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Indirect Electrochemical Oxidation of Cyclic Ketones: Influence of Ring Size, Mediator and Supporting Electrolyte on the Result of the Reaction

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Abstract: The result of the indirect electrochemical oxidation of cyclic ketones in methanol in an undivided cell in the presence of sodium halides depends on the ring size of ketone and the type of mediator. Selectivity of the reaction in some cases and current efficiency are increased by addition of supporting electrolyte - sodium hydroxide. Formation of cyclic 2,2-dimethoxycycloalkanols and the electrochemically induced Favorskii rearrangement with the formation of methyl cycloalkencarboxylates containing in the ring one carbon atom less than starting ketone are the main ways of the indirect electrochemical oxidation of cyclic ketones.© 1997 Elsevier Science Ltd.

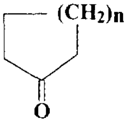
The oxidation of ketones is a way for preparing carboxylic acids and their derivatives, bifunctional compounds such as α-hydroxyketones, diketones and other useful intermediates in organic synthesis.[1] The formation of adipic acid from cyclohexanone is an important industrial process. In the case of aryl alkyl ketones the corresponding α-hydroxyketones and α-hydroxyketals are convenient compounds for synthesis of the pharmacologically active 2-arylalkanoic acids.[2,3]

The advance of electrooxidation procedures in recent years has provided organic chemists with a new versatile synthetic device of great promise.[4] But in the case of the electrooxidation of ketones only some reactions which could provide product-selectivity are known.

The first attempts of the electrochemical oxidation of ketones resulted in the formation of a mixture of acids, saturated and unsaturated hydrocarbons, carbon monoxide and dioxide.[5-8] Non selective remote oxidative functionalization of ketones was carried out in acetonitrile or trifluoroacetic acid as a result of the subsequent transformation of the initially produced cation radical $R^1R^2C{=}O^{+\cdot}$.[9,10] The anodic oxidation of cycloalkanones in aqueous alcohols usually gave mixtures of lactones of different types.[11,12]

In some oxidative transformations of ketones as in the Favorskii rearrangement the preliminary α-halogenation of ketones is necessary.[13] So for certain cases selective indirect electrooxidation of ketones with the electrochemically generated halides is also known. Thus, cyclohexanone and tetrahydropyran-4-one are converted into α-hydroxyketals by electrooxidation in basic potassium iodide - methanol solution,[14] aryl alkyl ketones being electrolysed in methyl orthoformate in the presence of iodides give rise to methyl 2-arylalkanoates.[15] The electrocatalytic variant of the haloform reaction, the procedure to prepare carboxylic acids esters by the electrooxidation of methyl ketones in methanol in the presence of bromides is also known.[16]

Continuing our studies on the electrooxidation of ketones[17-19] we have accomplished indirect electrochemical oxidation of cyclic ketones **1a-e** in the presence of sodium halides.

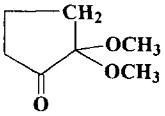


1a-e

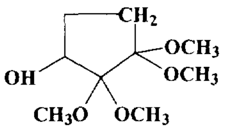
a n=1 **d** n=4
b n=2 **e** n=8
c n=3

Results

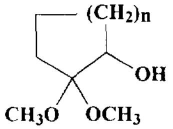
It has been found that the result of electrooxidation of cyclic ketones **1a-e** in methanol in the presence of sodium halides in an undivided cell depends on the ring size of cyclic ketone, mediator and supporting electrolyte - sodium hydroxide (Table 1).[20]



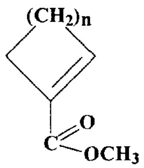
2
(n=1)



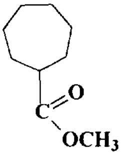
3
(n=1)



4a-d
a n=2 c n=4
b n=3 d n=8



5a-c
a n=3 c n=8
b n=4



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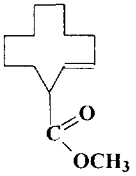

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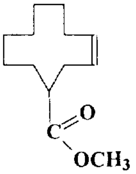


8

Table 1. Electrooxidation of cyclic ketones.

