Electroinduced oxidative transformation of 2,5-dioxabicyclo[4.4.0]decanes into 5-(1,3-dioxolan-2-yl)- and 5-(dimethoxymethyl)pentanoates

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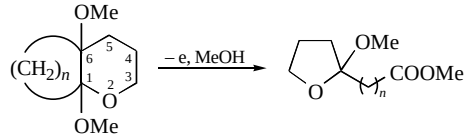
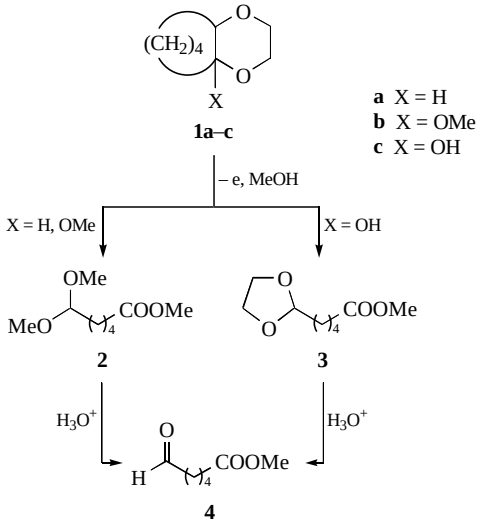
Anodic oxidation of 2,5-dioxabicyclo[4.4.0]decane **1a**, 1-methoxy-2,5-dioxabicyclo[4.4.0]decane **1b** and 1-hydroxy-2,5-dioxabicyclo[4.4.0]decane **1c** in methanol in the presence of tetrabutylammonium fluoroborate as a supporting electrolyte induces the electrooxidative transformation of substrates **1a** and **1b** into methyl 5-(dimethoxymethyl)pentanoate and of substrate **1c** into methyl 5-(1,3-dioxolan-2-yl)pentanoate.

Recently, we found the electroinduced oxidative rearrangement of 1,6-dimethoxy-2-oxabicyclo[*n*.4.0]alkanes into *ω*-(2-methoxytetrahydrofur-2-yl)alkanoates:[1]



This finding provoked us to investigate the behaviour of 2,5-dioxabicyclo[4.4.0]decane **1a**, 1-methoxy-2,5-dioxabicyclo[4.4.0]decane **1b** and 1-hydroxy-2,5-dioxabicyclo[4.4.0]decane **1c** under similar electrolysis conditions.† In this communication, we report the results obtained by the electrolysis. Methyl 5-(dimethoxymethyl)pentanoate **2** is formed as the main product from bicyclodecanes **1a** and **1b** in 75% yield, and methyl 5-(1,3-dioxolan-2-yl)pentanoate **3** is formed from bicyclodecane **1c** in 90% yield (Scheme 1).



Scheme 1

The transformation of **1a–c** into esters **2** and **3** resulted from the electrolysis of **1a–c** at room temperature in methanol in the presence of tetrabutylammonium fluoroborate as a supporting electrolyte in an undivided cell equipped with a platinum or graphite anode and a stainless steel cathode under passages of 2–4 F mol^{-1} of electricity (Table 1).‡

The structures of esters **2** and **3** were established on the basis of ^{1}H and ^{13}C NMR spectra,§ which contained signals due to dimethoxymethyl (δ_H 3.28, 4.31; δ_C 52.5, 64.7 and 104.1), methoxycarbonyl (δ_H 3.63; δ_C 51.3, 173.8) and 1,3-dioxolanyl (δ_H 3.87, 4.81) groups, and by comparison of their hydrolysis product with the authentic methyl 6-oxohexanoate.[6]

The formation of two types of products from structurally similar starting substrates indicates a difference in the mechanisms of their electrochemical transformations. A rearrangement related to that observed for 1,6-dimethoxy-2-oxabicyclo[*n*.4.0]alkanes,[1] occurs only in the case of bicyclodecane **1c**. The electrolysis of bicyclodecanes **1a** and **1b** gives ester **2** and is not accompanied by the rearrangement. Ester **2** is formed from substrate **1a** through the intermediate formation of bicyclodecane **1b**. Scheme 2 illustrates the proposed mechanism for the transformation of substrates **1a–c** into esters **2** and **3**.

