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Anodic Ring Opening Reaction of 2-Methoxy-1-cyclopentene-1-carboxylic Acids

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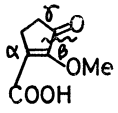
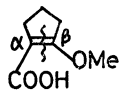
Electrolysis of 2-methoxy-1-cyclopentene-1-carboxylic acids **2** and **12a** gave α,β- or β,γ-ring opening products **4**, **5a**, **7a**, and **15**. Electrolysis of **2** without separation of anode and cathode compartments gave **6a** in a notable yield. **6a** is expected to be formed by the reduction of a key intermediate **8**, which can be rationalized by leading to **4** and **5**. The results from the anodic oxidation of **12** suggest that the C=C double bond function of **12** was initially oxidized giving **14** followed by discharge of the carboxylate anion to afford **15**. A possible mechanism for the anodic reaction of **2** and **12** has been discussed.

During the course of a study on the anodic oxidation of α,β-unsaturated carboxylic acids,[1a-d] it was found that the anodic reaction of α-methoxy-γ,γ-dimethylaconic acid in protic solvents gives lactone carbonate[1c] and the electrolysis of 5-substituted 2-furoic acids affords α,β-unsaturated butenolides along with the ring opening products.[1b,d] In both cases, the C=C double bond functions were initially oxidized to afford dimethoxy derivatives followed by further two electron oxidation of the carboxyl group.

Our interest in the anodic reaction of α,β-unsaturated carboxylic acids led us to investigate the oxidation of substituted cyclic α,β-unsaturated carboxylic acids. We wish here to report on the α,β- and β,γ-ring cleavage reactions of β-methoxy-α,β-unsaturated carboxylic acids (**2** and **12a**) by electrolysis.

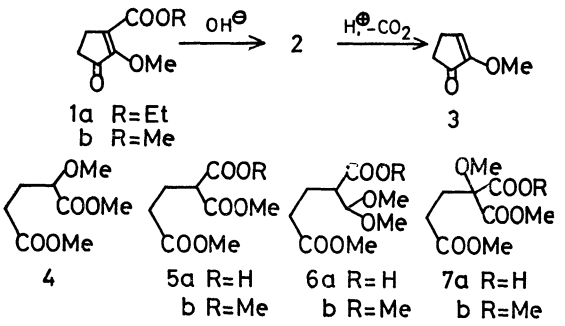


2



12a

Compound **2** obtained by hydrolysis of readily available ethyl ester **1a**[2] was electrolyzed in methanol containing a drop of concentrated sulfuric acid using one or two compartment cells fitted with platinium foil electrodes under a constant current.



In Experiment 1 (Table 1), the major products were **3**[3] and **4**.[4]

In Experiment 2, a prominent portion of acidic component was obtained together with **3** and **4** when electrolysis was interrupted at an early stage. On being treated with diazomethane the acidic products could be converted into methyl esters **1b**, **7**, and a small amount of minor products. However, when a cell without separation of the electrolysis compartments was used, compounds **5b**,[5] **6b**, and **7b** were isolated after esterification (Experiment 3). Details of experimental conditions along with the results are given in Table 1. Identification of products **3**, **4**, **5b**, **6b**, and **7b** were carried out by their spectral data and microanalyses (see Experimental).

Mechanistic consideration suggests that the electrolysis of **2** (Scheme 1), would give rise to a cationic

1) a) A. Takeda, S. Torii, and H. Oka, *Memoirs of School of Eng., Okayama Univ.*, **3**, 107 (1968); b) S. Torii, H. Tanaka, H. Ogo, and S. Yamasita, This Bulletin, **44**, 1079 (1971); c) S. Torii, T. Furuta, T. Miyaoka, H. Sako, H. Tanaka, and K. Uneyama, *ibid.*, **44**, 2258 (1971); d) S. Torii, H. Tanaka, and T. Okamoto, *ibid.*, **45**, 2783 (1972).

