Electrochemical transformations of monooxa- and dioxabicycloalkenes and -bicycloalkanes*

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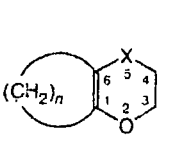
Electrolysis of 2-oxa- and 2,5-dioxabicyclo[*n*.4.0]alk-1(6)-enes (*n* = 4, 10) under conditions of direct undivided anodic oxidation in methanol results in their electrochemical mono- and dimethoxylation; electrolysis of the corresponding 2-oxa- and 2,5-dioxabicycloalkanes involves electrochemical cleavage of the bridging carbon—carbon bonds followed by electrooxidative transformation into methyl ω-(2-methoxytetrahydrofuryl)-, ω-(dimethoxymethyl)-, and ω-(1,3-dioxolan-2-yl)alkanoates.

Key words: 2-oxa- and 2,5-dioxabicyclo[*n*.4.0]alkenes and alkanes (*n* = 4, 10), electrochemical cleavage of bridging carbon—carbon bonds, ω-substituted methyl alkanoates.

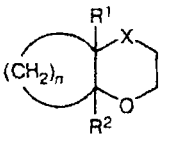
Previously we studied electrooxidation of α-arylalkenes,[2] α-aryl- and benzo[*c*]cycloalkenes,[3] acenaphthylene, and acenaphthenes[4] in methanol in an undivided cell; the reaction involves initially electrochemical cleavage of the π-C—C bonds in the ethylene fragments, which are thus transformed into α,β-dimethoxyethane fragments. Further oxidation involves cleavage of the σ-C—C bonds and gives dimethylacetals (ketals). The process can be terminated at the first step; this gives the products of dimethoxylation of the starting olefins with high selectivity.

As a continuation of these investigations, in this work, we studied cleavage of the bridging carbon—carbon bonds in 2-oxa- (**1a,b**) and 2,5-dioxabicycloalkenes (**1c,d**) and substituted 2-oxa- (**2a,b**) and 2,5-dioxabicycloalkanes (**2c—g**) in order to find out whether it is practically possible to transform them into monocyclic structures with medium and large rings. No study of this type had been performed previously. It had only been known that monocyclic vicinal glycols,[5] their mono- and dialkyl ethers,[5,6] tri- and tetramethoxy derivatives,[7,8] and hydroxy, alkoxy, and acetoxy ketones and ketals[9] are oxidized in methanol at a carbon anode with electrochemical cleavage of carbon—carbon bonds similar to the cleavage of these in glycols by chemical oxidants ($NaIO_4$, lead tetraacetate, *etc.*); thus, the initial compounds are converted into acetals of dicarbonyl compounds or oxoalkanoate acetals.

Electrolysis of these bicyclic compounds was carried out under the same conditions as that of α-arylolefins,[2,3] namely, in methanol with tetrabutylammonium tetrafluoroborate (TBTF) or potassium hydroxide in an undivided cell with a platinum or graphite anode and a stainless-steel cathode; the anode current density was 50—150 mA cm^{-2}, the temperature was 20—40 °C, and the amount of electricity ensuring an 80—100% degree of conversion of the substrates (2—10 F mol^{-1}) was passed. In addition, to estimate the influence of possible cathodic reactions on this process, electrolysis of oxabicycloalkene **1a** and dioxabicycloalkane **2d** was carried out in a divided cell under similar conditions.



1a—d



2a—g

1	*n*	X
a	4	CH_2
b	10	CH_2
c	4	O
d	10	O

2	*n*	X	R^1	R^2
a	4	CH_2	OMe	OMe
b	10	CH_2	OMe	OMe
c	4	O	OMe	OMe
d	4	O	H	H
e	4	O	H	OMe
f	4	O	H	OH
g	10	O	H	OH

Electrolysis of 2-oxa- and 2,5-dioxabicyclo[*n*.4.0]alkenes (1a—d). When potassium hydroxide is used as the electrolyte and 2—3 F mol^{-1} of electricity is passed, this process occurs as electrooxidative transformation of oxabicycloalkenes **1a,b** into 1,6-dimethoxy- (**2a,b**) and 1-methoxy-2-oxabicyclo[*n*.4.0]alkanes (**3a,b**). Electrolysis of these oxabicycloalkenes with TBTF as the supporting electrolyte gives only the methoxylation products, for example, product **3a** is formed from oxabicyclodecene **1a**. Conversely, electrolysis of dioxabicyclodecene **1c** under similar conditions involves selective di-

* For preliminary communication, see Ref. 1.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 11, pp. 2115—2122, November, 1999.