The electrochemical process begins with electron transfer from electrophorus ethylenedioxy fragments of bicyclodecanes **1a–c**. It is possible by two routes of further transformation of the resulting radical cations; one route starts with the deprotonation of radical cations and the formation of radicals **A** (route i), and the other route starts with the cleavage of the bridgehead C–C bond and the formation of distonic radical cation[8] **B** (route ii). Similar radical cations also arise from subsequent electrochemical transformations of radicals **A**. The transformations of radical cations derived from bicyclodecanes **1a** and **1b**,**c** follow routes i and ii, respectively. The conversion of distonic ions **B** (X = OH) electrogenerated from substrate **1c** into the final product (ester **3**) is accompanied by the deprotonation, rearrangement and decyclization *via* oxonium ions **F**.¶

† Starting materials. *trans-2,5-Dioxabicyclo[4.4.0]decane* **1a**[2] was prepared from epoxycyclohexane by the acid-catalysed reaction with 2-chloroethanol followed by the treatment of the resulting 2-(β-chloroethoxy)-cyclohexanol with an alcoholic potassium hydroxide solution (60% overall yield). *1-Methoxy-2,5-dioxabicyclo[4.4.0]decane* **1b**[3] was the product of the acid-catalysed addition of methanol to 2,5-dioxabicyclo-[4.4.0]dec-1(6)-ene.[4] *1-Hydroxy-2,5-dioxabicyclo[4.4.0]decane* **1c** was synthesised by a known procedure[4] from cyclohexanone in 40% yield; ethylene ketal of 2-hydroxycyclohexanone was formed along with **1c** in the same yield.

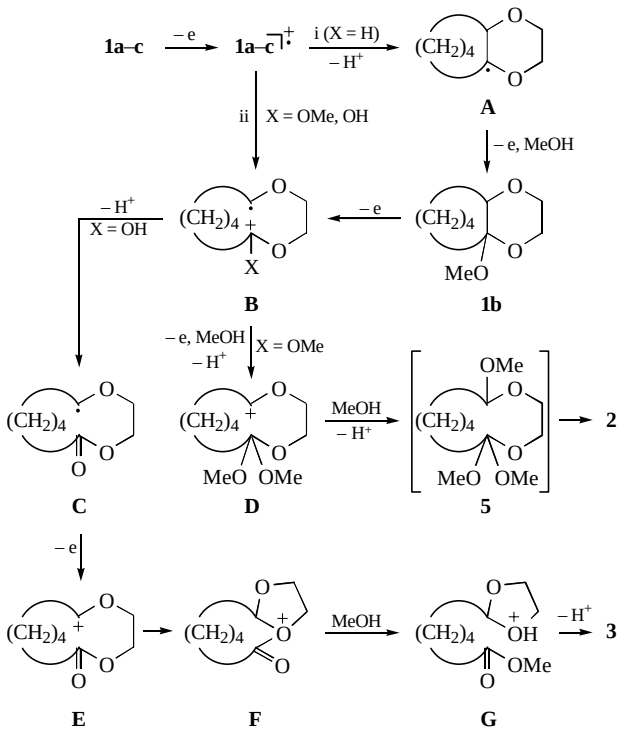
‡ *Electrolysis of dioxabicycloalkanes* **1a–c** *(typical procedure)*. A solution of an electrolyte (9 mmol), compound **1** (5 mmol) and *n*-decane (internal standard, 3 mmol) in MeOH (15–25 ml) was placed in an undivided cell[5] and then electrolysed at a constant current (0.5 A) and room temperature under intense stirring until more than 90% of **1** was converted. The solvent was removed, the residue was extracted with hexane (2×20 ml), and the combined extracts were concentrated. The products were isolated by vacuum distillation or flash chromathography with hexane–ethyl acetate (1%) as an eluent and then analysed.

§ *1-Methoxy-2,5-dioxabicyclo[4.4.0]decane* **1b**.[3] ^{1}H NMR (200 MHz, $CDCl_3$) δ: 1.55–1.80 (m, 8H, CH_2), 3.23 (s, 3H, MeO), 3.30 (m, 1H, CH), 3.46 and 3.82 (m, 4H, OCH_2CH_2O). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 96.4 (O–C–O), 80.8 (CH–O), 64.8, 60.2 (O–C–C–O), 46.9 (MeO), 29.82, 27.96, 24.18, 21.82 (CH_2).

Methyl 5-(dimethoxymethyl)pentanoate **2**.[6] ^{1}H NMR (200 MHz, $CDCl_3$) δ: 1.35 (m, 2H, CH_2), 1.60 (m, 4H, CH_2), 2.30 (t, 2H, CH_2COO), 3.28 (s, 6H, OMe), 3.63 (s, 3H, MeOCO), 4.31 (t, 1H, CHOMe). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 178.8 (O=C–O), 104.1 (O–CH–O), 64.7, 52.5, 51.3 (OMe), 33.8, 32.8, 24.6, 24.0 (CH_2).