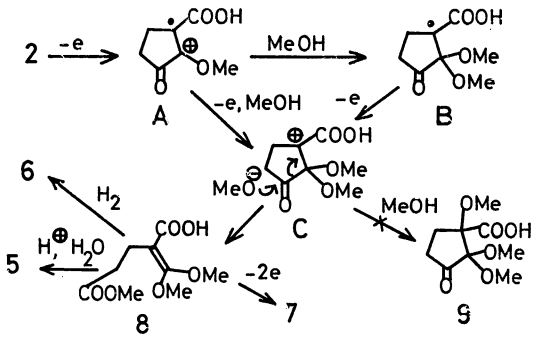
2) O. T. Schmidt and R. Eckert, *Ann.*, **618**, 71 (1958).

3) K. Bernauer, *ibid.*, **588**, 230 (1954); R. M. Acheson, *J. Chem. Soc.*, **1956**, 4232.

4) A. S. Matthews, W. G. Overend, F. Shafizaden, and M. Stacey, *ibid.*, **1955**, 2511; A. J. Birch, J. H. Birkinshaw, P. Chaplen, L. Mo, A. H. Manchanda, A. Pelter, and M. M. Riano, *Aust. J. Chem.*, **22**, 1933 (1969).

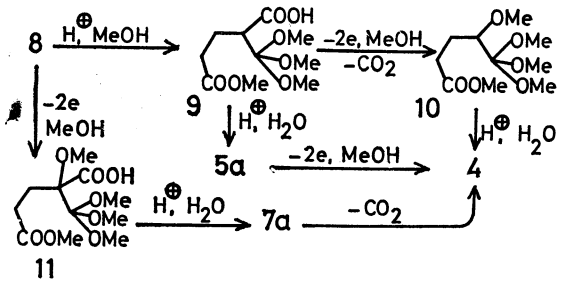
5) F. L. M. Pattison, R. L. Buchanan, and F. H. Dean, *Can. J. Chem.*, **43**, 1700 (1965); K. Schank and N. Moell, *Chem. Ber.*, **102**, 71 (1969).

intermediate **C**, which is expected to be formed from either radical intermediate **A** or **B** by one electron oxidation. On the other hand, most of our attempts to isolate a trimethoxy derivative **9** expected to be formed from the intermediate **C** with subsequent reaction with methanol failed. However, the formation of **4**, **5a**, **6a**, and **7a** *via* **8** reveals that the cation **C** would be attacked by a solvent leading to the cleavage of β,γ-bond of the intermediate **C**. Because of the high chemical instability under the acidic work-up conditions **8** was hydrolyzed rapidly to give **5a**. The formation of **8** *in situ* was also demonstrated by the isolation of **6b** as a result of reduction of the double bond when electrolysis was carried out in one compartment cell (Experiment 3).



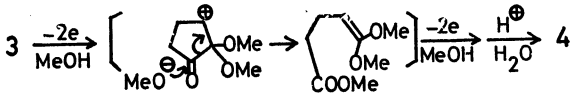
Scheme 1.

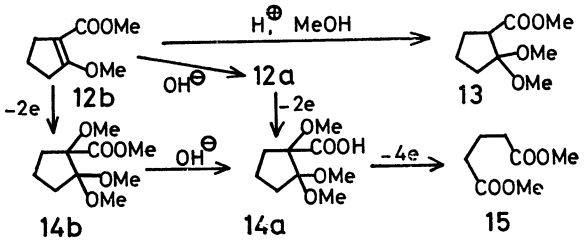
Conversion of **8** into **4** *via* **5a** and **7a** might be also explained as follows (Scheme 2). Most of the ortho ester intermediates **9**, **10**, and **11** would be readily hydrolyzed to **4**, **5a**, and **7a** under acidic conditions, *in situ* or during after treatment.



