(%): C, 50.31; H, 3.16; N, 5.43. $C_{11}H_9F_4NO_2$. Calculated (%): C, 50.18; H, 3.47; N, 5.34. IR, ν/cm^{-1}: 3150 (OH). ^{1}H NMR ($CDCl_3$), δ: 3.36 (d, 1 H, H_A, J_{AB} = 18.07 Hz); 3.75 (d, 1 H, H_B, J_{AB} = 18.01 Hz); 3.43 (s, 1 H, OH)*; 6.13 (tt, 1 H, HCF_2, $^2J_{H,F}$ = 53 Hz, $^3J_{H,F}$ = 6.1 Hz); 7.35—7.70 (m, 5 H, Ph).

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* The signal disappears when CD_3COOD is added.

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Electrochemical oxidative ring opening of 1-methylcyclobutanol

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The manganese(III) acetate-mediated electrooxidative ring opening of 1-methylcyclobutanol (**1**) in acetic acid affords pentane-2-one (**2**) as the major product. The reaction of 1-methylcyclobutanol with $Mn(OAc)_3$—LiCl gives 5-chloropentane-2-one (**4**).

Key words: 1-methylcyclobutanol, manganese(III) acetate, electrochemical oxidation; pentane-2-one, 5-chloropentane-2-one; β-cleavage.

The oxidative ring opening of tertiary cyclic alcohols with salts and complexes of multivalent metals proceeds *via* the formation of cycloalkoxyl radicals, which isomerize to oxoalkyl radicals. These radicals transform into the final products by three pathways, thus participating in the oxidation reactions, recombination and the hydrogen transfer.

In the series of homologs differing in the ring size, 1-methylcyclobutanol (**1**) is of the highest reactivity in the oxidation processes with Ce^{IV} and Pb^{IV} compounds. Cerium(IV) sulfate oxidizes compound **1** in pentane-2-one (**2**),[1] and cerium(IV) ammonium sulfate gives a mixture of pent-4-en-2-one and decane-2,9-dione (**3**).[2] The $Mn(OAc)_3$—LiCl,[3] $Pb(OAc)_4$—LiCl,[3] and $Ca(OCl)_2$—$FeSO_4$ [4] systems selectively oxidize alcohol **1** to 5-chloropentane-2-one (**4**).

The peculiarity of 1-methylcyclobutanol with respect to oxidizers is its ability to be oxidized with $Mn(OAc)_3$, the latter does not react under similar conditions with cycloalkanols containing more than four C atoms in the cycle.[3]

A solution of $Mn(OAc)_3$ in AcOH oxidizes compound **1** affording ketones **2** and **3**. The reaction of alcohol **1** with the $Mn(OAc)_3$—LiCl system gives only chloroketone **4**. In these reactions, $Mn(OAc)_3$ was used in stoichiometric amounts.[3]

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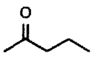
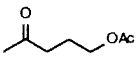
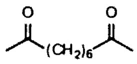
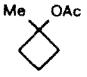
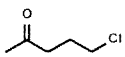
Table 1. Electrochemical oxidation of 1-methylcyclobutanol (**1**)

Reaction conditions[a]				Conversion **1** (%)	Product yields (%)[b]				
$[Mn(OAc)_2 \times 4H_2O]$ /mmol	Electrolyte (content /mmol)	T/°C	I/mA		 **2**		 **3**		 **4**
–	$LiClO_4$ (15)	100	–	20	–	–	–	96 (19)	–
–	$LiClO_4$ (15)	100	500	72	–	–	–	100 (72)	–
5	KOAc (15)	100	50	97	78 (76)	4 (4)	4 (4)	7 (6)	–
5	NaOAc (15)	100	500	95	67 (64)	–	4 (4)	4 (4)	–
0.5	NaOAc (15)	100	500	85	39 (33)	–	5 (4)	16 (14)	–
0.5	NaOAc (15)	50	500	36	78 (28)	–	–	–	–
0.5	LiCl—NaOAc (10) (5)	50	50	74	8 (6)	–	–	20 (15)	43 (32)
0.5	LiCl (10)	100	500	57	–	–	–	35 (20)	25 (14)
0.5	LiCl (10)	100	50	60	–	–	–	–	42 (25)

[a] AcOH was used as the solvent (15 mL), the content of alcohol **1** is 5 mmol, the amount of electricity is 1 F mol^{-1}.

[b] The data are calculated from transformed **1** and the yields calculated from starting alcohol **1** are given in parentheses.

This report presents the results of electrochemical oxidation of 1-methylcyclobutanol using $Mn(OAc)_3$ as the mediator. The electrolysis of alcohol **1** was carried out in an undivided cell in AcOH containing $Mn(OAc)_2 \cdot 4H_2O$ and potassium or sodium acetate. In the absence of manganese(II) acetate, the β-ring opening of **1** does not occur. Heating a solution of compound **1** in AcOH at 100 °C affords only 1-methylcyclobutanol acetate, while the electrolysis significantly increases the process of acylation (Table 1).

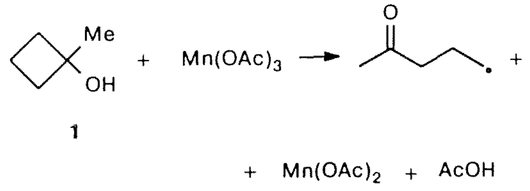
The reaction conditions and the composition of the products formed, when manganese(II) acetate is used in the stoichiometric and catalytic amounts, are given in Table 1. The process was not optimized. In both cases, ketone **2** is the major reaction product accompanied by a small amounts of diketone **3** and 5-acetoxypentane-2-one; their formation proceeds according to Scheme 1.

