



A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

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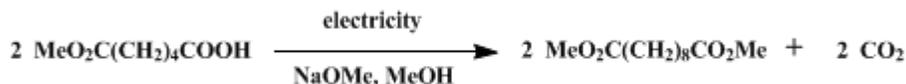
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ANODIC OXIDATION OF ACIDS: DIMETHYL DECANEDIOATE

[Decanedioic acid, dimethyl ester]



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1. Procedure

The electrode assembly (Note 1) is constructed; the platinum electrodes are positioned vertically, parallel, and about 5 mm apart by careful bending of the lower platinum wire connections.

To a 500-mL, round-bottomed flask having a central 34/45 standard taper neck and two 24/40 standard taper necks are added 120 g (0.75 mol) of methyl hydrogen hexanedioate (Note 2), 250 mL of methanol, 4.1 g (0.075 mol) of sodium methoxide, 10 mL of pyridine, and a magnetic stirring bar. The electrode assembly is inserted so that the platinum electrodes are immersed in the solution. A thermometer and reflux water condenser are attached. The mixture is heated to 60°C and stirred until the sodium methoxide dissolves.

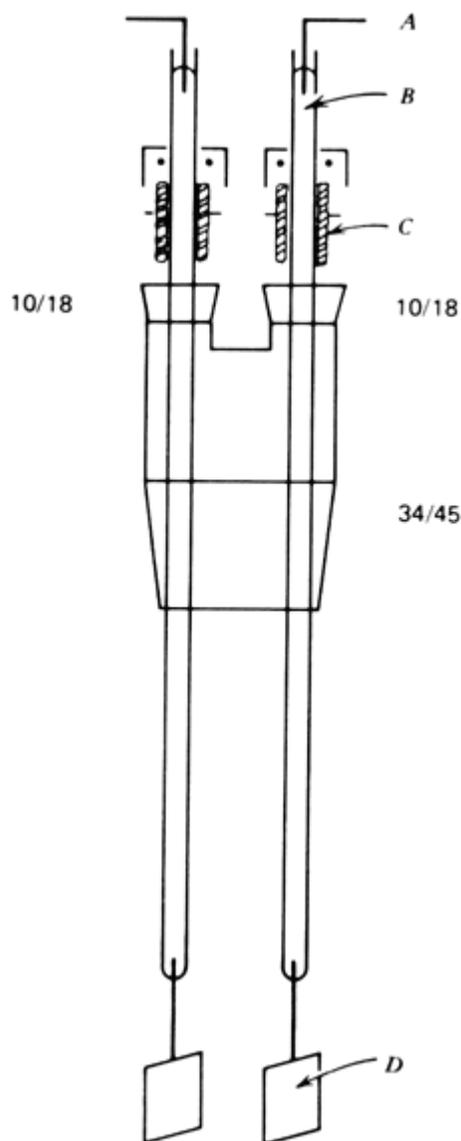
The mixture is electrolyzed with a constant current of 1.1 A (Note 3) until GLC analysis (Note 4) of the solution shows the absence of the peak due to methyl hydrogen hexanedioate. This requires about 23 hr; electrolysis is continued for an additional 2.5 hr at the same current (Note 5). Throughout the electrolysis the reaction mixture is maintained at 62–65°C by passage of the current. After about 1 hr of electrolysis, when conditions are stabilized, the reaction may be left unattended.

The yellow reaction mixture is allowed to cool and then is acidified with 20 mL of glacial acetic acid. The acidified solution is transferred with methanol washing to a 1-L round-bottomed flask and evaporated (70–80°C, 12 mm) to dryness. The solid residue is stirred with 500 mL of diethyl ether for 1 hr. Undissolved solids are removed by filtration and the residue is washed twice with 100-mL portions of diethyl ether. The combined filtrate and washings are washed with aqueous sodium carbonate until neutral and then three times with 200-mL portions of water. The ether solution is dried over anhydrous calcium sulfate. Filtration and evaporation of the ether afford a yellow oil that is distilled under reduced pressure through a Vigreux column (30 × 2.5 cm). This gives 6–7 g of dimethyl hexanedioate (bp 69–71°C, 0.02 mm), 3–4 g of a mixed fraction (bp 72–105°C, 0.02 mm) (Note 6), and 60–61 g (70–71%) of dimethyl decanedioate (bp 105–107°C, 0.02 mm). The dimethyl decanedioate crystallizes on standing at room temperature, mp 26.5–27.2°C (Note 7) and (Note 8).

2. Notes

1. The electrode assembly shown (Figure 1) is fairly versatile and has been used by the submitter in flasks with electrolyte volumes of ca. 40 mL to 4 L. Additionally, the platinum electrodes may be replaced by other electrodes that fit directly into the thermometer adaptor, e.g., commercially available 1/4 in. graphite or stainless-steel rods. In the present example the electrodes are positioned vertically and are of opposite polarity. In other cases they may be positioned horizontally (parallel to a mercury cathode), and both are anodic.

Figure 1. Electrode assembly: (A) platinum wire; (B) mercury-filled 6-mm-o.d. glass tubing; (C) "thermometer" adaptor, 10/18 standard taper joint, Teflon; (D) platinum electrodes 25 mm × 30 mm.



