Electrohydrocyclodimerisation of Dimethyl Benzene-1,2-diacrylate

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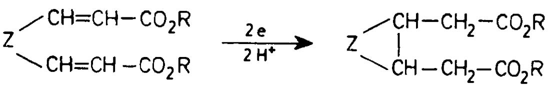
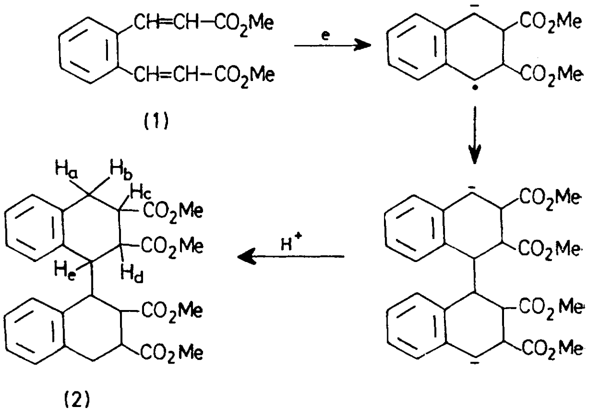
Summary On cathodic reduction, dimethyl benzene-1,2-diacrylate yields a cyclic hydrodimer, the tetramethyl ester of 1,1′-bi(tetrahydronaphthalene-2,3-dicarboxylic acid), which is formed in a novel reaction, an electrohydrocyclodimerisation.

The electrochemical hydrodimerisation (EHD) of activated olefins is a well known reaction.[1] If the activated double bonds are part of the same molecule, they can react with each other in a so-called electrohydrocyclisation (EHC) reaction[2] (equation 1). All known examples of EHC involve diolefins in which Z is a nonconjugated group isolating the two double bonds.



$$Z\begin{cases}CH{=}CH{-}CO_2R\\ CH{=}CH{-}CO_2R\end{cases}\xrightarrow[2H^+]{2e}Z\begin{cases}CH{-}CH_2{-}CO_2R\\ |\\ CH{-}CH_2{-}CO_2R\end{cases}\qquad(1)$$

In the course of a study on the cathodic reduction of some $\alpha\beta$-unsaturated dicarboxylic acid derivatives in which Z contains double bonds so that the $\alpha\beta$ double bonds are conjugated with each other, we investigated dimethyl benzene-1,2-diacrylate (**1**). The cyclic voltammogram of (**1**) on a hanging drop mercury electrode (with added activated alumina[3]) shows two reversible waves at E_p −1·60 and −1·87 V and an irreversible peak at −2·62 V *vs.* S.C.E. [dimethylformamide (DMF), tetraethylammonium tosylate, 10 V min^{-1}]. With 5% water present, the position and appearance of the first two waves were essentially unchanged whereas the third peak was shifted to E_p −2·20 V.



Scheme

A preparative reduction of (**1**) in DMF containing 4% water was carried out at −1·25 V on a mercury cathode. When 1·1 F/mol had passed, all (**1**) had reacted. G.l.c.

showed three major products (constituting 7, 28, and 59%, respectively, of the product mixture) of which the two minor ones were the result of hydrogenation of one and two double bonds, respectively.

The main product, m.p. 157—157·5 °C, after two recrystallizations from 80% methanol–water, comprised 62% of the total amount of dimer in the product mixture [29% yield based on (**1**)] and was shown to have structure (**2**) on the basis of the following evidence. According to its mass spectrum, the molecular weight of (**2**) is 494 [twice that of (**1**)+2]. The ^1H n.m.r. (no olefinic protons) and i.r. (carbonyl band at 1735 cm^{-1}) spectra showed it to be a saturated product. The ^{13}C n.m.r. spectrum ($CDCl_3$, rel. to Me_4Si) showed the tertiary aromatic carbon resonances at 137·2 and 136·2 p.p.m., characteristic for tetralins,[4] compared with the corresponding resonance in dimethyl *cis*-tetrahydronaphthalene-2,3-dicarboxylate at 134·7 p.p.m.

The ^1H n.m.r. spectrum (100 MHz, $CDCl_3$) of (**2**) shows two sets of signals at δ 2·74 and 2·88, each set consisting of four lines [each 1H, H_a and H_b, $J(H_a{-}H_b)$ 16 Hz], an unresolved multiplet at δ 3·28 (2H), and a broad peak at δ 3·82 (1H, H_c). The multiplet splits up into a triplet (H_d) and a doublet of doublets (H_e) on addition of $Eu(fod)_3$.

Since dimethyl *cis*- and *trans*-tetrahydronaphthalene-2,3-dicarboxylate are among the minor products, a probable reaction sequence could involve a one-electron reduction to the anion radical which would cyclise and then couple. Subsequent protonation would afford (**2**) as shown in the Scheme.

Coupling through the α-positions is exceptional[5] but has been observed as a minor pathway in the EHD of, *e.g.* cinnamonitrile,[6] but never as the major route. To the best of our knowledge, it has not been reported for an EHC. The case studied here is exceptionally favourable for $\alpha\alpha'$-coupling because of the steric restraints upon $\beta\beta'$-coupling (formation of a benzocyclobutene derivative).

Compound (**2**) in principle can exist in 20 isomeric forms[7] of which 16 are enantiomeric pairs and 4 *meso* forms. From its physical properties, especially the appearance of its ^{13}C n.m.r. spectrum, the specimen isolated here seems to be a single isomer.

(*Received*, 3*rd May* 1976; *Com.* 493.)

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[1] M. M. Baizer in 'Organic Electrochemistry, ed. M. M. Baizer, Marcel Dekker, New York, 1973, p. 688.
[2] J. D. Anderson, M. M. Baizer, and J. P. Petrovich, *J. Org. Chem.*, 1966, **31**, 3890.
[3] O. Hammerich and V. D. Parker, *Electrochim. Acta*, 1973, **18**, 537; B. S. Jensen and V. D. Parker, *J.C.S. Chem. Comm.*, 1974, 367.
[4] J. B. Stothers, 'Carbon-13 NMR Spectroscopy,' Academic Press, New York, 1972, p. 99.
[5] Reference 1, p. 689.
[6] J. P. Petrovich, M. M. Baizer, and M. R. Ort, *J. Electrochem. Soc.*, 1969, **116**, 749.
[7] H. Landolt, 'Das optische Drehungsvermögen,' Vieweg und Sohn, Braunschweig, 1898, p. 50.