Scheme 1

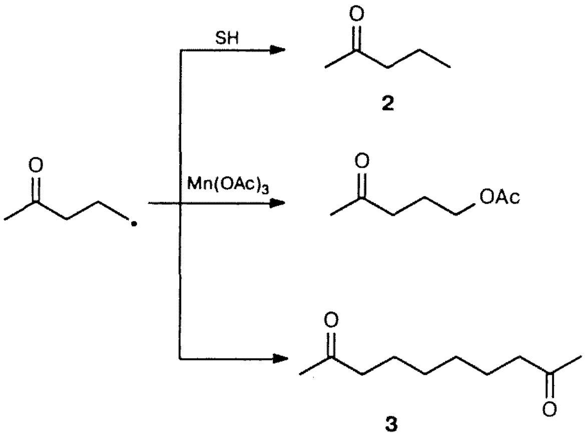
On an anode:

$$Mn(OAc)_2 \xrightarrow[AcOH]{-\bar{e}} Mn(OAc)_3$$

In a solution:



1



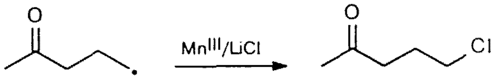
2

3

SH is a hydrogen donor

A change in the current density by an order of magnitude with a constant amount of electricity being conducted does not affect substantially the product composition and the conversion of 1-methylcyclobutanol; the conversion of alcohol **1** decreases, when the temperature decreases from 100 °C to 50 °C (see Table 1).

Upon the electrolysis of compound **1** with the mediator, *i.e.*, $Mn(OAc)_3$, in conjunction with lithium chloride, the generated 4-oxopentyl radicals are mainly oxidized to chloroketone **4**.



4

Thus, the chemical oxidation of alcohol **1** with a stoichiometric amount of manganese(III) acetate and the electrochemical Mn^{III}-mediated oxidation **1** with a catalytic amount of $Mn(OAc)_3$ result in similar compositions of the products. However, in the first case, diketone **3** and monoketone **2** are formed in practically equal amounts, whereas in the second case, diketone **3** and the product of acylation of compound **1** are minor components (at 100 °C) or are absent altogether (at 50 °C). The decrease in the concentration of mediator slightly decreases the conversion of alcohol **1** and strikingly decreases the yield of ketone **2**.

Experimental

GLC analysis was carried out with a LKhM-80 chromatograph equipped with a flame-ionization detector and stainless-steel columns (2000×3 mm) with 5 % SE-30 and 5 % PEG 20M on Inerton Super (0.16—0.20 mm); nitrogen was used as the carrier gas (30 mL min^{-1}). The ^1H and ^{13}C NMR spectra were recorded with Bruker WM-250 and Bruker AM-300 spectrometers in $CDCl_3$. The IR spectra were recorded with a Specord M-80 instrument in a thin film. Manganese diacetate $Mn(OAc)_2 \cdot 4H_2O$ ("pure" grade) was used without additional treatment. 1-Methylcyclobutanol was distilled prior to the reaction. The electrolytes $LiClO_4$, NaOAc ("pure"), LiCl ("chemically pure" grade), and KOAc ("extra pure" grade) were used without additional purification. The electrodes: graphite plate (20×60×2 mm) was used as the anode and titanium wire was used as the cathode (2 mm diameter). Glacial acetic acid was used as the solvent.

Electrochemical oxidation of 1-methylcyclobutanol (1) (general procedure). Compound **1** (5 mmol), electrolyte (15 mmol), AcOH (15 mL), and $Mn(OAc)_2 \cdot 4H_2O$ (0.5 or 5 mmol) were placed in an undivided cell (volume 30 mL, the distance between electrodes *ca.* 15 mm) equipped with a magnetic stirrer, thermometer, and a reflux condenser, and 1 F mol^{-1} of electricity was passed. The electrolysis was carried out at 50—100 °C, current was 50—500 mA (see Table 1), and current density on the anode was 15—150 mA cm^{-2}. The reaction mixture was analyzed by GLC using an internal standard. To isolate the products, the reaction mixture was treated with an aqueous solution of Na_2CO_3, extracted with ether, and dried over Na_2SO_4, and the solvent was removed. The products of electrolysis were isolated by distillation and identified by NMR and IR spectroscopy and GLC (by comparison with authentic samples).

Pentan-2-one (2). ^1H NMR, δ: 1.12 (t, 3 H, CH_3); 1.90—2.08 (m, 2 H, CH_2); 2.10 (s, 3 H, CH_3CO); 2.62 (t, 2 H, CH_2CO).

Electrochemical oxidation of 1-methylcyclobutanol (1) in the presence of LiCl. Using LiCl or LiCl—NaOAc mixture as the electrolyte in the general procedure, a mixture of 1-methyl-1-acetoxycyclobutane and 5-chloropentan-2-one was obtained from alcohol **1**.

1-Methyl-1-acetoxycyclobutane. ^1H NMR, δ: 1.51 (s, 3 H, CH_3); 1.90 (s, 3 H, CH_3CO); 1.92—2.30 (m, 6 H, $(CH_2)_3$).

5-Chloropentan-2-one (4). ^1H NMR, δ: 1.85—2.02 (m, 2 H, $CH_2\underline{CH_2}CH_2$); 2.05 (s, 3 H, CH_3); 2.65 (t, 2 H, $COCH_2$); 3.42 (t, 2 H, CH_2Cl).

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