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Electrooxidation of α-Methoxy-γ,γ-Dimethylaconic Acid

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Recently anodic alkoxylation of alkenes has been investigated extensively.[1] However, few studies have been made on the application of the reaction to cyclic olefins[1] or cyclic α,β-unsaturated carboxylic acids.[2] It is of interest that the acids have two reaction points (olefinic double bond and carboxy group) which may suffer anodic oxidation. Further one-electron oxidation of the acyloxy radical to an acyloxy cation can be possible since decarboxylation of the radical is not favorable.[3] Thus, we have examined the anodic oxidation of α-methoxy-γ,γ-dimethylaconic acid(I) in methanol as a model reaction of α,β-unsaturated cyclic carboxylic acids.

Experimental

Electrolysis of I. A stirred mixture containing 2.2 g of I[4] and 0.2 m*l* of sulfuric acid in 70 m*l* of commercial grade methanol was electrolyzed[5] using 3 cm^2 bright Pt electrodes for 3 hr at 20°C. Anode potential of electrolysis was 2.2±0.1 *vs.* SCE at current density of 0.1 A/cm^2. Under the electrolysis conditions, starting carboxylic acid I was almost completely consumed. The acidic portion (1.36 g) was recrystallized from benzene - ethanol to give 1.06 g of trimethoxy compound II and 0.30 g of IV.

The structural assignment of II was made by elemental analysis and IR and NMR spectra; mp 192.5—193°C, IR (Nujol) 1795 (lactone C=O) and 1760 (COOH) cm^{-1}, NMR (methyl ester) in $CDCl_3$, τ 8.53 (3H, s, CH_3), 8.42 (3H, s, CH_3), 6.50 (3H, s, CH_3O), 6.47 (3H, s, CH_3O), 6.37 (3H, s, CH_3O), 6.21 (3H, s, CO_2CH_3), M$^+$, *m/e* 262 (methyl ester).

Found: C, 47.99; H, 6.59%. Calcd for $C_{10}H_{16}O_7$: C, 48.39; H, 6.50%.

The structure of IV was assigned by mp, IR spectrum and vpc retention time of its methyl ester compared with authentic samples.[6]

The neutral portion (0.24 g) was fractionated by vpc using a SE-30 column at 150°C to give 0.20 g of carbonate III. The structure of III was established by spectral and elemental analyses; IR (neat) 1780, 1750 (C=O), 1210, 1170, 1130 cm^{-1}, NMR ($CDCl_3$) τ 8.35 (6H, s, gem. CH_3), 6.26 (3H, s, CH_3O), 6.10 (3H, s, CH_3O), M$^+$-60, *m/e* 172.

Found: C, 46.29; H, 5.43%. Calcd for $C_9H_{12}O_7$: C, 46.59; H, 5.21%.

Electrolysis of II. A mixture of 0.30 g of II and 0.08

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[1] N. L. Weinberg and H. R. Weinberg, *Chem. Revs.*, **68**, 449 (1968); H. Schafer, *Chem.-Ing-Techn.*, **41**, 179 (1969); *Angew. Chem.*, **81**, 940 (1969), and references cited therein.

[2] No report on anodic oxidation of cyclic α,β-unsaturated carboxylic acids except for benzoic acid has been found in literature.

[3] B. C. L. Weedon, "Advances in Organic Chemistry," Vol. 1, Interscience Publishers, Inc., N. Y. (1960).

[4] S. Torii, S. Endo, H. Oka, Y. Kariya, and A. Takeda, This Bulletin, **41**, 2707 (1968).

[5] Electrolyses were carried out by a procedure similar to that described in the paper: A. Takeda, S. Wada, S. Torii and Y. Matsui, This Bulletin, **42**, 1047 (1969).

[6] A. Takeda and S. Torii, *Memoirs of School of Engineering, Okayama Univ.*, **1**, 44 (1966).

m*l* of sulfuric acid in 30 m*l* of commercial grade methanol was electrolyzed with a terminal voltage of 15 V at a current density of 0.1 A/cm^2 (anode cell voltage, 1.95±0.05 *vs.* SCE). After recovery of 0.20 g of unchanged II, 0.05 g of neutral materials obtained was subjected to preparative vpc (SE-30, 3 m, 150°C) to afford 0.03 g of III.