1066-5285/99/4811-2091 $22.00

methoxylation and transformation into 1,6-dimethoxy-2,5-dioxabicyclo[4.4.0]decane (**2c**). Under conditions of electrochemical dimethoxylation of **1c**, its homolog, dioxabicyclohexadecene **1d** is converted into 1-methoxy-2,5-dioxabicyclo[10.4.0]hexadec-6-ene (**4**) rather than into the expected 1,6-dimethoxy-2,5-dioxabicyclohexadecane (Scheme 1) (Table 1, entries 1—9).

Electrolysis in the presence of basic electrolytes (KOH and MeONa) affords di- (**2**) and monomethoxylation (**3**) products in 3 : 1 ratio; product **2a** is mostly formed as the *cis*-isomer, compound **2c** is produced as a mixture of *cis*- and *trans*-isomers (~1 : 1), and products **3a,b** are formed as only *trans*-isomers.

Electrolysis of bicycloalkene **1a** in a divided cell led to similar results (see Table 1, entry 2).

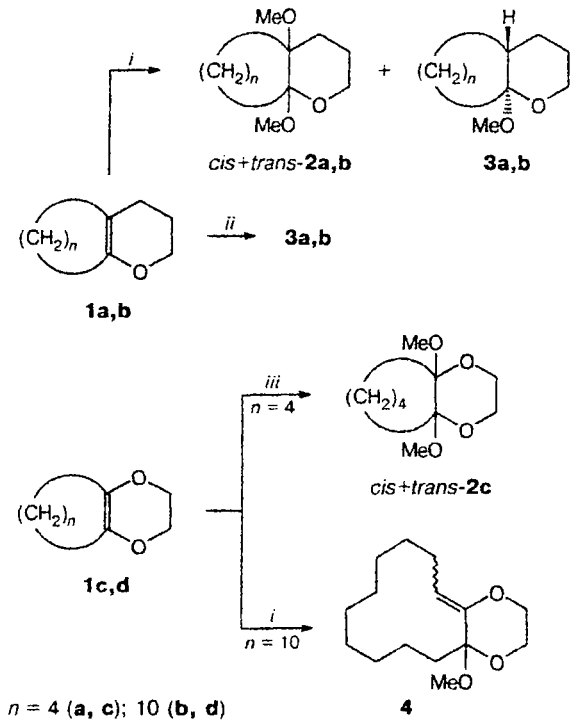
Electrolysis of bis(methoxy)-substituted bicyclo[*n*.4.0]alkanes (2a—c). Under the conditions that provide the transformation of bicycloalkenes **1a—c** into products **2a—c** and **3a,b**, only compound **2c** undergoes further electrooxidation on passing of more than 2—3 F mol^{-1} of electricity. Electrolysis of **2c** in the presence of TBTF results in the cleavage of the bridging carbon—carbon bond followed by transformation into dimethyl adipate (**5**) (see Table 1, entries 8 and 12). Compounds **2a,b** behave in the electrolysis with TBTF similarly to **2c**, being converted into methyl ω-(2-methoxytetra-

Table 1. Electrolysis of 2-oxa- and 2,5-dioxabicyclo[*n*.4.0]alk-1(6)-enes (**1a—d**) and the corresponding bicycloalkanes **2a—g**