N	Ketone	n	Mediator	Electricity passed, F/mol	Conversion of ketone [%]	Products, yield [%][a]
1	**1a**	1	NaI	5.0	82	**2**, 66 (51)
2	**1a**	1	NaBr	6.0	89	**3**, 40 (22)
3	**1b**	2	NaI	3.5	95	**4a**, 82 (70)
4	**1b**	2	NaBr	3.5	98	**4a**, 78 (65)
5	**1c**	3	NaI	3.5	93	**4b**, 47; **5a**, 31
6	**1c**	3	NaI [b]	2.3	100	**4b**, 80 (65)
7	**1c**	3	NaBr	6.0	92	**4b**, 18; **5a**, 55
8	**1c**	3	LiBr [c]	6.0	97	**5a**, 64 (50)
9	**1d**	4	NaI	11.0	100	**5b**, 82 (68); **6**, 13
10	**1d**	4	NaI [d]	4.0	100	**5b**, 71; **6**, 14; **4c**, 9
11	**1d**	4	NaI [b]	4.0	100	**5b**, 57; **6**, 17; **4c**, 26 (10)
12	**1d**	4	NaBr	9.0	92	**5b**, 56; **6**, 15
13	**1e**	8	NaI	8.0	100	**5c**, 43; **7**, 8; **8**, 14,
14	**1e**	8	NaI [d]	3.6	98	**5c**, 55 (60) [e]; **8**, 16;
15	**1e**	8	NaI [b]	3.6	100	**5c**, 40; **4d**, 29 (8)
16	**1e**	8	NaBr	7.5	97	**5c**, 35; **8**, 29 (13)

[a] Determined by gas chromatography and NMR-spectra, in parenthesis - isolated yields.

[b] 10 mmol of NaOH were added as supporting electrolyte.

[c] Current density 50 mA/cm^2.

[d] 1 mmol of NaOH was added as supporting electrolyte.

[e] Reaction mixture after electrolysis was heated 1 hour with additional 10 mmol of NaOH, under these conditions **8** is completely transformed into in **5c**.

Electrooxidation of cyclopentanone **1a** in the presence of NaI results in formation of 2,2-dimethoxycyclopentanone **2**. Under the same conditions in the presence of NaBr complex mixture of mono-, di-, tri- and tetramethoxylated compounds was obtained. The main component of this mixture 2,2,3,3-tetramethoxycyclopentanol **3** was formed in 40% yield (GC) and isolated by distillation in 22% yield after passing 6.0 F/mol of electricity through under standard conditions of the electrooxidation. Using NaOH as supporting electrolyte did not give sufficient effect on the selectivity of the electrooxidation of **1a**.

The result of the electrooxidation of cyclohexanone **1b** is nearly the same in the presence of NaI and NaBr - the formation of 2,2-dimethoxycyclohexanol **4a** in ~80% yield. There is little influence of NaOH on this reaction. The latter fact was also mentioned earlier for the case of the electrooxidation of **1b** in the presence of NaI.[14] Electrooxidation of **1b** in the presence of NaCl results in formation of a complex mixture of products, among them **4a** was formed in 33% yield.

The electrooxidation of cycloheptanone **1c** depends on the mediator used. In the presence of NaI 2,2-dimethoxycycloheptanol **4b** is predominantly formed. In the presence of NaBr, electrochemically induced Favorskii rearrangement with the formation of methyl 1-cyclohexene-1-carboxylate **5a** is the main reaction pathway. Conditions for preparing both **4b** and **5a** were optimised: for **4b** by using NaOH as the supporting electrolyte, for **5a** by employing LiBr as the mediator. In the last case it is necessary to decrease the current density from 100 mA/cm^2 up to 50 mA/cm^2 to depress the reduction on the cathode of **1c** into cycloheptanol.

Under all the conditions studied the main pathway of the electrooxidation of cyclooctanone **1d** and cyclododecanone **1e** is electrochemically induced Favorskii rearrangement. The best selectivity for the electrooxidation of **1e** was achieved under standard conditions in the presence of NaI and 1 mmol of NaOH as supporting electrolyte. In the presence of NaOH in this case the current efficiency was also increased (2 times). Using NaOH as supporting electrolyte also increases current efficiency in the case of electrooxidation of **1d**, but in the latter case under these conditions less selectivity of the reaction was achieved.

