



A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

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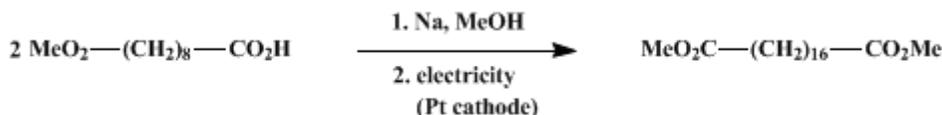
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 5, p.463 (1973); Vol. 41, p.33 (1961).

DIMETHYL OCTADECANEDIOATE

[Octadecanedioic acid, dimethyl ester]



Submitted by Sherlock Swann, Jr. and W. E. Garrison, Jr.¹

Checked by James Cason, John A. Carlson, and Stanley Wood.

1. Procedure

To 500 ml. of absolute [methanol](#) ([Note 1](#)) in a 1-l. electrolytic (tall form) beaker is added 1.1 g. (0.05 g. atom) of clean [sodium](#) metal. After solution of the [sodium](#), 216 g. (1.0 mole) of [methyl hydrogen sebacate](#) ([Note 2](#)) is dissolved in the [sodium methoxide](#) solution. A magnetic stirring bar is placed in the beaker which is then fitted with a large neoprene stopper ([Note 3](#)) holding a platinum sheet anode, 12 cm.² in area; and two platinum sheet cathodes, approximately 5.3 cm.² in area, spaced equidistantly on either side of the anode at a distance of approximately 1.5 cm. ([Note 4](#)). The stopper is also provided with a stoppered entry tube and an efficient reflux condenser ([Note 5](#)).

The electrodes are connected to a suitable variable source of direct current ([Note 6](#)), the magnetic stirrer is started, and a potential of about 50 volts is applied. This results in a current flow of 1–2 amperes. The solution soon comes to boiling; the voltage is then regulated so that a rapid reflux is maintained ([Note 7](#)).

Completion of the run, after 30–40 hours, is indicated when a few drops of the solution show an alkaline reaction to [phenolphthalein](#). No harm is done if the electrolysis is carried a few hours beyond this point; however, after excessively long periods, formation of polymeric material lowers the yield and renders purification of the product rather troublesome.

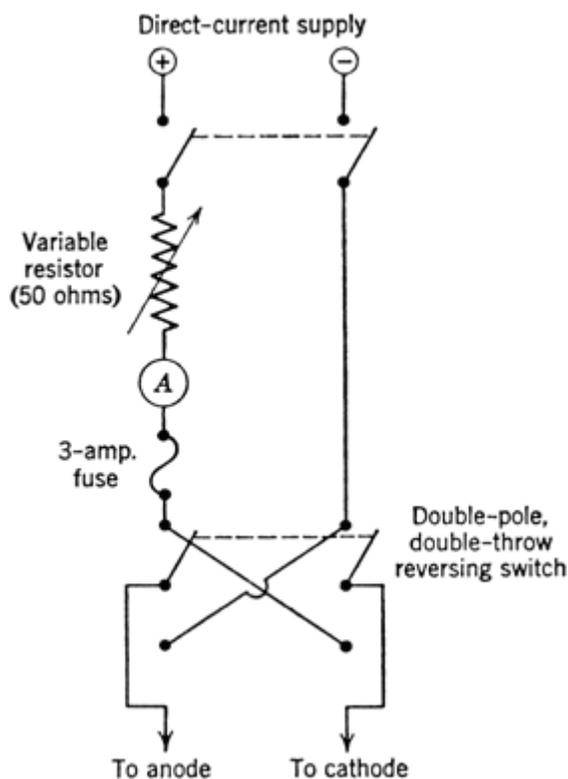
Upon completion of the reaction ([Note 8](#)) the solution is acidified with [acetic acid](#), and the solvent removed under reduced pressure. The residue is dissolved in about 1.4 l. of [ether](#) and filtered into a 2-l. separatory funnel through fluted paper. After the ether solution has been washed with two 300-ml. portions of 5% aqueous [sodium bicarbonate](#) solution ([Note 9](#)), the [ether](#) is removed on a steam bath. The residue is dissolved in about 1.5 l. of warm [methanol](#), and the solution is allowed to cool to room temperature. The crystallized product is collected by suction filtration on a Büchner funnel and pressed well. The product is rather waxy and is best washed by transferring it to a beaker and stirring thoroughly with about 150 ml. of cold [methanol](#). The white crystals are then collected and pressed well again. If the filtrate is colored, the crystals are washed again with a smaller quantity of [methanol](#). The combined filtrate and washings are concentrated to one-half the original volume and chilled in ice to yield a few grams of additional product of the same melting point. The combined lots are dried in a vacuum desiccator. The yield amounts to 116–126 g. (68–74%) of white, microcrystalline [dimethyl octadecanedioate](#), m.p. 57–58°.