The thermometer adaptors are available commercially (Ace Glass Company, Vineland, NJ). The platinum wire to platinum electrode connection was made by laying the wire on the foil, heating both parts to red heat with an oxygen–naturalgas flame, and forcing the two together with a sharp hammer blow.

2. [Methyl hydrogen hexanedioate \(adipic acid, monomethyl ester\)](#) was obtained from Aldrich Chemical Company, Inc.

3. The cell voltage, initially 25 V, increased slowly to 27 V. A power supply operating in a constant current mode was used to supply the current. [Since there is little change in cell voltage, a constant voltage power supply capable of delivering 24 V (e.g., two automobile batteries) could also be used.] The cell voltage is important only in connection with the amount of heat generated in the solution by the passage of current. This depends on the product of current and voltage. The voltage should not be so high that the reflux cannot cope with the heat generated or so low that the reflux temperature is not attained. It should be in the range 20–30 V. If the voltage should not fall within this range, the electrode separation should be adjusted. Decreasing the separation decreases the cell voltage. However, contact of the electrodes should not, of course, occur.

4. The column used was a 6 ft × 1/8 in. stainless-steel column packed with 5% OV17 on 100–120-mesh Chromosorb W. The column temperature was increased at 10°C per minute from 60 to 260°C.

5. The additional current passed is to allow for the conversion of that portion of the starting material that is converted to the sodium salt by the added [sodium methoxide](#) and that is not detected by gas

chromatography.

6. The quantity of ester obtained (0.26 mol) theoretically requires 0.52*F*. Actual current passed was 28 A-hr [1.05*F* (Faradays)], corresponding to a current efficiency of 50%.

7. The melting point was determined by remelting the product and allowing it to cool with a thermometer inserted into it. Occasional stirring with the thermometer was necessary to prevent supercooling.

8. The product shows ¹H NMR (CDCl₃) δ: 1.2–1.8 (complex, 12, internal methylenes), 2.28 (4, α-CH₂), 3.65 (6, OCH₃).

3. Discussion

The present preparation is based on that of [dimethyl tetradecanedioate](#),² with the inclusion of some [pyridine](#) into the electrolyte, which has been shown³ to be effective in preventing anode coating. The reaction used is an example of the Crum Brown-Walker reaction⁴ (anodic oxidation of half-esters of α,ω-dicarboxylic acids), which is itself an example of the Kolbe reaction (anodic oxidation of carboxylic acids). The latter is a very general reaction, and its scope and mechanism have been reviewed recently.^{5,6} The particular example detailed here has some commercial interest and has been extensively examined. For example, the effects of current density (optimum 0.1–0.4 A/cm²), degree of neutralization (optimum < 10%), nature of the base used for neutralization, and the nature of the solvent used have been examined.^{7,8} These optimized results were obtained^{7,8} in a specially constructed cell with an electrode gap of ca. 0.15 mm. To obtain reasonable results with the larger electrode gap used in this example (ca. 5 mm; if the gap is made any smaller, inadvertent contact of the electrodes and short circuiting become a strong possibility) and maintain the cell voltage fairly low (within range of inexpensive power supplies), the current density used (0.14 A/cm²) was kept toward the low end of the desirable range and the degree of neutralization (10%) at the highest value consistent with a good yield. In a small-gap cell a current efficiency of 66% together with a chemical yield of 85% has been obtained⁷ in the same solvent and electrolyte system.

In addition to the route described here, [dimethyl decanedioate](#) has been prepared by esterification of [decanedioic acid](#) with [methanol](#)^{9,10,11,12,13} or [diazomethane](#),¹⁴ hydrogenation of [dimethyl 2,5,8-decatrienedioate](#),¹⁵ and by thermal decomposition of [bis\(1-methoxy-1-cyclopentyl\)pentoxide](#).¹⁶

The present procedure offers an alternative electrochemical setup to accomplish the Kolbe electrolysis of half esters to that reported earlier for the preparation of [dimethyl octadecanedioate](#).¹⁷ In the present case the apparatus offers general versatility and electrode coating is prevented by an additive ([pyridine](#)). In the earlier case periodic current reversal was necessary.

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 7, 479](#)

References and Notes

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

acetic acid (64-19-7)

methanol (67-56-1)

ether,
diethyl ether (60-29-7)

sodium carbonate (497-19-8)

platinum (7440-06-4)

calcium sulfate (7778-18-9)

sodium methoxide (124-41-4)

pyridine (110-86-1)

Diazomethane (334-88-3)

decanedioic acid (111-20-6)

methyl hydrogen hexanedioate,
adipic acid, monomethyl ester (627-91-8)

Dimethyl decanedioate,
Decanedioic acid, dimethyl ester (106-79-6)

dimethyl hexanedioate (627-93-0)

Dimethyl octadecanedioate (1472-93-1)

dimethyl tetradecanedioate (5024-21-5)

dimethyl 2,5,8-decatrienedioate

bis(1-methoxy-1-cyclopentyl)pentoxide