Discussion

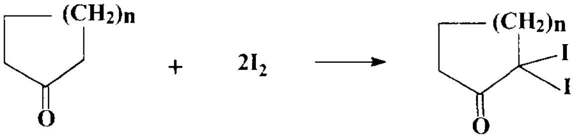
The reactions at the electrodes which take place during the process are shown below:

$$\textbf{anode: } 2\mathrm{Hal}^- - 2e \longrightarrow \mathrm{Hal}_2$$

$$\textbf{cathode: } 2\,\mathrm{CH_3OH} + 2e \longrightarrow 2\mathrm{CH_3O}^- + \mathrm{H_2}$$

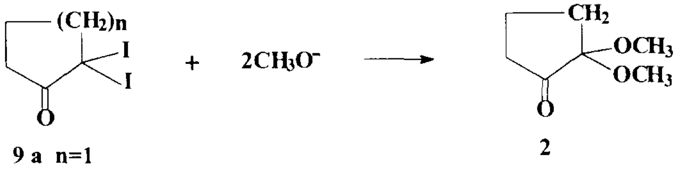
The formation of iodine or bromine at the anode is observed by the corresponding colour when electrolysis is conducted without stirring of the reaction mixture.

In the case of electrooxidation of cyclopentanone **1a** in the presence of NaI then α-monoiodination takes place in the solution. α-Iodocyclopentanone thus formed undergoes the second iodination more easily than starting cyclopentanone **1a**, so the general equation of the iodination reaction looks like the one given below:

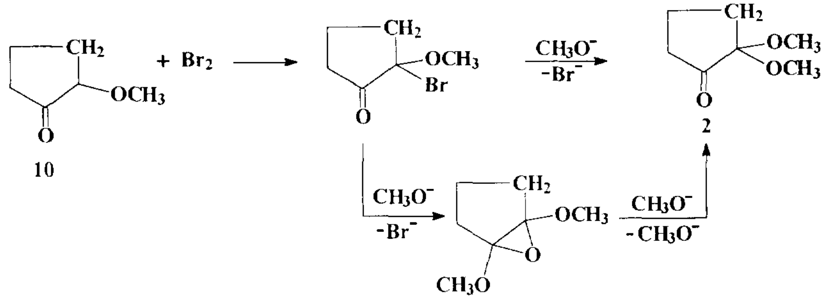


1a n=1 **9 a n=1**

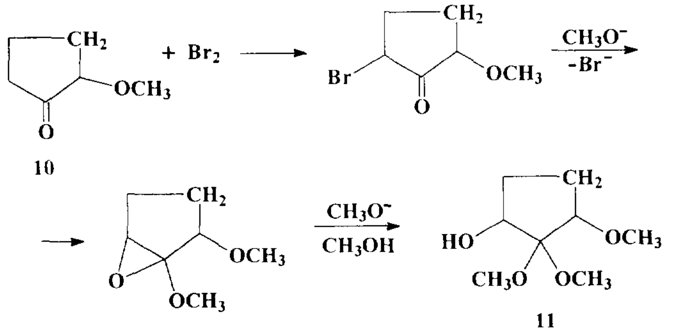
Further reaction of **9a** with CH_3O^--anions generated at the cathode results in the formation of the end product of the electrochemical process - compound **2**:



