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Working with Hazardous Chemicals

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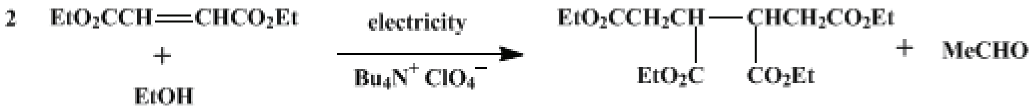
ELECTROHYDRODIMERIZATION OF AN ACTIVATED ALKENE: TETRAETHYL 1,2,3,4-BUTANETETRACARBOXYLATE

[1,2,3,4-Butanetetracarboxylic acid, tetraethyl ester]



$$2\ EtO_2CCH{=}CHCO_2Et + EtOH \xrightarrow[Bu_4N^+\ ClO_4^-]{electricity} EtO_2CCH_2CH(CO_2Et){-}CH(CO_2Et)CH_2CO_2Et + MeCHO$$

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1. Procedure

The cell consists of a commercially available four-necked, 500-mL, round-bottomed flask equipped with a 34/45 standard-taper joint electrode assembly (Note 1), a 24/40 standard-taper joint purge and vent assembly, a mercury pool cathode (Note 2), a cathode contact (Note 3), a magnetic stirring bar (Note 4), and thermometer (inserted in a 10/18 standard-taper joint neck). The two platinum anodes of the electrode assembly (Note 1) are positioned in a horizontal plane ca. 1 cm above (Note 4) the mercury (cathode) surface.

To the cell are added diethyl fumarate (172 g, 1.0 mol) (Note 5), absolute ethanol (200 mL), and tetrabutylammonium perchlorate (3.41 g, 0.1 mol) (Note 6). The mixture is allowed to stand for 0.5 hr to allow complete dissolution of the tetrabutylammonium perchlorate. The cell is placed in a flowing-water bath in a hood.

The solution is electrolyzed with continuous magnetic stirring and nitrogen purging at a constant current (Note 7) until the theoretical quantity of electricity ($1.0F \equiv 1e^-$ per mole of diethyl fumarate) has been passed. The rate at which the cooling water in the bath flows is adjusted to maintain the electrolyte solution at 35°C during the first 2 hr of the electrolysis. It is then kept constant for the remainder of the electrolysis. After conditions have stabilized (ca. 1–2 hr of electrolysis), the reaction does not need constant attention, and may be allowed to run overnight.

The reaction mixture is transferred to a 2-L, round-bottomed flask with ethanol washing and the ethanol is removed by rotatory evaporation. Diethyl ether (1 L) is added to precipitate the electrolyte salt, which is collected by filtration and washed with ether. The crude electrolyte is obtained as a white solid (32–32.5 g, theory 34.1 g). The filtrate and washings were combined and evaporated to give a viscous brown oil, which was vacuum-distilled through a short Vigreux column (15 cm × 2.5 cm). After a forerun of 70 mL of material boiling below 150°C (0.15 mm), the product (92–96 g, 53–56%), bp 150–155°C (0.1 mm), is collected (Note 8) and (Note 9). The forerun contained diethyl maleate, diethyl fumarate, diethyl succinate, and diethyl ethoxysuccinate. The product is a mixture of diastereomers; on standing some meso isomer, mp 74–75°C, crystallizes.

2. Notes

1. The electrode assembly has been described (see synthesis of dimethyl decanedioate, Note 1 and Figure 1, p. 182). In this case the electrodes have the same polarity and are electrically connected with a platinum wire dipping into the mercury contacts.
2. About 65 mL (860 g) of mercury was used, giving a pool with a surface diameter of ca. 6 cm.
3. A mercury-filled 6-mm o.d. glass tube with a platinum wire sealed through the lower end was used. The tube was bent to fit the contour of the flask. It was connected to the flask through a 24/40 standard-taper joint Teflon thermometer adapter (Ace Glass, Vineland, NJ). Contact to the mercury was made with a platinum wire as shown (Figure 1, p. 183).
4. A 20-cm × 0.5-cm Teflon coated stirring bar was used. This thickness (0.5 cm) is close to the maximum usable with an electrode gap of 1 cm. The rate of stirring was the maximum possible without

breaking the mercury surface into droplets.

