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Indirect Electrochemical Oxidation of Cyclic Ketones: Strong Influence of Ring Size on the Result of the Reaction

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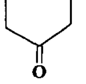
Abstract: The result of the indirect electrochemical oxidation of cyclic ketones in methanol in the undivided cell in the presence of sodium iodide depends on the ring size. Cyclopentanone affords 2,2-dimethoxycyclopentanone. While cyclohexanone gives rise 2,2-dimethoxycyclo-hexanol, and cyclic ketones with higher ring size undergo new type of the electrochemically induced Favorskii rearrangement with the formation of methyl cycloalkencarboxylates containing in the ring on the one carbon atom less than starting ketone. So the simple electrocatalytic system can distinguish the ring size of cyclic ketones. Copyright © 1996 Elsevier Science Ltd

The first attempts of the electrochemical oxidation of ketones resulted in the formation of a mixture of acids, saturated and unsaturated hydrocarbons, carbon oxide and dioxide[1-4]. Non selective remote oxidative functionalization of ketones was carried out in acetonitrile or trifluoroacetic acid as a result of subsequent transformation of initially produced cation radical $R^1R^2C{=}O^{+\cdot}$ [5-6]. The anodic oxidation of cycloalkanones in aqueous alcohols gave usually mixtures of lactones of different types[7-8].

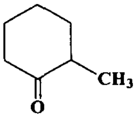
For certain cases selective indirect electrooxidation of ketones is known. Thus, ketones are converted into α-hydroxyketals by electrooxidation in basic potassium iodide - methanol solution[9], aryl alkyl ketones give rise methyl 2-arylalkanoates being electrolysed in methyl orthoformate in the presence of iodides[10]. The electrocatalytic variant of haloform reaction is also known[11].

Continuing our studies on electrooxidation of ketones[12-14] we have accomplished indirect electrochemical oxidation of cyclic ketones **1a-e** and **2** in the presence of sodium iodide.



1a-e

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



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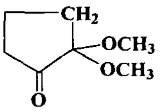
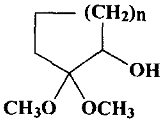
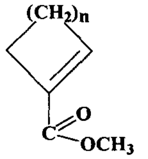
It has been found that the result of electrooxidation of cyclic ketones **1a-e** in methanol in the presence of sodium iodide in an undivided cell is strongly depends on the ring size of cyclic ketone (Table 1).



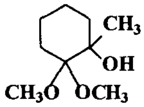
3
(n=1)



4a,b
a n=2
b n=3



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



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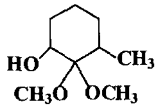

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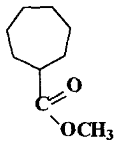

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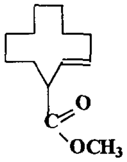

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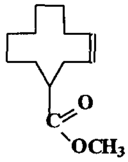

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Table 1. Electrooxidation of cyclic ketones.

Ketone	n	Electricity passed, F/mol	Conversion of ketone [%]	Products,[25] yield [%][a]
1a	1	5.0	82	**3**[15], 66 (51)
1b	2	3.5	95	**4a**[16], 82 (70)
1c	3	3.5	93	**4b**[17], 47; **5a**[18], 31
1d	4	11.0	100	**5b**[19], 82 (68); **8**[22], 13
1e	8	8.0	100	**5c**[20], 43 (49)[b]; **9**[23], 8; **10**[24], 14
2		3.5	100	**6**[21], 47; **7**[21], 37 (72)[d]

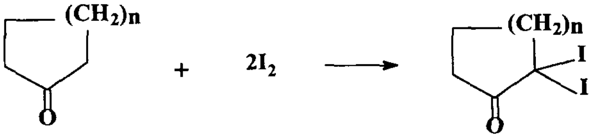
[a] Determined by gas chromatography and NMR-spectra, in parenthesis - isolated yields.
[b] Reaction mixture after electrolysis was heated 1 hour with 10 mmol of NaOH, under this conditions **9** and **10** are completely transformed into in **5c**.
[d] As a mixture of isomers.

