



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.

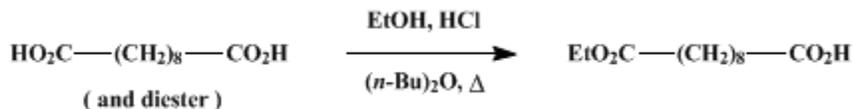
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 2, p.276 (1943); Vol. 19, p.45 (1939).

ETHYL HYDROGEN SEBACATE

[Sebacic acid, ethyl acid ester]



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1. Procedure

In a 1-l. modified Claisen flask (Note 1), the side arm of which is corked, is placed a mixture of 202 g. (1 mole) of [sebacic acid](#), 150 g. (0.58 mole) of [diethyl sebacate](#) (Note 2), 50 cc. of [di-*n*-butyl ether](#) (Note 3), and 30 g. (25 cc.) of concentrated [hydrochloric acid](#) (sp. gr. 1.19). A reflux condenser is connected to the top of the distilling flask.

The flask is heated in a Wood's metal bath at 160–170° until the mixture is completely homogeneous. The temperature of the bath is then lowered to 120–130°, and 60 cc. (1 mole) of 95 per cent [ethyl alcohol](#) is added to the solution through the condenser. The mixture is allowed to reflux for two hours. At the end of this period an additional 20-cc. portion of [ethyl alcohol](#) is poured into the solution and refluxing is continued for two hours longer.

The Wood's metal bath is allowed to cool to about 75° and the reaction mixture is subjected to distillation under reduced pressure, using a water pump (Note 4). The temperature of the bath is increased slowly and distillation is continued, with a water pump, until the bath reaches a temperature of about 125°. The bath is again cooled to 75–80° and the distillation is continued at lower pressure, using an oil pump.

The first fractions consist of a little alcohol, water, and [*n*-butyl ether](#) (Note 5). The next fraction is [ethyl sebacate](#), b.p. 156–158° at 6 mm. (Note 6). [Ethyl hydrogen sebacate](#) is collected at 183–187° at 6 mm. The product melts at 34–36° and weighs 114–124 g. (50–54 per cent of the calculated amount, based on the [sebacic acid](#) used). Refractionation of the fore-run (b.p. 175–183°/6 mm.) and after-run (b.p. 187–195°/6 mm.) gives an additional 24–26 g. of pure monoester. The total yield is 138–150 g. (60–65 per cent of the theoretical amount) (Note 7) and (Note 8).

2. Notes

1. The column of the flask should be at least 35 cm. in length and well insulated. Wrapping the column with 10-mm. asbestos rope is satisfactory.
2. The addition of diester at the beginning of the reaction decreases its formation from the reactants so that the monoester becomes the main product.
[Ethyl sebacate](#) is prepared conveniently by refluxing 130 g. (0.65 mole) of [sebacic acid](#) with 250 g. of [ethyl alcohol](#) and 25 cc. of concentrated [sulfuric acid](#). The yield is about 90 per cent, and the product boils at 156–158° at 6 mm. See, also, [Note 8, p. 265](#).
3. [*n*-Butyl ether](#) is used in preference to other possible compounds because it permits the formation of a homogeneous reaction mixture.
4. At the beginning of the distillation the liquid in the flask foams excessively. It is advisable, therefore, to reduce the pressure gradually and not to use low pressures until the foaming subsides.
5. The [*n*-butyl ether](#) may be recovered in pure condition by a simple distillation after the water has been separated from it.
6. After the [ethyl sebacate](#) has distilled, it is well to drain the cooling water from the condenser in order to prevent the monoester from solidifying before reaching the receiver. The recovered [ethyl sebacate](#) weighs 150–175 g. and may be used directly in a subsequent preparation.

7. In subsequent runs the distillation residue is allowed to remain in the flask. In this way the yield is increased to 70–77 per cent for runs of one and two moles.
8. The submitters report that [ethyl hydrogen adipate](#), b.p. 155–157°/7 mm., has been prepared in 71–75 per cent yields on a one-mole scale by the same procedure.

3. Discussion

[Ethyl hydrogen sebacate](#) has been prepared by the direct esterification of [sebacic acid](#) with [ethyl alcohol](#),¹ by the half-saponification of [ethyl sebacate](#),² and by heating equimolecular quantities of [sebacic acid](#) and [diethyl sebacate](#) for several hours.³

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 2, 154](#)
- [Org. Syn. Coll. Vol. 3, 401](#)
- [Org. Syn. Coll. Vol. 3, 613](#)
- [Org. Syn. Coll. Vol. 4, 635](#)
- [Org. Syn. Coll. Vol. 5, 463](#)

References and Notes

1. Neison, J. Chem. Soc. **29**, 319 (1876).
 2. Walker, *ibid.* **61**, 713 (1892).
 3. Fourneau and Sabetay, Bull. soc. chim. (4) **43**, 859 (1928); (4) **45**, 834 (1929).
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Appendix Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

Sebacic acid, ethyl acid ester

[ethyl alcohol](#) (64-17-5)

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

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

[Ethyl hydrogen adipate](#) (626-86-8)

[di-n-butyl ether](#),
[n-butyl ether](#) (142-96-1)

[Ethyl sebacate](#),
[Ethyl hydrogen sebacate](#) (693-55-0)

[sebacic acid](#) (111-20-6)

[diethyl sebacate](#) (110-40-7)