5. Diethyl fumarate, obtained from Aldrich Chemical Company, Inc., was used without prior purification. The submitters used diethyl maleate.

6. Tetrabutylammonium perchlorate, obtained from Eastman Organic Chemicals, was recrystallized from aqueous methanol (75%) and dried in vacuo.

7. The checkers used a Heath Schlumberger Model SP-2711 (30 V, 3 A) power supply at a current of 1.5 A. The cell voltage, initially 25 V, slowly rose to 30 V at the end of the electrolysis and the current dropped to ca. 1 A. The electrolysis required 17–24 hr. The submitters used a current of 1.0 A.

8. The submitters reported a yield of 135 g (78%). In part the reduced yields found by the checkers were caused by mechanical losses during distillation.

9. The product showed ^{1}H NMR ($CDCl_3$) δ: 1.25 (t, 12 H, CH_3), ca. 2.6 (m, 4 H,-$COCH_2$), ca. 3.3 (m, 2 H, CH), 4.2 (two overlapping q, 8 H, OCH_2). Analysis calculated for $C_{16}H_2O_8$: C, 55.5; H, 7.6%. Found: C, 55.5; H, 7.8. Molecular weight calculated: 346. Found (osmometrically in $CHCl_3$): 340, 338.

3. Discussion

This synthesis is an example of electrohydrodimerization of activated alkenes, the scope and mechanism of which have been recently reviewed.[2,3] The individual reactions combining to give the overall result. are the cathodic reduction of the alkene to a dimer dianion (in the general case there are two major mechanisms by which the dianion may be formed and these are discussed in the references cited[2,3]), the protonation of the dianion by ethanol, and the anodic oxidation of ethanol.

In addition to providing an anode reaction (a suitable reaction at the "other" electrode is a necessity in any electrochemical reaction), reaction (4) also maintains the pH constant by producing protons to neutralize the ethoxide ions originating from reaction (3).

The present synthesis is an adaptation of a previously reported synthesis[4] in a divided cell (i.e., separate anode and cathode compartments). The overriding consideration in making this modification has been to simplify the operations involved and render the synthesis more attractive to chemists not well acquainted with electrochemical procedures. The main simplification achieved is that the pH is controlled internally via the anodic generation of protons as noted above (in the reported procedure,[4] this is achieved by periodic addition of acetic acid to the cathode compartment). A further simplification has been to run the reaction with a constant current rather than at controlled cathode potential. After the electrolysis has been initiated, the reaction requires no special attention. A small price is paid for the simplicity of the present synthesis in that the yield is somewhat lower than that obtained previously.[4] The major by-product formed is diethyl succinate, which results from a $2e^-$ reduction of diethyl fumarate or diethyl maleate: [cf. (2), which consumes $1e^-$ per mole of ester]. The occurrence of reaction (5) leads to incomplete consumption of ester after passage of the theoretical quantity of electricity (there may also be contributions from other sources).

The by-product, diethyl 2-ethoxybutanedioate, may be formed via base-catalyzed reaction in the vicinity of the cathode, where conditions may become quite basic.

References and Notes

1. Corporate Research Department, Monsanto Company, St. Louis, MO.
2. Baizer, M. M. In "Organic Electrochemistry," Baizer, M. M., Ed.; Marcel Dekker: New York, 1973.
3. Baizer, M. M.; Petrovich, J. P. *Progr. Phys. Org. Chem*. **1970**, *7*, 189–227.
4. Petrovich, M. M.; Baizer, M. R. *J. Electrochem. Soc*. **1969**, *116*, 749–756.

Appendix
Chemical Abstracts Nomenclature (Collective Index Number);

(Registry Number)

ethanol (64-17-5)

acetic acid (64-19-7)

methanol (67-56-1)

diethyl ether (60-29-7)

mercury (7439-97-6)

platinum (7440-06-4)

diethyl fumarate (623-91-6)

diethyl maleate (141-05-9)

ethoxide

Diethyl succinate (123-25-1)

Dimethyl decanedioate (106-79-6)

Tetraethyl 1,2,3,4-butanetetracarboxylate,
1,2,3,4-Butanetetracarboxylic acid, tetraethyl ester (4373-15-3)

tetrabutylammonium perchlorate (1923-70-2)

diethyl ethoxysuccinate,
diethyl 2-ethoxybutanedioate