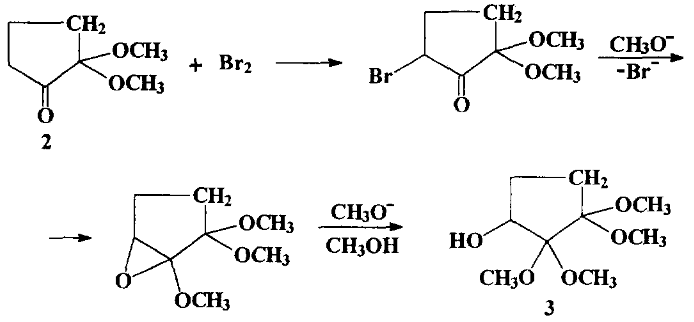
In the electrooxidation of **1a** in the presence of NaBr under conditions of low conversion both α-monomethoxy- and α,α-dimethoxycyclopropanonones **10** and **2** were identified. Thus when conversion of **1a** was 30% **10** and **2** were prepared in 17 and 28% yield respectively together with **3**, 5% yield (on converted **1a**). The main feature of the electrolysis of **1a** in the presence of NaBr is that the thus formed **10** and **2** also react with bromine formed at the anode. The main pathway of the oxidation of **10** under these conditions is formation of **2** by two possible variants of the mechanism:



Bromination of **10** in α'-position with next attack of CH_3O^--anion on the carbonyl group should lead to 2,2,3-trimethoxycyclopentanol **11** which was also identified in the reaction mixture:

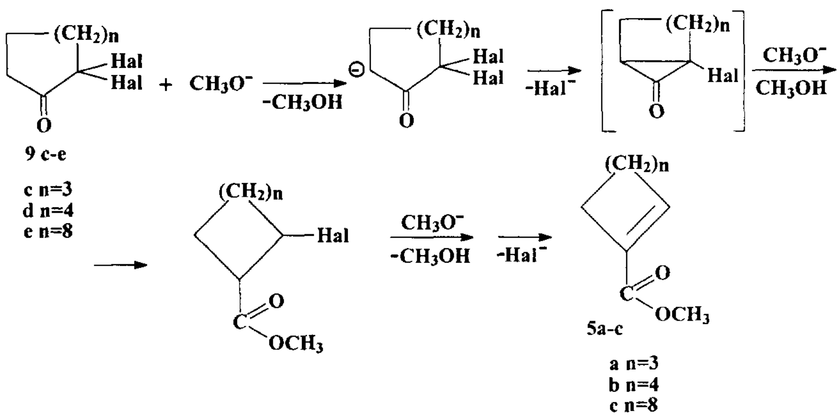


The analogous process for **2** leads to **3** which is the main product of the reaction under conditions of substantial conversion of **1a**. Thus under conditions of 60% conversion of cyclopentanone **1a** compounds **10**, **2** and **3** were prepared in 5, 12 and 28% yields respectively.



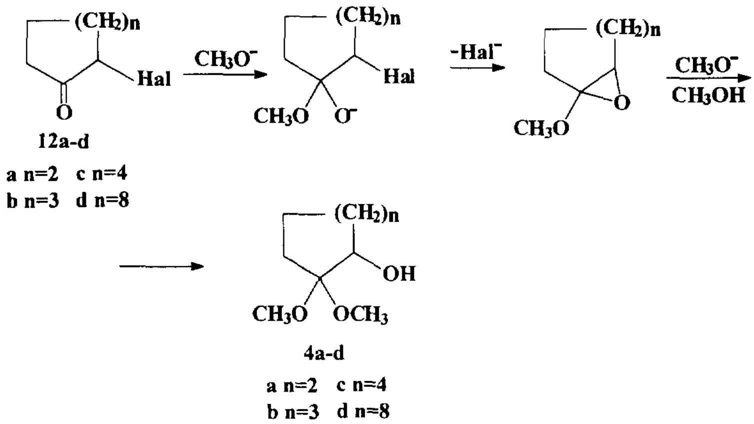
The general process of the electrooxidation of **1a** in the presence of NaBr has low selectivity. The similar low selectivity was also mentioned in the case of electrooxidation of **1b** in the presence of NaCl. Probably both these processes could also have a free radical pathway, which lead to low selectivity. A free radical pathway has already been suggested for the indirect electrooxidation of malonate ester in the presence of NaCl.[21]

In the electrooxidation of all other cyclic ketones except cyclohexanone the formation of double α-halogenated intermediate of the type **9** also takes place. But for cyclic ketones with the ring size more than 6 carbon atoms the main reaction of this intermediate in solution is Favorskii rearrangement:



In the case of the electrooxidation of **1c** the formation of **5a** is the main pathway of the reaction only in the presence of bromides as mediators. This coincides with the result of the analogous chemical variant of Favorskii rearrangement of corresponding iodides and bromides of **1c**.[22] When LiBr is employed as mediator less current density should be used because of the higher reduction potential of Li^+ compared to Na^+ to avoid substantial electrochemical reduction of **1c** into cycloheptanol.