2. Notes

1. Analytical reagent absolute [methanol](#) is sufficiently pure for this purpose.
2. The [methyl hydrogen sebacate](#) used by the submitters was prepared by the method described by Pattison and co-workers,² which is a modification of the method described in *Organic Syntheses, Coll. Vol. 2, 276 (1943)*, for [ethyl hydrogen sebacate](#). The methyl rather than the ethyl ester is preferred because of the greater ease of purification of [methyl hydrogen sebacate](#) and [dimethyl octadecanedioate](#). The checkers prepared [methyl hydrogen sebacate](#) by the convenient procedure which has been described for [methyl hydrogen hendecanedioate](#).³ Absence of diacid in the half ester is imperative, for each molecule of diacid (in low concentration) will couple with two molecules of half ester.

3. A rubber stopper will suffice, but neoprene is more durable.
4. Convenient dimensions are 3×4 cm. for the anode, and 2.3×2.3 cm. for the cathode. The bottom of the anode should extend to about 3 cm. from the bottom of the beaker, and the centers of the cathodes should be lined up with the center of the anode. The submitters and checkers used 0.002-in. platinum sheet. Thinner material is easily distorted by the action of the stirrer and may thus develop a short circuit. Platinum wire may be attached to the sheet by heating both parts to redness and hammering them together. The wire may then be sealed in a piece of Pyrex tubing, which is passed through a properly located hole in the stopper, and mercury is used to make contact with the lead-in wire.⁴ In a run one-half the size here described, the checkers obtained similar results by using the same geometry of electrodes with the same concentrations of reactants in a 700-ml. tall-form beaker, with one-half the electrolysis time.
5. It is most convenient to insert a 24/40 outer joint in the stopper to accommodate the condenser. A 14/20 outer joint makes a convenient entry tube for withdrawing samples in order to determine when alkalinity has been reached. This joint must be stoppered during the electrolysis, which is under reflux.
6. A variable field d-c motor generator was used by the submitters. In lieu of such equipment, the checkers used a 120-volt d-c source with a heavy-duty resistor in the circuit. Occasionally, a film of polymeric material may form on the anode and reduce the current flow. This condition may be corrected by reversing the current flow for a period of 5–10 seconds. A suitable control circuit is diagrammed in Fig. 1.

Fig. 1



7. It is usually necessary to increase the applied voltage toward the end of the electrolysis in order to keep the current flow at a high rate. The submitters usually finished the electrolysis at 140 volts; however, the checkers found that a limit of 120 volts resulted in no significant delay in completion of the electrolysis.
8. The electrodes should be removed promptly from the warm reaction mixture, for the solution sets to a solid mass on cooling. It is most convenient to proceed with work-up of the warm solution.
9. An insignificant amount of half ester is recovered by acidification of the bicarbonate washings, followed by extraction with ether.

3. Discussion

Dimethyl and diethyl octadecanedioate have been prepared by the electrolysis of the sodium or potassium salts of methyl or ethyl hydrogen sebacate in water⁵ or in [methanol](#).⁶

4. Merits of Preparation

The advantages of this preparation of [dimethyl octadecanedioate](#) over that described earlier⁵ are purity of product, no foaming of the electrolyte, higher yields, and elimination of the use of large quantities of the salt of the acid ester as supporting electrolyte. The procedure is regarded as near the optimum for a Kolbe electrolysis.

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 5, 445](#)
- [Org. Syn. Coll. Vol. 7, 181](#)

References and Notes

1. Department of Chemistry, University of Illinois, Urbana, Ill. This work was supported by a grant from the National Science Foundation for polymer research.
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Appendix Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

Dimethyl and diethyl octadecanedioate

sodium or potassium salts of methyl or ethyl hydrogen sebacate

[acetic acid](#) (64-19-7)

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

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

[sodium bicarbonate](#) (144-55-8)

[mercury](#) (7439-97-6)

[sodium methoxide](#) (124-41-4)

sodium (13966-32-0)

phenolphthalein (77-09-8)

Ethyl hydrogen sebacate (693-55-0)

methyl hydrogen sebacate (818-88-2)

Methyl hydrogen hendecanedioate (3927-60-4)

Dimethyl octadecanedioate,
Octadecanedioic acid, dimethyl ester (1472-93-1)