Scheme 2

Formation of **3** from **2** could be rationalized as the result of acid-catalyzed decarboxylation, since stirring of **2** in methanol containing a drop of concentrated sulfuric acid provided **3** in a moderate yield. The presence of an appreciable amount of **3** in the earlier stage of electrolysis of **2** suggests that the anodic oxidation of **3** would afford **4** as follows. Actually, electrolysis of **3** under the same conditions as in Experiment 1 (Table 1) gave **4** in 57% yield.





Scheme 3.

In order to compare the electrochemical nature of **2** with that of its analogous compound, electrolysis of the acid **12a** prepared by hydrolysis of **12b**[6] was attempted. The reaction conditions and the results are listed in Table 1. As a major product, methyl glutarate **15** was isolated from the neutral product including several minor constituents. On the other hand, electrolysis of **12b** gave **13** and **14b** without producing other notable products. It is clear that the acetal ester **13** was derived from **12b** by acid-catalyzed solvation with methanol (Scheme 3). After hydrolysis of **14b** with aqueous potassium hydroxide, electrolysis of the alkaline solution in acetonitrile gave rise to the ring opening of **14a** to give **15**. These results reveal that **14a** should be precursors of **15** in the case of anodic oxidation of **12a**.

It is considered that the differences in the products resulting from electrolyses of **2** and **12** are apparently consistent with the intrinsic chemical nature of the postulated intermediate **C** and the electrochemical behavior of **14a**.

Experimental[7]

Electrolysis. Procedure A. The cell used was a water-jacketed beaker, 3.2 cm or 5.5 cm in diameter, 10 cm high, fitted with a gas lead pipe, a thermometer, and magnetic stirrer. The electrodes were two platinum foils (1.5×2.0 cm^2) about 1 mm apart from each other. The current was controlled manually, its direction being changed every 30 sec by means of a commutator. The reaction temperature was controlled by cooling externally with circulating water.

Procedure B. Electrolysis was carried out with two platinium foil electrodes (1.5×2.0 cm^2) under a constant current. The cell used consists of two compartments separated by a glas-filter.[1]

2-Methoxy-3-oxo-1-cyclopentene-1-carboxylic Acid (2). A solution of ethyl 2-methoxy-3-oxo-1-cyclopentene-1-carboxylate(**1a**),[2] (1.00 g), Na_2CO_3 (1.00 g), and water (25 ml) was stirred for 24 hr at room temperature. The aqueous solution was washed with ether, neutralized with dilute HCl, and

6) F. Lacasa, J. Pascual, and L. V. Arco, *Anales real soc. espãn. fis. y guin.*, **52B**, 549 (1956); *Chem. Abstr.*, **51**, 5711 (1957); R. Mayer and B. Gebhardt, *Chem. Ber.*, **93**, 1212 (1960).

7) Preparative and analytical glpc were performed with a a partially modified Yanagimoto GCG-550T type apparatus using a column packed with 10% coated SE-30 Silicone grease on Celite 545, 80/100 mesh, 3 m long (4 ϕ), carrier gas H_2 at 120 °C or 140 °C. All melting and boiling points are uncorrected. Infrared spectra were determined with a Hitachi EPI/S2 spectrophotometer. NMR spectra were obtained on a Japan Electron Optics Laboratory Spectrometer (JNM-C-60) in deuterochloroform with TMS as an internal reference. Microanalyses were carried out by Miss M. Harada.

Table 1. Electrolytic conditions and results for compounds **2**, **12a**, **12b** and **14**