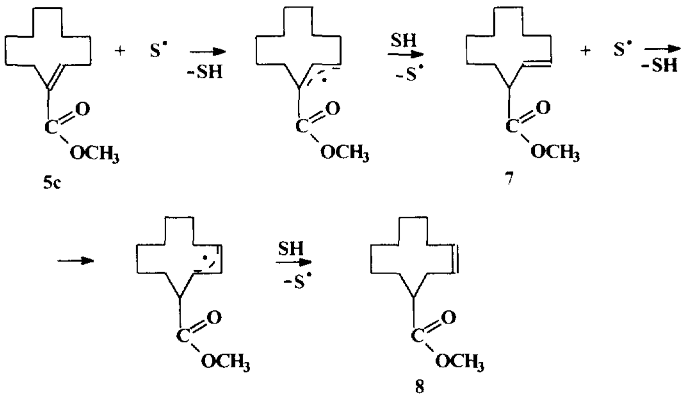
Using NaOH as additional electrolyte to NaI in the case of the electrooxidation **1c** led to the selective formation of **4b** by the following general reaction scheme:



This reaction is the main process for the electrooxidation of **1b** into **4a** in the presence both NaI and NaBr even in the absence of NaOH. **4c** and **4d** were identified in quantities up to 30% in the case of the electrooxidation of **1d** and **1e** in the presence of NaI with adding NaOH as supporting electrolyte.

The results of the formation **4a,b** under conditions of the electrolysis in the absence of NaOH could be due to the fact that the quantity of the keto-form in α-monohalogenated cyclic ketone in the case of cyclohexanone **1b** and cycloheptanone **1c** is more than in the case of the other cyclic ketones studied. So in the electrooxidation of cyclohexanone **1b** and cycloheptanone **1c** one more route of the reaction leading to **4a,b** takes place even in the absence of additional electrolyte - NaOH. The addition of NaOH has two effects. First it increases the concentration of CH_3O^--anions in the solution and thus facilitates the pathway of the formation of α,α-dimethoxycycloalkanols **4**. This effect has been already mentioned for the case of the electrooxidation of tetrahydropyran-4-one.[14] The second it increases the quantity of enol form in starting ketone and thus increases the general efficiency of the electrooxidation of ketone (current yield).

Methyl 1-cycloundecene-1-carboxylate **5c** formed in the electrooxidation of cyclododecanone **1e** undergoes the migration of double bond under the conditions of the electrolysis with the formation of **7** and **8**. The isomerization of **5c** could also be connected with the free radical pathway of the reaction, for example by the following scheme:



According to this scheme at least one relatively stable isomer **8** is formed under different reaction conditions. Another possibility is acid catalysed migration of double bond in **5c** near the surface of anode. It should be also mentioned that under basic conditions **8** is completely isomerized into **5c**.

Experimental

GC analysis was carried out on Hewlett-Packard Model 5890 chromatograph with a flame-ionisation detector. Columns: 1) fused-silica capillary column HP-1 (5 m x 0.53 mm x 2.65 μm), 2) glass column 3 m x 3 mm with 10% FFAP on Chromaton N-Super (0.13-0.16 mm). ^{1}H-NMR and ^{13}C-NMR spectra were run for solutions in $CDCl_3$ and recorded with Varian Unity 300 (300 MHz) or Varian Unity 500-PLUS (500 MHz) spectrometers. Chemical shifts are presented in δ scale with tetramethylsilane (TMS) used as internal standart. Mass-spectra (70 eV) were determined directly or with chromatographic injection using Hewlett-Packard Model 5988A spectrometer.

General electrolysis procedure.