Results and Discussion

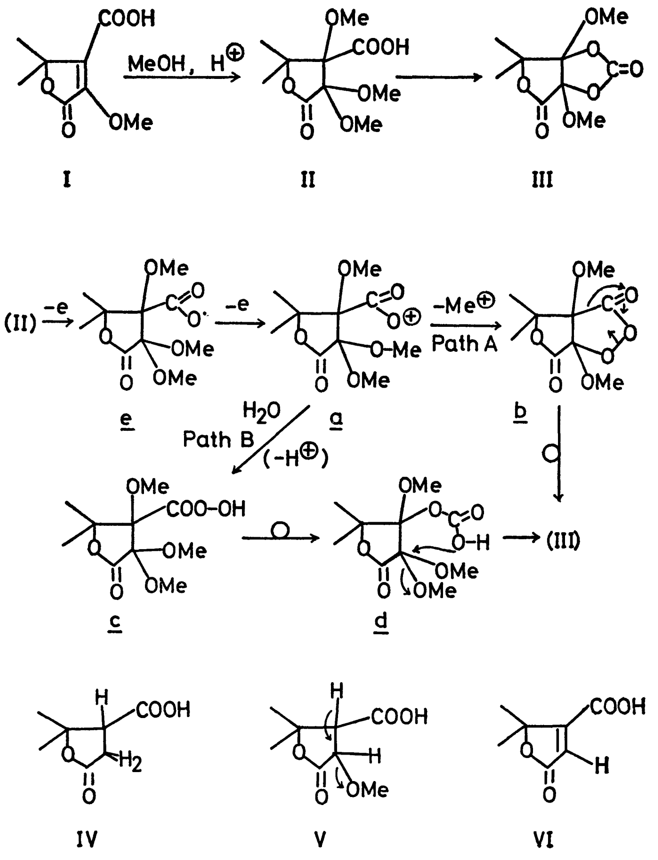
Products were α,α,β-trimethoxy-γ,γ-dimethylparaconic acid(II) (36%), terebic acid(IV) (16%), and γ,γ-dimethyl-α,β-carbonyldioxy-α,β-dimethoxybutyrolactone(III) (7.3%). Predominant formation of acidic compounds (II and IV) as compared with neutral compound III indicates that the olefinic double bond in I undergoes oxidation more readily than carboxy group. Trimethoxy compound II would result from two electron oxidation of I followed by methanolysis. Carbonate III would be produced from further oxidation of II, since electrolysis of II in a methanol-sulfuric acid mixture afforded III as the main neutral product.

Table 1. Products and their yields of the anodic oxidation of α-methoxy-γ,γ-dimethylaconic acid (I) in MeOH

Product	I$^{b)}$	II	III	IV
Yield$^{a)}$ (%)	trace	36	7.3	16

a) Yield based on carboxylic acid I.
b) Recovered I.

A tentative mechanism for the formation of carbonate III is described in scheme 1. Assuming formation of acyloxonium ion **a**[7] in the carbonation reaction of II, one can rationalize the result by postulating the rearrangement of the peroxide intermediates (**b** or **c**), *viz.* (Path A) intramolecular peroxide rearrangement[8] of **b** to III and (Path B) peracid rearrangement of **c** and reclosure of **d** to III. The mechanism of the formation of terebic acid IV can involve the following processes: i) electrochemical reduction of I to V, ii) demethoxylation with the aid of acid, and iii) further reduction of VI.[9] We found that IV was not detected by vpc analysis when I was electrolyzed in an anode compartment separated by a glass filter and VI could be subjected to reduction for a very short period without separation of electrolysis compartments.



Scheme 1

Further details of the carbonation mechanism can not be deduced from these preliminary results.

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7) P. G. Gassman and F. V. Zalar, *J. Amer. Chem. Soc.*, **88**, 2252 (1966); T. Shono, I. Nishiguchi, S. Yamane, and R. Oda, *Tetrahedron Lett.*, **1969**, 1965.

8) D. B. Denney, *J. Amer. Chem. Soc.*, **78**, 590 (1956).

9) R. Fitting and B. Frost, *Ann. Chem.*, **226**, 370 (1884).