (0.106 mole) of hendecanedioic acid (p.510) under reflux for 2 hours with a solution of 8 ml. of concentrated sulfuric acid in 80 ml. of methanol. After the reaction mixture has been diluted with 3 volumes of water, it is extracted with two 75-ml. portions of benzene. The benzene extracts are washed successively with 250-ml. portions of water, 5% aqueous sodium carbonate solution, and water. After the benzene has been removed under reduced pressure, the residue (Note 1) is transferred to a 250-ml. Erlenmeyer flask containing 127 ml. of a 0.915*N* solution of barium hydroxide (0.058 mole) in commercial anhydrous methanol (Note 2). The flask is immediately closed with a soda-lime tube and swirled to mix the solution. The barium salt of the half ester begins to precipitate after about 2 minutes.

After the flask has been allowed to stand at room temperature (20–25°) for at least 17 hours (Note 3), the barium salt is collected by suction filtration and washed with about 20 ml. of methanol (Note 4). The moist barium salt is shaken for a few minutes in a separatory funnel with a mixture of 100 ml. of 4*N* hydrochloric acid and 100 ml. of ether. The aqueous layer, together with any precipitated barium chloride, is removed and extracted again with 100 ml. of ether. The two ether extracts are combined and washed with three 100-ml. portions of water, the solvent is removed, and the residue (Note 5) is distilled through a half-meter column (Note 6). There is essentially no fore-run (see (Note 4)). The pure half ester is collected at 165–168°/2 mm., weight 14.6–15.7 g. (60–64%), m.p. 44–46° (Note 7).

2. Notes

1. The submitters state that the residue may be distilled to give dimethyl hendecanedioate in 98% yield (25.5 g.).
2. An approximately 1.0*N* solution of anhydrous barium hydroxide in methanol is prepared, and the exact normality is determined by titration. The checkers employed 143 ml. of an 0.814*N* solution of barium hydroxide in anhydrous methanol. This procedure is not suitable for making ethyl esters on account of the low solubility of barium hydroxide in ethanol.
3. Periodic titration of aliquots of the reaction mixture has shown that after 16 hours about 95% of the original barium hydroxide has reacted.
4. If an insufficient amount of methanol is employed to wash the precipitate, a considerable quantity of recovered diester, b.p. ca. 145°/2 mm., is obtained as a fore-run in the fractional distillation of the product. The diester may be recovered by dilution of the filtrate with water and extraction.
5. The crude product obtained directly from the barium salt is 90–95% half ester, and the remainder is diacid. This material may be used directly in reactions where small amounts of diacid are not objectionable; however, distillation is necessary in order to obtain a pure sample of half ester. This distillation is simplified because there is no lower-boiling diester and only a small amount of higher-boiling diacid.
6. The submitters used a simple type of Podbielniak column.² The checkers used a 122-cm. column of similar design.

7. Titration of this half ester gives an equivalent weight, within experimental error, of the calculated value of 230.3. The yield in this preparation may be regarded as close to theoretical on the basis of recovery and re-use of diacid and diester.

3. Discussion

Methyl hydrogen hendecanedioate has been reported as a by-product in the ozonolysis of methyl 11-dodecenoate,³ but the only preparative procedure reported is that presently described.⁴ Half esters have usually been prepared by partial esterification⁵ and direct fractional distillation of the three products of the reaction; however, some modification⁶ of this procedure is required for the higher-boiling half esters. The present method^{4,7} is considerably less laborious than the partial esterification procedure and is a particular advantage for higher-boiling esters where a prolonged fractional distillation at high temperatures permits disproportionation of the half ester. This method is not satisfactory for lower-molecular-weight half esters, for their salts are too soluble in methanol. Sebacic acid gives satisfactory results by this method; azelaic acid, poor results; and lower-molecular-weight dibasic acids fail to give significant amounts of half ester.

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 5, 463](#)

References and Notes

1. University of California, Berkeley, California.
2. Cason and Rapoport, *Laboratory Text in Organic Chemistry*, 2nd ed., p. 293, Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1962.
3. Lycan and Adams, *J. Am. Chem. Soc.*, **51**, 625 (1929).
4. Cason, Taylor, and Williams, *J. Org. Chem.*, **16**, 1187 (1951); Cason and McLeod, *J. Org. Chem.*, **23**, 1497 (1958).
5. *Org. Syntheses Coll. Vol. 2*, 276 (1943).
6. Jones, *J. Am. Chem. Soc.*, **69**, 2350 (1947).
7. Signer and Sprecher, *Helv. Chim. Acta*, **30**, 1001 (1947).

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

[ethanol](#) (64-17-5)

[sulfuric acid](#) (7664-93-9)

[hydrochloric acid](#) (7647-01-0)

[Benzene](#) (71-43-2)

[methanol](#) (67-56-1)

[ether](#) (60-29-7)

[sodium carbonate](#) (497-19-8)

barium chloride (10361-37-2)

barium hydroxide (17194-00-2)

Azelaic acid (123-99-9)

sebacic acid (111-20-6)

Hendecanedioic acid (1852-04-6)

Methyl hydrogen hendecanedioate,
Undecanedioic acid, methyl ester (3927-60-4)

Dimethyl hendecanedioate (4567-98-0)

methyl 11-dodecenoate