A solution of cyclic ketone (0.02 mol) and sodium halide (0.015 mol) in methanol (20 ml) was electrolysed in an undivided cell equipped with C-anode and Fe-cathode at 30^{0}C under constant current density 110 mA/cm^2 until the quantity of the electricity indicated in Table 1 was passed. The solvent was then removed and the reaction mixture extracted with ether, washed with a solution of $Na_2S_2O_3$ in water then with water and dried with Na_2SO_4 (procedure of isolation A). In the cases when NaOH was used as supporting electrolyte reaction mixture was neutralized by dilute HCl, the solution was then removed and the reaction mixture extracted with ether, washed with a solution of $Na_2S_2O_3$ in water then with water and dried with Na_2SO_4 (procedure of isolation B). After distillation compounds **2-5** were isolated.

Compounds **2**,[20, 23] **4a**[14, 20] have been already discribed sufficiently.

2,2,3,3-Tetramethoxycyclopentanol (**3**), b. p. 55-58^{0}C (0.12 torr), H^1-NMR ($CDCl_3$): 1.39 (m, 1H, CH_2), 1.72 (m, 1H, CH_2), 1.91 (m, 1H, CH_2), 2.11 (m, 1H, CH_2), 2.95 (d, 1H, OH), 3.33 (s, 3H, OCH_3), 3.36 (s, 3H, OCH_3), 3.42 (s, 3H, OCH_3), 3.45 (s, 3H, OCH_3), 3.89 (m, 1H, CH-O); C^{13}-NMR ($CDCl_3$): 27.8 (t), 28.7 (t), 49.9 (q), 50.78 (q), 50.80(q), 51.0 (q), 73.4 (d), 105.4 (s), 107.7 (s); MS (70 eV): m/z (relative intensity %): 206 (M$^+$, 1), 191(2), 175 (8), 159 (99), 143 (21), 131 (22), 127 (25), 101 (100), 99 (27), 71 (37), 59 (33). Anal. Calcd. for $C_9H_{18}O_5$: C, 52.41; H, 8.78. Found: C, 52.33: H, 8.89.

2,2-Dimethoxycycloheptanol (**4b**),[24] b. p. 48-51^{0}C (0.12 torr), H^1-NMR ($CDCl_3$): 1.20-1.85 (m, 10H, CH_2), 2.12 (d, 1H, OH), 3.21 (s, 6H, OCH_3), 3.79 (m, 1H, CH); C^{13}-NMR ($CDCl_3$): 20.2 (t), 20.7 (t), 26.9 (t), 29.5 (t), 30.8 (t), 48.4 (q), 48.8 (q), 72.1 (d), 103.4 (s); MS (70 eV): m/z (relative intensity %): 174 (M$^+$, 4), 143 (11), 101 (100), 88 (23), 59 (19), 55 (26).

2,2-Dimethoxycyclooctanol (**4c**), was identified in reaction mixtures (procedure of isolation A) of exp. 10,11 by mass-spectrometry and signals in ^{1}H-NMR-spectra. MS (70 eV): m/z (relative intensity %): 188 (M$^+$, 5), 157 (7), 115 (5), 101 (100), 88 (21), 59 (17), 55 (23); H^1-NMR ($CDCl_3$): 3.22 (s, 3H, OCH_3), 3.26 (s, 3H, OCH_3), 3.82 (m, 1H, CH-O). After repeating electrolysis under conditions of exp. 11 using procedure of isolation B and further silica gel column chromatography (hexane - ethyl acetate 10 : 1) 2-hydroxycyclooctanone[25] was isolated in 10% yield as viscous oil, H^1-NMR ($CDCl_3$): 0.80-1.95 (m, 10H, CH_2), 2.23 [m, 1H, CH(C=O)] 2.95 [m, 1H, CH(C=O)], 3.53 (d, 1H, OH), 4.18 (m, 1H, CH-O); C^{13}-NMR ($CDCl_3$): 21.7 (t), 25.2 (t), 25.8 (t), 26.9 (t), 31.8 (t), 38.4 (t), 76.8 (d), 213.5 (s).