Experiment[a]		1	2	3	4	5	6
Substrate		**2**	**2**	**2**	**12a**	**12b**	**14**
(g)		1.00	1.00	0.96	0.50	4.00	0.20
Supporting	H_2SO_4 (mg)	70	70	70	—	—	—
Electrolyte	$LiClO_4$ (g)	6.0	6.0	—	0.50	2.00	—
	1 M-KOH (ml)	—	—	—	—	—	10
Solvent	MeOH	130	130	40	30	120	—
(ml)	MeCN	—	—	—	—	—	30
Current	(A)	0.25	0.25	0.25	1.00	0.70	0.80
Terminal voltage	(V)	11.5—18.5	19.5—28.0	8.5—12.0	14.5—15.5	8.2	12.0
Temperature	(°C)	10.0—12.0	11.5—13.5	11.0—12.0	26.0	26.0	19.0—20.3
Time	(hr)	5.5	2.75	5.75	2.0	14	0.5
Product (g)							
Neutral component		0.90	0.70	0.43	0.31	3.95	0.08
Acidic component		trace	0.23	0.38	0.07	trace	0.05
Neutral component[b]	(%)						
3		17.0	30.0	6.0	—	—	—
4		72.0	13.0	72.0	—	—	—
15		—	—	—	59.2	—	76.0
2-Methoxycarbonylcyclopentanone		—	—	—	—	6.0	—
13		—	—	—	—	43.0	—
14b		—	—	—	—	24.0	—
12b (Recovered)		—	—	—	—	9.0	—
Acidic component[b,c]	(%)						
5b		—	—	23.0	—	—	—
6b		—	—	53.0	—	—	—
7b		—	47.0	15.0	—	—	—
1b (Recovered)		—	26.0	—	—	—	—

a) Experiments 3, 4, 5, and 6 were carried out without separation of anode and cathode compartments.
b) The product abundances calculated are based on the peak area of glpc.
c) Isolated acidic products were treated with diazomethane before analysis.

extracted with chloroform. The extract was washed with water and dried(Na_2SO_4). Evaporation of the solvent gave 0.49 g of **2**, mp 148.5—149.5 °C (Benzene); IR (Nujol) 3450—2200, 1709 (COOH), 1672 (C=O), 1614 (C=C) cm^{-1}; NMR ($CDCl_3$) δ 2.39—2.90 (m, 4H), 4.27 (s, 3H, CH_3O), 8.81 (s, 1H, COOH).

Found: C, 53.83; H, 5.03%. Calcd for $C_7H_8O_4$: C, 53.85; H, 5.16%.

Electrolysis of **2**. *(Procedure B).* A mixture of lithium perchlorate (6.00 g) and concd H_2SO_4 (70 mg) in MeOH (130 ml) was poured into the anode and cathode compartments. The carboxylic acid **2**(1.00 g) was charged in the anode compartment and electrolyzed under a constant current (0.25 A) at 10—12 °C for 1.5 hr. The anode solution was concentrated by suction and taken up in chloroform. The solution was washed with water followed by aqueous $NaHCO_3$ and dried (Na_2SO_4). Removal of the solvent gave a crude liquid (0.90 g). The constituent of the oil was elucidated by glpc as shown in Table, Exp. 1. The major component **4**[4] was isolated by preparative glpc: IR (Neat) 2845 (CH_3O), 1741 (C=O) cm^{-1}; NMR ($CDCl_3$) δ 1.80—2.20 (m, 2H, CH_2), 2.30—2.60 (m, 2H, CH_2CO), 3.39 (s, 3H, CH_3O), 3.68 (s, 3H, CH_3OOC), 3.77 (s, 3H, CH_3OOC), 3.92 (m, 1H, CH). Microanalyses gave correct results.

The spectral data of **3**[3] (minor product) isolated by preparative glpc are as follows: IR (Neat) 3098 (HC=C), 1715 (C=O), 1631 (C=C) cm^{-1}; NMR ($CDCl_3$) δ 2.98 (broad, 4H, CH_2), 3.76 (s, 3H, CH_3O), 6.39 (t, J=2.5 Hz, HC=C).

(Procedure A). A mixture of **2** (0.96 g) in MeOH (40 ml) containing H_2SO_4 (*ca.* 70 mg) was electrolyzed (Table 1, Exp. 3). The mixture was concentrated under reduced pressure and the residue was taken up in chloroform. The solution was washed successively with water, aqueous $NaHCO_3$, and water, and then dried (Na_2SO_4). Removal of the solvent gave an oil (0.43 g), whose glpc results are shown in Table 1 (Exp. 3). Components **3** and **4** were isolated by preparative glpc from the oil. Spectral data of **3** and **4** were identical with those of the corresponding authentic samples.