Methyl 5-(1,3-dioxolan-2-yl)pentanoate **3**.[7] ^{1}H NMR (200 MHz, $CDCl_3$) δ: 1.42–1.63 (m, 6H, CH_2), 2.30 (t, 2H, CH_2COO, *J* 7.5 Hz), 3.63 (s, 3H, MeO), 3.87 (m, 4H, OCH_2CH_2O), 4.81 (t, 1H, OCHO, *J* 4.9 Hz).

¶ The participation of cyclic oxonium ions in the isomerization of linear aliphatic methoxy-substituted carbonium ions was found in ref. 9.



Scheme 2

A gain in energy as a result of decyclization of the strained 10-membered ring system seems to be a driving force for this process. Distonic ions **B** (X = OMe) derived from substrates **1a** and **1b** are likely to be turned to the final product (ester **2**) as a result of simultaneously occurring electrooxidation and alcoholysis of radical and cationic centres and by the interaction of cationic intermediates **D** and cyclic ortho ether **5** with methanol. The protons generated during the electrooxidation of methanol and the alcoholysis of intermediates **B** and **D** are a possible catalyst for the reaction of this ortho ether with methanol. The reduction of the protons at a cathode to produce molecular hydrogen does not permit them to be accumulated in the electrolysis products in a concentration sufficient for catalysing the complete conversion of the ortho ether into ester **2**. This was supported by the presence of signals typical of protons of the methoxy group (δ_H 3.13) and ^{13}C nuclei (δ_C 115.5) of the ortho ether group[10] in the NMR spectra of the electrolysis products of **1a**.

Thus, the electroinduced oxidative rearrangement of 2-oxa- and 2,5-dioxabicycloalkanes is not a general case, and it is typical of only a limited range of compounds of this kind, such as 1,6-dimethoxy-2-oxabicyclo[*n*.4.0]alkanes and 1-hydroxy-2,5-dioxabicyclo[4.4.0]decane.

Table 1 Electroinduced transformation of 2,5-dioxabicyclo[4.4.0]decane **1a**, 1-methoxy-2,5-dioxabicyclo[4.4.0]decane **1b**, and 1-hydroxy-2,5-dioxabicyclo[4.4.0]decane **1c** to methyl 5-(dimethoxymethyl)pentanoate **2** and methyl 5-(1,3-dioxalan-2-yl)pentanoate **3**.

Entry	Bicyclo-alkane	Anode	Q/F mol^{-1}	Conversion (%)	Product	Yield (%)[a]
1	**1a**	Pt	2.0	85	**1b** + **2**	50 + 28
2	**1a**	Pt	3.0	95	**1b** + **2a**	34 + 44
3	**1a**	Pt	4.0	100	**1b** + **2a**	23 + 57
4	**1b**	Pt	2.0	90	**2**	80
5	**1c**	C	4.0	100	**3**	90

[a]On a converted bicyclodecane basis.

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References

1 Yu. N. Ogibin, A. O. Terent'ev, A. I. Ilovaisky and G. I. Nikishin, *Mendeleev Commun*., 1998, 239.
2 F. R. Larsen and A. Neese, *J. Am. Chem. Soc*., 1975, **97**, 4345.
3 D. Lalandais, C. Baequet and J. Einhorn, *Tetrahedron*, 1981, **37**, 3131.
4 I. R. Fjeldskaar, P. Rongved and L. Skattebol, *Acta Chem. Scand*., 1987, **B41**, 477.
5 Yu. N. Ogibin, A. I. Ilovaisky and G. I. Nikishin, *Izv. Akad. Nauk, Ser. Khim*., 1994, 1624 (*Russ. Chem. Bull*., 1994, **43**, 1536).
6 G. A. Tolstikov, M. S. Miftakhov, F. A. Valeev, R. R. Akhmetvaleev, L. M. Khalilov and A. A. Panasenko, *Zh. Org. Khim*., 1985, **21**, 72 [*J. Org. Chem. USSR* (*Engl. Transl.*), 1985, **21**, 65].
7 T. Nakamura, H. Sawada and M. Nakayma, *Jpn. Kokai Tokyo Koho, Japanese Patent* 02 48.585 (90 48.585), 1991 (*Chem. Abstr*., 1991, **113**, P 41219).
8 K. M. Stirk, L. K. Kiminkinen and H. I. Kenttamaa, *Chem. Rev*., 1992, **92**, 1649.
9 (*a*) E. L. Allred and S. Winstein, *J. Am. Chem. Soc*., 1967, **89**, 3991; (*b*) E. L. Allred and S. Winstein, *J. Am. Chem. Soc*., 1967, **89**, 4012.
10 (*a*) P. Deslongchamps, J. Lessard and Y. Nadeau, *Can. J. Chem*., 1985, **63**, 2485; (*b*) P. Deslongchamps, J. Lessard and Y. Nadeau, *Can. J. Chem*., 1985, **63**, 2493.

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