



A Publication  
of Reliable Methods  
for the Preparation  
of Organic Compounds

## Working with Hazardous Chemicals

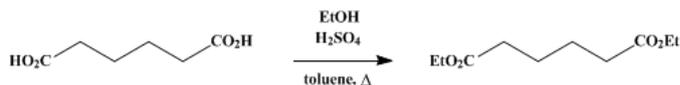
The procedures in *Organic Syntheses* are intended for use only by persons with proper training in experimental organic chemistry. All hazardous materials should be handled using the standard procedures for work with chemicals described in references such as "Prudent Practices in the Laboratory" (The 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](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.*

## ETHYL ADIPATE [Adipic acid, diethyl ester]



Submitted by V. M. Micovic  
Checked by Reynold C. Fuson and E. A. Cleveland.

### 1. Procedure

Four hundred thirty-eight grams (3 moles) of adipic acid, 1080 cc. (9 moles) of absolute alcohol, 540 cc. of toluene, and 2.5 cc. of concentrated sulfuric acid (Note 1) are placed in a 3-l. distilling flask. The flask is connected with a downward condenser and heated on an oil bath (Note 2). An azeotropic mixture of alcohol, toluene, and water begins to distil at 75°. Distillation is continued until the thermometer in the neck of the flask rises to 78°, when further heating is suspended.

The distillate is collected in a 2-l. flask containing 450 g. of anhydrous potassium carbonate (Note 3). It is well shaken, filtered through a Büchner funnel, and returned to the distilling flask (Note 4). The flask is again heated until the temperature rises to 78–80°, when distillation is discontinued (Note 5). The residual liquid (Note 6) is emptied into a 1-l. flask, the large flask being rinsed with a little alcohol, and distilled under vacuum. Alcohol and toluene distil first; then the temperature rises and ethyl adipate distils at 138°/20 mm. (Note 7). The yield is 580 to 588 g. (95–97 per cent of the theoretical amount) (Note 8) and (Note 9).

### 2. Notes

1. For esterification by this method, three times the theoretical quantity of absolute alcohol is taken. If only twice the theoretical amount is used, esterification is not complete. The quantity of sulfuric acid required is 1 per cent of the weight of adipic acid used. For smaller quantities of organic acid, a few drops of sulfuric acid are sufficient.

2. It is necessary to maintain the temperature of the bath at about 115° until the mixture dissolves and distillation begins. Later a temperature of 100–110° is sufficient.

3. For each mole of adipic acid to be esterified, 150 g. of anhydrous potassium carbonate is required.

4. Filtering through a fluted filter paper directly into a distillation flask is entirely satisfactory when smaller quantities are used.

5. The distillate, which contains alcohol, toluene, and water, can be dried, distilled, and used again for esterification after the addition of the necessary quantity of absolute alcohol; or, by the addition of water, toluene alone may be separated, dried over calcium chloride, and distilled.

6. If the solution is allowed to cool, small crystals of unesterified acid separate. The quantity is negligible.

7. Towards the end of the distillation, the temperature rises several degrees; but distillation should be continued, for when redistilled the ester does not leave a residue.

8. According to the submitter, ethyl esters of the dibasic acids from oxalic through sebacic have been prepared in yields of 94–98 per cent by this same procedure.

9. Ethyl adipate can also be prepared<sup>1</sup> by refluxing 175 g. (1.2 moles) of adipic acid, 175 g. (222 cc.) of ethyl alcohol, 450 cc. of benzene, and 80 g. (43.5 cc.) of concentrated sulfuric acid for five hours on the steam bath. The yield of ester boiling at 136–137/19 mm. is 218 g. (90 per cent of the theoretical amount). (Private communication from P. S. Pinkney. Checked by Louis F. Fieser and T. L. Jacobs.)

### 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](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.

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

### 3. Discussion

Ethyl adipate is obtained by boiling adipic acid, alcohol, benzene, and sulfuric acid;<sup>1</sup> from adipic acid, alcohol, and hydrogen chloride;<sup>2</sup> from adipic acid, absolute alcohol, and sulfuric acid;<sup>3</sup> by distilling a mixture of ethyl alcohol, toluene, and adipic acid with the addition of some hydrochloric acid which acts as a catalyst;<sup>4</sup> and by the procedure described above.<sup>5</sup>

This preparation is referenced from:

- Org. Syn. Coll. Vol. 2, 116
- Org. Syn. Coll. Vol. 2, 276
- Org. Syn. Coll. Vol. 2, 325
- Org. Syn. Coll. Vol. 4, 819

### References and Notes

1. Van Rysselberge, Bull. soc. chim. Belg. **35**, 312 (1926).
2. Arppe, J. prakt. Chem. (1) **95**, 208 (1865).
3. Curtius, *ibid.* (2) **91**, 4 (1915); Bouveault and Locquin, Bull. soc. chim. (4) **3**, 439 (1908).
4. Locquin and Elghozy, *ibid.* (4) **41**, 445 (1927).
5. Micovic, *ibid.* (5) **4**, 1661 (1937).

### Appendix

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

ethyl alcohol,  
alcohol (64-17-5)

calcium chloride (10043-52-4)

potassium carbonate (584-08-7)

sulfuric acid (7664-93-9)

hydrogen chloride,  
hydrochloric acid (7647-01-0)

Benzene (71-43-2)

Adipic acid (124-04-9)

Ethyl adipate (626-86-8)

toluene (108-88-3)

Adipic acid, diethyl ester (141-28-6)

Copyright © 1921-2015, Organic Syntheses, Inc. All Rights Reserved

---