Entry	Starting compound	Electrolyte	Anode	Q /F mol^{-1}	*T* /°C	Degree of conversion (%)	Product	Yield[a] (%)
1	**1a**	KOH	Pt	2	25	95	**2a**[c]	68
							3a	20
2[b]	**1a**	KOH	Pt	2	25	95	**2a**[c]	64
							3a	25
3	**1a**	MeONa	Pt	5.4	30	95	**2a**[c]	44
							3a	15
4	**1a**	Bu_4NBF_4	Pt	2	20	85	**3a**	80
5	**1b**	KOH	Pt	3	20	95	**2b**	65
							3b	20
6	**1c**	Bu_4NBF_4	C	2	20	80	**2c**[d]	85
								(70)
							5	2
7	**1c**	Bu_4NBF_4	C	3	20	88	**2c**[d]	75
							5	10
8	**1c**	Bu_4NBF_4	C	10	20	100	**2c**[d]	12
							5	70
9	**1d**	KOH	C	2	60	70	**4**	58
								(44)
10	**2a**	Bu_4NBF_4	Pt	7	25	95	**6a**	(75)
11	**2b**	Bu_4NBF_4	Pt	7	20	90	**6b**	(40)
12	**2c**	Bu_4NBF_4	C	10	20	95	**5**	80
								(75)
13	**2d**	Bu_4NBF_4	Pt	2	20	85	**2e**	50
							9	28
14	**2d**	Bu_4NBF_4	Pt	4	20	100	**2e**	23
							9	57
15[b]	**2d**	Bu_4NBF_4	Pt	4	20	100	**2e**	28
							9	51
16	**2e**	Bu_4NBF_4	Pt	2	20	90	**9**	82
17	**2f**	Bu_4NBF_4	C	4	20	100	**10**	90
								(60)
18	**2g**	Bu_4NBF_4	C	8	20—25	90	**11**	(54)
							12	(30)

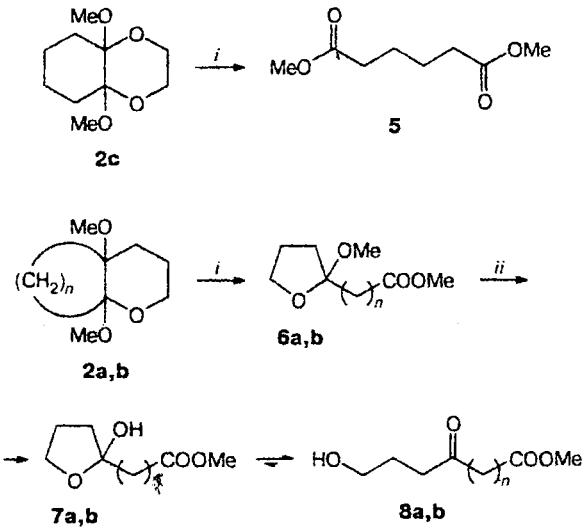
[a] Data of GLC with an internal standard based on the converted substrate and based on the product isolated by flash chromatography (or distillation, in parentheses).
[b] This entry was carried out in a divided cell.
[c] The *cis*/*trans*-**2a** ratios in entries 1—3: 7 (1), 8 (2), and 10 (3).
[d] The *cis*/*trans*-**2c** ratio in entries 6—8 was ~1 : 1.

Scheme 1



Reagents and conditions: (*i*) −e, MeOH, KOH, Pt anode, steel cathode, 2 F mol^{-1}, 20–60 °C; (*ii*) −e, MeOH, Bu_4NBF_4, Pt anode, steel cathode, 2 F mol^{-1}, 20 °C; (*iii*) −e, MeOH, Bu_4NBF_4, C anode, steel cathode, 2 F mol^{-1}, 20 °C.

Scheme 2

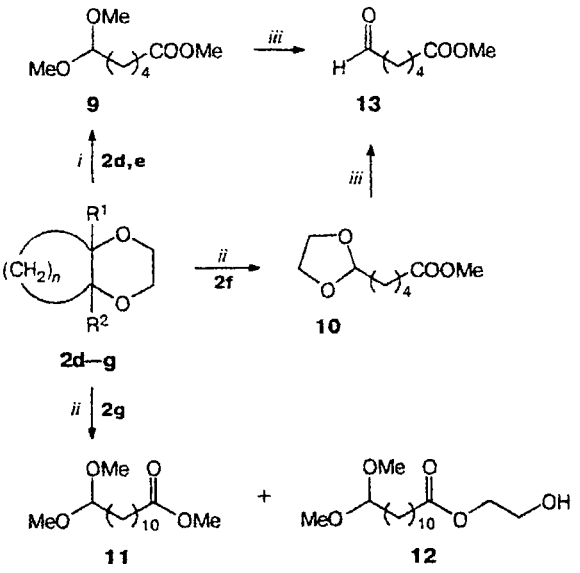


Reagents and conditions: (*i*) −e, Bu_4NBF_4, MeOH, Pt or C anode, steel cathode, 7–10 F mol^{-1}, 20 °C; (*ii*) 10% HCl, 20 °C, 20 min.

hydrofur-2-yl)alkanoates (**6a,b**) (Scheme 2) (see Table 1, entries 10 and 11).