The aqueous alkaline solution was acidified with dilute HCl to pH 3—4 and extracted with chloroform. The extracts were washed with water and dried (Na_2SO_4). Removal of the solvent gave the acidic material as an oil (0.38 g). By treating with diazomethane, the acidic fraction was converted into the corresponding methyl esters, whose glpc results[8a] showed the presence of three major compounds: **5b** (Peak area 23%, R_t 8.2 min), **6b** (53%, 9.6 min), and **7b** (15%, 14.2 min) along with several minor peaks (total 9%). The major products **5b**, **6b**, and **7b** were isolated by preparative glpc.

Compound **5b**[5]: IR (Neat) 2850 (CH_3O), 1740 (C=O) cm^{-1}; NMR ($CDCl_3$) δ 2.00—2.60 (m, 4H, CH_2), 3.51 (t, 1H, CH), 3.70 (s, 3H, CH_3OOC), 3.78 (s, 6H, CH_3OOC).

8) a) Carrier gas flow rate: 35 ml/min at 140 °C. b) 20 ml/min at 140 °C.

Compound **6b**: IR (Neat) 2840 (CH_3O), 1741 (C=O) cm^{-1}; NMR ($CDCl_3$) δ 1.80—2.80 (m, 5H), 3.42 (s, 6H, gem CH_3O), 3.73 (s, 3H, CH_3OOC), 3.76 (s, 3H, CH_3OOC), 4.58 (d, J=7.5 Hz, 1H, CH).

Found: C, 51.56; H, 7.75%. Calcd for $C_{10}H_{18}O_6$: C, 51.27; H, 7.75%. Compound **7b**: IR (Neat) 2880 (CH_3O), 1745 (C=O) cm^{-1}; NMR ($CDCl_3$) δ 2.44 (s, 4H, CH_2), 3.43 (s, 3H, CH_3O), 3.73 (s, 3H, CH_3OOC), 3.86 (s, 6H, CH_3-OOC).

Found: C, 48.76; H, 6.60%. Calcd for $C_{10}H_{16}O_7$: C, 48.39; H, 6.50%.

*2-Methoxy-2-cyclopentenone (**3**).* A solution of **2** (0.50 g) in MeOH (40 ml) containing a drop of concd H_2SO_4 was stirred for 5.5 hr 11—13 °C. After removal of the solvent, the residue was taken up in chloroform. The solution was washed with water and aqueous $NaHCO_3$ and dried (Na_2SO_4). Removal of the solvent gave an oil (91 mg), whose glpc[8b] results showed the presence of two major components: **3** (Peak area 70%, R_t 4.3 min), unknown (30%, 6.0 min). Isolation of **3** was carried out by preparative glpc, its structure being confirmed by comparison with the spectral data of an authentic sample.[3]

*Electrolysis of 2-Methoxy-1-cyclopentenone (**3**). (Procedure B).* A mixture of lithium perchlorate (6.00 g) in MeOH containing concd H_2SO_4 (70 mg) was poured into both compartments. In the anode compartment **3** (0.20 g) was charged and electrolyzed under a constant current of 0.25 A at 10.0—11.0 °C for 2.0 hr with stirring. The solution of the anode compartment was then worked up as described above to give a crude oil (230 mg), which was chromatographed on 5 g of silica gel (Wakogel C-200) with AcOEt–Benzene (1 : 5) to give a clean oil (144 mg). Glpc analysis of the oil showed the presence of methyl 2-methoxyglutarate (**4**) (79%). Analytical specimen of **4** was obtained by preparative glpc. IR and NMR spectra of **4** were identical with those of an authentic sample.