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

$$\textbf{anode: } 2I^- - 2e \longrightarrow I_2$$

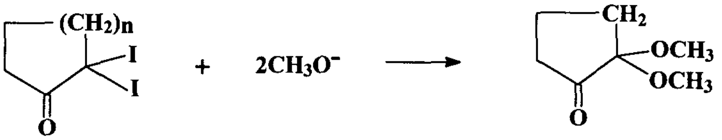
$$\textbf{cathode: } 2\,CH_3OH + 2e \longrightarrow 2CH_3O^- + H_2$$

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



1a n=1 **11a** n=1

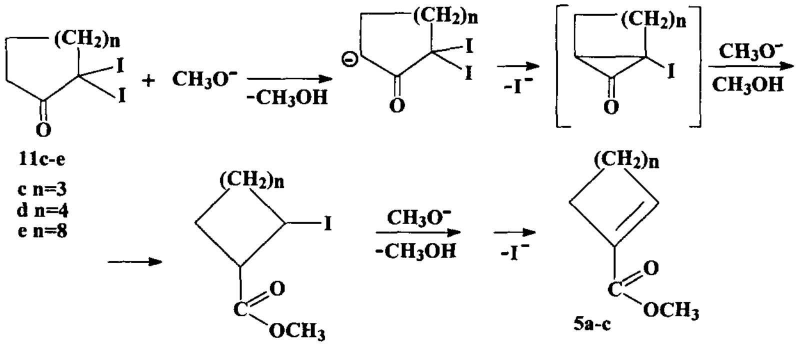
Further reaction of **11a** with CH_3O^--anions generated at the cathode results in the formation of the end product of the electrochemical process - compound **3**:



11a n=1

3

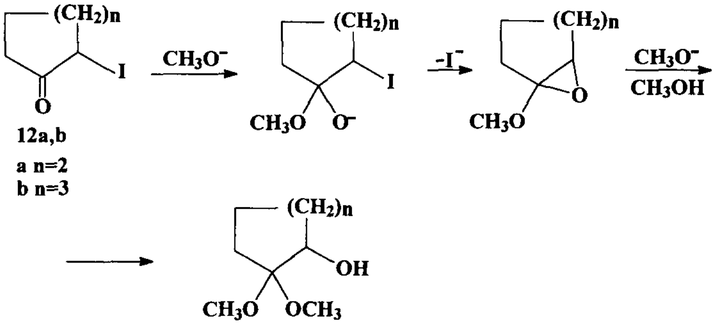
In the electrooxidation of the all other cyclic ketones except cyclohexanone the formation of double α-iodinated intermediate **11** also takes place. But for cyclic ketones with the ring size more than 6 carbon atoms the main reaction of this intermediate in solution is Favorskii rearrangement:



11c-e
c n=3
d n=4
e n=8

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

The quantity of ketoform in α-monoiodinated 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 takes place:



12a,b
a n=2
b n=3

4a,b
a n=2
b n=3

Methyl cycloundec-1-encarboxylate **5c** formed in the electrooxidation of cyclododecanone **1e** undergoes the migration of double bond under the conditions of the electrolysis with formation of **9** and **10**.

Experimental procedure.

A solution of cyclic ketone (0.02 mol) and NaI (0.015 mol) in methanol (20 ml) was electrolysed in an undivided cell equipped with C-anode and Fe-cathode at 30^0C under constant current density $110 mA/cm^2$ until the quantity of the electricity indicated in Table 1 was passed. The solvent was than removed and the reaction mixture extracted with ether, washed with water and dried with Na_2SO_4. The products were isolated by distillation or identified by comparison with authentic samples and by using GC, chromatomass-spectrometry and NMR (500 MHz).

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15. **3**, b. p. 75-78^{0}C (10 torr), H^1-NMR ($CDCl_3$): 1.87 (m, 2H, CH_2), 2.00 (t, 2H, CH_2), 2.27 (t, 2H, CH_2), 3.27 (s, 6H, OCH_3); C^{13}-NMR ($CDCl_3$): 16.6 (t), 33.3 (t), 34.9 (t), 50.4 (q), 100.8 (s), 209.7 (s).
16. **4a**, b. p. 42-43^{0}C (0.1 torr), H^1-NMR ($CDCl_3$): 1.20 -1.75 (m, 8H, CH_2), 2.23(d, 1H, OH), 3.14 (s, 3H, OCH_3), 3.16 (s, 3H, OCH_3), 3.75 (m, 1H, CH); C^{13}-NMR ($CDCl_3$): 19.6 (t), 22.0 (t), 27.8 (t), 29.1 (t), 47.3 (q), 48.0 (q), 68.0 (d), 100.6 (s).
17. **4b**, (65% isolated yield) when 10 mmol of NaOH was added as supporting electrolyte, 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).
18. **5a**, Krabbenholf H.O., *J. Org. Chem.*, 1979, *44*, 4293.
19. **5b**, 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=,); 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).
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23. **9**, mass-spectrum (70eV) M/e: 210 (M+, 48), 95(100); H^1-NMR ($CDCl_3$): 5,18 dt (1H, CH=), 6.88 dd (1H, CH=).
24. **10**, Cameron A. G., Knight D. W., *J. Chem. Soc. Perkin Trans. I*, 1986, 161-7.
25. All main compounds were characterised by their H^1- and C^{13}-NMR-spectra. We are grateful to Dr. M. V. Galakhov for the performance of NMR-spectra.

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