Electrolysis of 2,5-dioxabicyclo[*n*.4.0]alkanes (2d–g). Unsubstituted dioxabicyclodecane **2d** is electrolyzed in an undivided or divided cell to give 1-methoxy-2,5-dioxabicyclo[4.4.0]decane (**2e**); this product is converted into methyl dimethoxyhexanoate (**9**). In an undivided cell under similar conditions, methoxy-substituted dioxabicyclodecane **2e** is immediately converted into ester **9**, hydroxydioxabicyclodecane **2f** is converted into methyl 5-(1,3-dioxolan-2-yl)pentanoate (**10**), and hydroxydioxabicyclohexadecane **2g** is converted into methyl (**11**) and 2-hydroxyethyl (**12**) 11-(dimethoxymethyl)-undecanoate (Scheme 3) (see Table 1, entries 12–18).

Scheme 3

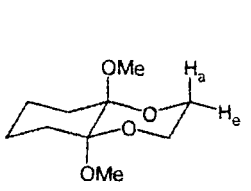


Reagents and conditions: (*i*) −e, MeOH, Bu_4NBF_4, Pt or C anode, steel cathode, 2–4 F mol^{-1}, 20 °C; (*ii*) −e, MeOH, Bu_4NBF_4, C anode, steel cathode, 4–8 F mol^{-1}, 20 °C; (*iii*) 10% HCl, 20 °C, 20 min.

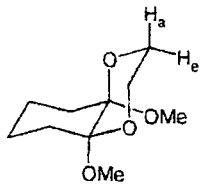
Determination of the structures of electrolysis products of mono- and dioxabicycloalkenes 1a–d and mono- and dioxabicycloalkanes 2a–g. The structures of electrolysis products were determined based on ^1H and ^{13}C NMR spectra and mass spectra and, for some of the products (**6** and **9–12**), also based on the products of their transformations. Acid hydrolysis of the electrolyzates obtained from substituted oxabicycloalkanes **2a,b** resulted in mixtures of tautomeric methyl ω-(2-hydroxytetrahydrofuran-2-yl)alkanoates (**7a,b**) (minor component) and methyl ω-hydroxy-(ω-3)-oxoalkanoates (**8a,b**) (major component) (see Scheme 2), and hydrolysis of the electrolyzates formed from dioxabicycloalkanes **2d–f** gave methyl 6-oxohexanoate **13** (see Scheme 3);

transesterification of ester **12** in methanol in the presence of *p*-toluenesulfonic acid yielded ester **11**.

The formation of products **2a,c** as *cis*- and *trans*-isomers upon electrochemical dimethoxylation of compounds **1a,c** was confirmed by separation of the stereoisomers by flash chromatography. The symmetrical *trans*-isomer of compound **2c** (R_f 0.3, hexane—ethyl acetate, 95 : 5), unlike the *cis*-isomer (R_f 0.15), is a solid; the OCH_2CH_2O fragment in its molecule is responsible for the multiplets at 3.42 (AA′, H_e) and 4.04 ppm (BB′, H_a) in the ^1H NMR spectrum. For the asymmetrical *cis*-isomer **2c**, the chemical shifts of the H_e and H_a protons of the OCH_2CH_2O group do not differ so much as those for the *trans*-isomer **2c**; therefore, their signals overlap, giving one complex multiplet at δ 3.72.



trans-**2c**



cis-**2c**

The isolated stereoisomers of compound **2a** were identified as *cis*- and *trans*-isomers based on their R_f values (0.19 for the major isomer and 0.3 for the minor isomer; hexane—ethyl acetate, 98 : 2), the relative rates of electrooxidation (*trans*-isomers are known to be oxidized more rapidly than the *cis*-isomers[10]), and also based on the fact that the minor stereoisomer is a solid, unlike the major isomer, which was isolated as an oil.

The conclusion that the monomethoxylation products are formed from oxabicycloalkenes **1a,b** as only *trans*-isomers was based on (1) the ^1H NMR spectra of these products, which contain only one singlet in the region typical of protons of methoxy groups, (2) the assumption that stereospecific *trans*-addition of methanol to bicyclic enol ethers **1a,b** can be catalyzed by electrochemically generated protons (this type of electrophilic addition of alcohols is typical of enol ethers[11]), and (3) the fact that the monomethoxylation product obtained in entry 4 is identical to the adduct obtained from ether **1a** and methanol in the presence of a catalytic amount of sulfuric acid.