2,2-dimethoxycyclododecanol (**4d**) was identified in reaction mixtures (procedure of isolation A) of exp. 15 by mass-spectrometry and signals in ^{1}H-NMR-spectra: MS (70 eV): m/z (relative intensity %): 244 (M$^+$, 6), 226 (1), 213 (5), 171 (4), 157 (4), 115 (6), 102 (12), 101 (100), 88 (23), 55 (17); H^1-NMR ($CDCl_3$):

3.28 (s, 3H, OCH_3), 3.39 (s, 3H, OCH_3), 3.87 (m, 1H, CH-O). After repeating electrolysis under conditions of exp. 15 using procedure of isolation B and further silica gel column chromatography (hexane - ethyl acetate 10 : 1) 2-hydroxycyclododecanone was isolated in 8% yield, m. p. 75-76^{0}C (lit.[26] 75-77^{0}C), H^1-NMR ($CDCl_3$): 0.75-1.95 (m, 18H, CH_2), 2.19 [m, 1H, CH(C=O)] 3.05 [m, 1H, CH(C=O)], 3.62 (d, 1H, OH), 4.43 (m, 1H, CH-O); C^{13}-NMR ($CDCl_3$): 18.5(t), 21.2 (t), 21.8 (t), 22.3 (t), 22.5 (t), 23.7 (t), 25.8(t), 26.0(t), 30.5 (t), 34.1 (t), 76.5 (d), 213.2 (s).

Methyl 1-cyclohexene-1-carboxylate (**5a**),[27] b. p. 94-97^{0}C (14 torr), H^1-NMR ($CDCl_3$): 1.53 (m, 2H, CH_2), 1.61 (m, 2H, CH_2), 2.21 (m, 2H, CH_2), 2.21 (m, 2H, CH_2), 3.69 (s, 3H, OCH_3), 6.95 (m, 1H, CH=); C^{13}-NMR ($CDCl_3$): 21.4 (t), 22.0 (t), 24.3 (t), 25.7 (t), 51.4 (q), 130.1(s), 139.7 (d), 168.1 (s); MS (70 eV): m/z (relative intensity %): 140 (M^+, 38), 109 (25), 108 (24), 97 (15), 81 (100), 80 (55), 79 (38), 67 (55), 59 (42), 55 (67).

Methyl 1-cycloheptene-1-carboxylate (**5b**),[28] b. p. 41-43^{0}C (0.12 torr), H^1-NMR ($CDCl_3$): 1.50 (m, 4H, CH_2), 1.75 (m, 2H, CH_2), 2.26 (m, 2H, CH_2), 2.49 (m, 2H, CH_2), 3.69 (s, 3H, OCH_3) 7.14 (t, 1H, CH=, *J*=7,5 Hz); C^{13}-NMR ($CDCl_3$): 25.7 (t), 26.2 (t), 27.4 (t), 28.8 (t), 32.0 (t), 51.7 (q), 136.5(s), 144.5 (d), 168.7 (s); MS (70 eV): m/z (relative intensity %): 154 (M^+, 49), 123 (28), 111 (17), 95 (100), 87 (56), 81 (25), 79 (59), 67 (85), 59 (38), 55 (62).

Methyl 1-cycloundecene-1-carboxylate (**5c**),[29] b. p. 76-80^{0}C (0.15 torr), mixture of (Z)- and (E)-isomers in ratio 3 : 1. (Z)-**5c**, MS (70 eV): m/z (relative intensity %): 210 (M+, 68), 179(15), 167(13), 153(75), 149(21), 95(86), 81(93), 79(72), 67(85), 59 (58), 55(100); H^1-NMR ($CDCl_3$): 1.15-1.75 (m, 14H, CH_2), 2.29 (m, 2H, CH_2), 2.49 (m, 2H, CH_2), 3.73 (s, 3H, OCH_3), 6.09 (t, 1H, CH=, *J*=8 Hz); C^{13}-NMR ($CDCl_3$): 131.6 (s) and 143.5 (d) (C=CH), 168.9 (s, C=O). (E)-**5c**, MS (70 eV): m/z (relative intensity %): 210 (M+, 86), 179(33), 167(19), 153(68), 149(17), 95(100), 81(97), 79(81), 67(79), 59 (54), 55(77); H^1-NMR ($CDCl_3$): 1.15-1.75 (m, 14H, CH_2), 2.33 (m, 2H, CH_2), 2.41 (m, 2H, CH_2), 3.71 (s, 3H, OCH_3), 6.69 (t, 1H, CH=, *J*=7.5 Hz); C^{13}-NMR ($CDCl_3$): 132.7 (s) and 144.4 (d) (C=CH), 168.5 (s, C=O).

