



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.

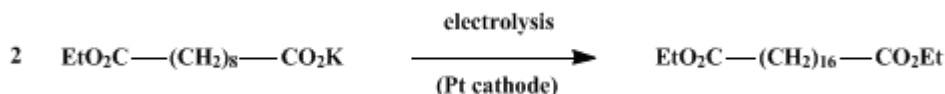
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 3, p.401 (1955); Vol. 21, p.48 (1941).

ETHYL 1,16-HEXADECANEDICARBOXYLATE

[Octadecanedioic acid, diethyl ester]



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1. Procedure

To 86.5 g. (0.38 mole) of [ethyl hydrogen sebacate](#) [*Org. Syntheses Coll. Vol. 2, 276 (1943)*] is added slowly and with cooling 125–130 ml. of approximately 3 *N* [potassium hydroxide](#). The solution is then diluted to approximately 250 ml., yielding a 1.5 *N* solution of [potassium ethyl sebacate](#).

The solution of [potassium ethyl sebacate](#) ([Note 1](#)) is poured into a 500-ml. tall beaker provided with a cooling coil ([Note 2](#)), a thermometer, a stirrer, a [platinum](#) sheet anode 45–55 sq. cm. in area ([Note 3](#)), and two [platinum](#) wire cathodes ([Note 4](#)). To the solution 10 g. of [monoethyl sebacate](#) ([Note 5](#)) is added.

The electrodes are connected to a suitable source of direct current, 10 amperes of which is allowed to pass through the cell. To the solution there is now added 40 g. more of [monoethyl sebacate](#) in portions of 10 g. each over a period of 10 minutes ([Note 6](#)). The temperature of the cell is held below 50° by running cold water through the cooling coil ([Note 7](#)).

The run is finished in 60–70 minutes. The reaction will have reached completion when a few drops of the electrolyte removed with a pipet show an alkaline reaction to [phenolphthalein](#). The alkalinity should be tested every 10 minutes after the first 45.

When the electrolyte has become alkaline, the oily product floating on the top is removed by means of a pipet ([Note 8](#)). The oil is washed with an equal volume of 10% [potassium carbonate](#) ([Note 9](#)), then with an equal volume of 3.5% [hydrochloric acid](#), and finally twice with half its volume of water (a little [ether](#) effectively breaks up any emulsions which may form at this point). It is then crystallized from [methanol](#), filtered by suction, and washed twice while in the funnel with ice-cold [methanol](#) ([Note 10](#)). The product, snow-white and waxy in appearance, is dried in a desiccator over [sulfuric acid](#). The yield is 16–22 g. (40–55%) of material melting at 41–42°. These figures for the percentage yields, however, are based only upon the 50 g. of [ethyl hydrogen sebacate](#) used in the second part and no account is taken of the 86.5 g. used in preparing the electrolyte solutions. This preparation becomes practicable, therefore, only when several consecutive runs are made ([Note 8](#)).

2. Notes

1. The reaction mixture may require slight warming on the water bath to make a homogeneous solution.
2. The checkers used a copper cooling coil. This was slightly attacked during the electrolysis: the solution became blue, and [copper](#) deposited on the cathodes.
3. Convenient dimensions for the anode are 3.75 by 6.0 cm. (the area of the anode [both sides] used by the checkers was 52 sq. cm.). Care should be taken to submerge it in the solution to a depth such that the oil that gathers on the top of the solution during the electrolysis will not insulate it, thus increasing the current density. The wire tab of the platinum sheet may be sealed into a glass tube so that only the sheet is exposed to the solution.
4. The cathodes should be equidistant from the anode to ensure uniform current density on both sides of the anode.
5. As the [potassium salt of monoethyl sebacate](#) is decomposed during the electrolysis, the free acid forms new salt. The alkalinity of the solution may, therefore, be used as the end point of the electrolysis.
6. If the 50 g. of [monoethyl sebacate](#) is added all at once, excessive foaming will occur.

7. Addition of more water (50 ml.) makes possible a much better control of the temperature.
8. If it is desired to prepare larger amounts of product, more free acid may be added to the solution without turning off the current after the product has been drawn off by the pipet. Between ten and fifteen batches of [monoethyl sebacate](#) may be converted in this way. The length of time for a run will gradually increase with the number of runs. After ten to fifteen runs, the time required to convert a 50-g. batch is 3.5–4 hours. The electrolyte should then be renewed.
9. Unchanged mono ester may be recovered by acidification of the carbonate washings, followed by extraction with [ether](#).
10. About the same amount of by-product as main product is in solution in the [methanol](#). The first material that crystallizes is pure main product.

3. Discussion

[Diethyl 1,16-hexadecanedicarboxylate](#) has been prepared by the electrolysis of [potassium ethyl sebacate](#)¹ and by the electrolysis of a mixture of sodium and hydrogen sebacates.²

This preparation is referenced from:

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

References and Notes

1. Brown and Walker, *Proc. Roy. Soc. Edinburgh*, **17**, 297 (1890); *Trans. Roy. Soc. Edinburgh*, **36**, 222 (1890); *Ann.*, **261**, 125 (1891); Fairweather, *Proc. Roy. Soc. Edinburgh*, **45**, 283 (1925); Shiina, *J. Soc. Chem. Ind. Japan*, **40**, Suppl. binding 324 (1937) [*C. A.*, **32**, 499 (1938)].
2. Drake, Carhart, and Mozingo, *J. Am. Chem. Soc.*, **63**, 617 (1941).

Appendix

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

[sodium and hydrogen sebacates](#)

[potassium carbonate](#) (584-08-7)

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

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

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

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

[platinum](#) (7440-06-4)

[copper](#) (7440-50-8)

[potassium hydroxide](#) (1310-58-3)

[phenolphthalein](#) (77-09-8)

Ethyl hydrogen sebacate,
monoethyl sebacate (693-55-0)

ETHYL 1,16-HEXADECANEDICARBOXYLATE

Octadecanedioic acid, diethyl ester,
Diethyl 1,16-hexadecanedicarboxylate (1472-90-8)

potassium ethyl sebacate,
potassium salt of monoethyl sebacate