The structures of the final products of electrochemical cleavage of the bridging carbon—carbon bond in dioxabicycloalkanes **2c—g** followed by electrically induced transformation of the intermediates were established as follows: ester **5** was identified using an authentic sample of dimethyl adipate; the products prepared from compounds **2a,b** and **2d—g** were identified based on the fact that their ^1H and ^{13}C NMR spectra contain signals corresponding to the protons and the ^{13}C nuclei of 2-methoxytetrahydrofuryl (δH 1.76—2.13, 3.14, 3.85; δC 47.5—47.8, 66.9—67.1, 108.8—109.1),[12] dimethoxymethyl (δH 3.28, 4.31; δC 52.5, 64.7, 104.1),[13] methoxycarbonyl (δH 3.63; δC 51.3, 173.8),[13] and 1,3-dioxolan-2-yl (δH 3.87, 4.81)[14] groups.

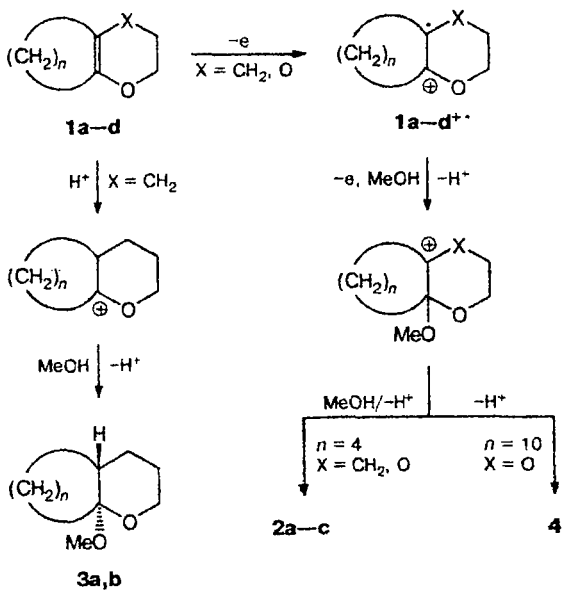
The formation of mixtures of tautomeric esters **7a,b** and **8a,b** upon hydrolysis of electrolyzates obtained from oxabicycloalkanes **2a,b** is confirmed by the presence of absorption bands typical of the ketone and ester carbonyl groups (1715 and 1735 cm^{-1}) in the IR spectrum and 20 lines in the ^{13}C NMR spectrum of the products of hydrolysis of the electrolyzate of **2a**.

The mechanism of the electrochemical processes under consideration. A typical feature of these processes is the fact that they occur in the near-anode layer. This follows from the fact that the electrolysis of oxabicyclodecane **1a** and dioxabicyclodecane **2d** in undivided and divided cells gives identical results. The facts that these processes are induced by electrochemical cleavage of bridging carbon—carbon π- and σ-bonds in the compounds under study and include ring opening in the intermediates thus formed are common features of these processes. In addition to the generation of methoxide anions (see, *e.g.*, Ref. 15), the cathodic reaction may involve partial discharge of the protons formed in the near-anode layer.

The fact that electrolysis of substrates with similar structures gives different types of products indicates that the mechanisms of the studied processes are somewhat different. The most probable mechanisms of the electrochemical transformations of all these compounds leading to the identified products are illustrated in Schemes 4—6.

For all compounds except for **2d**, the electrochemical process starts with the transfer of an electron from the oxygen-containing groups adjacent to the bridging carbon—carbon bond and cleavage of this bond to give