Methyl cycloheptancarboxylate (**6**), was isolated as mixture 1:1.5 with **5b** (0.3 g) from the reaction mixture exp. 12, b. p. 102-106^{0}C (14 torr). After hydrogenation this mixture under conditions[30] pure **6** was obtained in quantitative yield, b. p. 94-96^{0}C (12 torr), H^1-NMR ($CDCl_3$): 1.42-1.94 (m, 12H, CH_2), 2.46 (m 1H, CH), 3.63 (s, 3H, OCH_3); C^{13}-NMR ($CDCl_3$): 26.3 (t), 28.1 (t), 30.8 (t), 44.9 (d), 51.1 (q), 173.5 (s).

Methyl 2-cycloundecene-1-carboxylate (**7**) was isolated as mixture with **5c** and **8** in ratio 1:4:1 and identified by mass-spectra and characteristic signals in ^{1}H-NMR. **7**, mass-spectrum (70 eV) m/z (relative intensity %): 210 (M+, 48), 179 (21), 167 (15), 153 (45), 149 (21), 95(100), 79 (69), 67 (73), 59 (53), 55 (83); H^1-NMR ($CDCl_3$): 5.18 dt (1H, CH=), 6.88 dd (1H, CH=, J_1=12 Hz, J_2=2 Hz). After hydrogenation of this reaction mixture under conditions[30] methyl cycloundecane carboxylate[31] was obtained in quantitative yield.

Methyl 3-cycloundecen-1-carboxylate (**8**)[32] was isolated by silica gel chromatography (hexane-ethyl acetate 5 :1) from the reaction mixture exp. 16 in 13% yield, viscous oil, H^1-NMR ($CDCl_3$): 1.15-1.65 (m, 12H, CH_2), 2.01-2.17 (2H, m) 2.32-2.57 (3H, m), 3.64 (s, 3H, OCH_3); 5.49-5.63 m (m, 2H, CH=CH, *J*=14 Hz); C^{13}-NMR ($CDCl_3$): 24.4 (t), 25.3 (t) , 25.9 (t), 26.5 (t), 26.9 (t), 28.4 (t), 34.1 (t) 36.2 (t), 43.8 (d), 51.6 (q), 127.5 (d) , 133.6 (d), 175.4 (s). MS (70 eV): m/z (relative intensity %): 210 (M^+, 42), 179 (13), 167 (9), 153 (30), 95 (92), 81 (87), 79 (82), 67 (79), 59 (100), 55 (72).

2-Methoxycyclopentanone (**10**) was obtained by the method[33] and identified in reaction mixtures of the electrooxidation of **1a** by methods of GC and mass-spectrometry.

2,2,3-Trimethoxycyclopentanol (**11**) was isolated by p. g. c., H^1-NMR ($CDCl_3$): 1.38 (m, 1H, CH_2), 1.62 (m, 1H, CH_2), 1.86 (m, 1H, CH_2), 1.98 (m, 1H, CH_2), 2.71 (d, 1H, OH), 3.21 (s, 3H, OCH_3), 3.34 (s, 3H, OCH_3), 3.40 (s, 3H, OCH_3), 3.65 (m, 1H, CH-O), 3.93 (m, 1H, CH-O); MS (70 eV): m/z (relative intensity %): 176 (M^+, 9), 161 (14), 129 (66), 101 (CH_2=CH-C$(OCH_3)_2^+$, 100), 88 (41), 75 (35), 69 (33), 59 (40). Anal. Calcd. for $C_8H_{16}O_4$: C, 54.53; H, 9.15. Found: C, 54.27; H, 8.99.

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