*2-Methoxy-1-cyclopentene-1-carboxylic Acid (**12a**).* A mixture of **12b** (10 g),[6] K_2CO_3 (10 g), and water (35 ml) was stirred for 8 hr at room temperature. The resulting solution was cooled to 10 °C and acidified with dilute HCl to pH 6.0—6.5 and extracted with chloroform. The extracts were washed with water and dried (Na_2SO_4). Concentration of the solution gave crude **12a**, 4.5 g (49.4%), mp 148—148.3 °C (Benzene); IR (Nujol) 2600 (COOH), 1670, 1640, 1610, 1600 (C=O, C=C) cm^{-1}; NMR ($CDCl_3$) δ 1.95 (m, 2H, CH_2), 2.40—2.90 (m, 4H, CH_2), 3.89 (s, 3H, CH_3O), 9.57 (s, 1H, COOH).

Found: C, 59.43; H, 7.07%. Calcd for $C_7H_{10}O_3$: C, 59.14; H, 7.09%.

*Electrolysis of 2-Methoxy-1-cyclopentene-1-carboxylic Acid (**12a**). (Procedure A).* A mixture of **12a** (0.50 g) and lithium perchlorate (0.50 g) in MeOH was electrolyzed (Table 1, Exp. 4). The reaction mixture was concentrated *in vacuo* and the residue was taken up in chloroform. The solution was worked up in the usual manner. Removal of the solvent gave an oil (0.31 g), whose glpc results (Table 1) showed the presence of dimethyl glutarate (59.2%) as a major component isolated by preparative glpc.

*Electrolysis of Methyl 2-Methoxy-1-cyclopentene-1-carboxylate (**12b**). (Procedure A).* A mixture of **12b** (4.00 g) and lithium perchlorate (2.00 g) in MeOH (120 ml) was electrolyzed (Table 1, Exp. 5). The mixture was worked up in the usual manner to give an oil (3.95 g), whose glpc results[8] showed the presence of four major components: methyl 2-cyclopentanone-1-carboxylate (Peak area 6%, R_t 4.3 min), **13** (43%, 6.0 min), recovered **12b** (9%, 7.8 min), and **14b** (24%, 10.6 min) along with several minor compounds (18%). The major products were isolated by preparative glpc or by preparative tlc. The structural assignments of methyl 2-cyclopentanone-1-carboxylate, **12b**, and **13** were carried out by comparing their spectral data with those of the corresponding authentic specimen. The physical data of **14b** together with microanalyses are as follows: IR (Neat) 2845 (CH_3O), 1737 (C=O) cm^{-1}; NMR ($CDCl_3$) δ 1.50—2.50 (m, 6H, CH_2), 3.24 (s, 6H, CH_3O), 3.39 (s, 3H, CH_3O), 3.78 (s, 3H, CH_3OOC).

Found: C, 55.04; H, 8.30%. Calcd for $C_{10}H_{18}O_5$: C, 55.03; H, 8.31%.

*Electrolysis of 1,2,2-Trimethoxycyclopentane-1-carboxylic Acid (**14a**). (Procedure A).* A solution of **14b** (215 mg, purity 70%) obtained in the above procedure in 1 M aqueous KOH (1.26 ml) was stirred for 25 hr at room temperature. To this solution was added a mixed solution of acetonitrile (30 ml) and water (10 ml). The mixture was electrolyzed, reaction conditions and results being given in Table 1, Exp. 6.

*Methyl 2,2-Dimethoxycyclopentane-1-carboxylate (**13**).* A mixture of **12b** (0.50 g) and a drop of concd H_2SO_4 in MeOH (30 ml) was stirred at room temperature for 1 hr. The resulting solution was concentrated and taken up in chloroform. The solution was washed with water and dried (Na_2SO_4). Evaporation of the solvent gave an oil (0.31 g), consisting of two components (**13** and **12b**) as elucidated by glpc[8b]: **13** (Peak area 89%, R_t 6.0 min) and recovered **12b** (8%, 7.8 min). Both compounds isolated by preparative glpc were confirmed by comparison with authentic sepcimens.