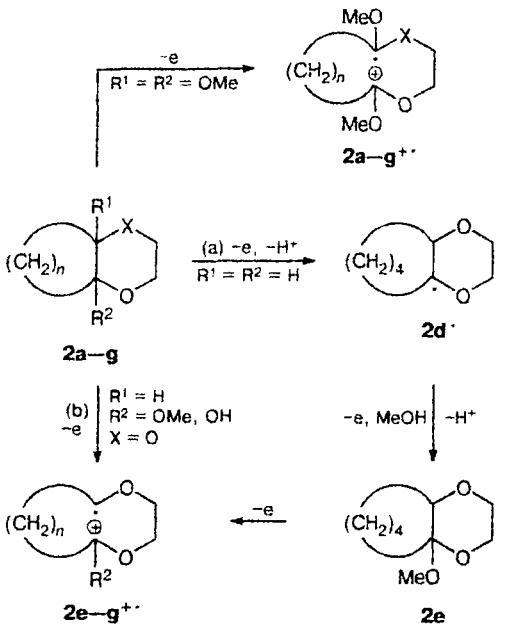
Scheme 4



radical cations with separated radical and cationic centers, $\mathbf{1}^{\bullet+}$ and $\mathbf{2}^{\bullet+}$. In the case of oxabicycloalkenes **1a,b**, the process is accompanied by the competing addition of methanol to these substrates; this reaction is apparently catalyzed by the protons resulting from electrooxidation of methanol and alcoholysis of cationic intermediates (Scheme 4).

In the case of dioxabicyclodecane **2d**, the electron transfer is followed by proton elimination yielding radical **2d**$^{\bullet}$, which undergoes electrooxidation and alcoholysis to give bicyclodecane **2e**, and the latter is converted into radical cation $\mathbf{2e}^{\bullet+}$ (Scheme 5).

Scheme 5



The subsequent transformation of radical cations $\mathbf{2a}^{\bullet+}$ and $\mathbf{2b}^{\bullet+}$ into products **6a,b** (Scheme 6) involves electrooxidative rearrangement, which proceeds apparently as electrooxidation and alcoholysis of the radical and cationic centers in these radical cations and isomerization of cationic intermediates **A** into **C** *via* oxonium ions **B**. Transformations of linear aliphatic methoxy-substituted carbenium ions with similar participation of cyclic oxonium ions have been reported previously.[16] The driving force of the isomerization of cationic intermediates **A** into species **C** is probably the energy gain due to the transformation of intermediate **A** into more stable cation **C** and, in the case of intermediate **A** (X = CH_2 and n = 4), also decyclization of the strained 10-membered cyclic system. Cationic intermediate **A** (X = O and n = 4) generated from radical cations $\mathbf{2c}^{\bullet+}$ is converted into ester **5** upon alcoholysis (Scheme 6).

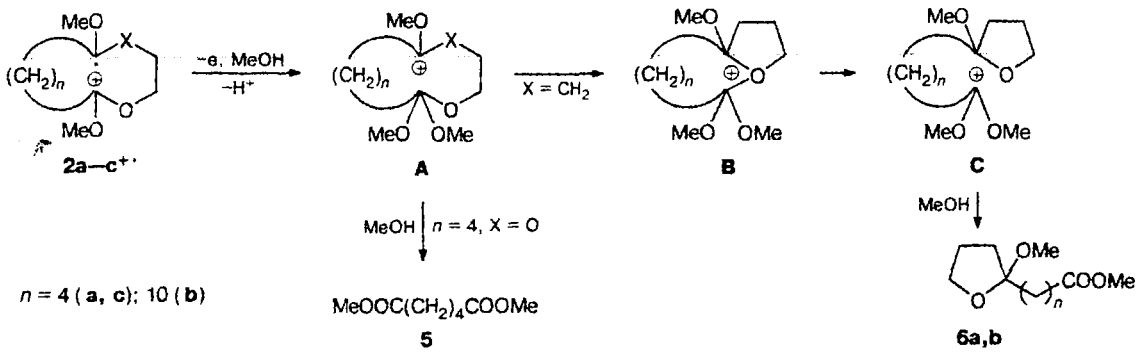
An electrooxidative rearrangement similar to that observed for radical cations $\mathbf{2a,b}^{\bullet+}$ occurs as well for radical cation $\mathbf{2f}^{\bullet+}$ (R^2 = OH, n = 4), which is converted into methyl 5-(1,3-dioxolan-2-yl)pentanoate (**9**) (Scheme 7).

Products **9**, **11**, and **12** are formed from radical cations $\mathbf{2e,g}^{\bullet+}$ upon their decyclization, which accompanies alcoholysis of cationic intermediates **D** and **F** and involves the intermediate formation of cyclic orthoester **14** and ester **15**. The intermediate formation of orthoesters is indicated by the presence of signals characteristic of the protons of the methoxy group (δH 3.13) and ^{13}C nuclei of the orthoester group (δC 115.5)[17] in the spectra of the fresh product of electrolysis of substrate **1a**. The protons that catalyze the alcoholysis of orthoesters and esters are generated upon electrooxidation of methanol.

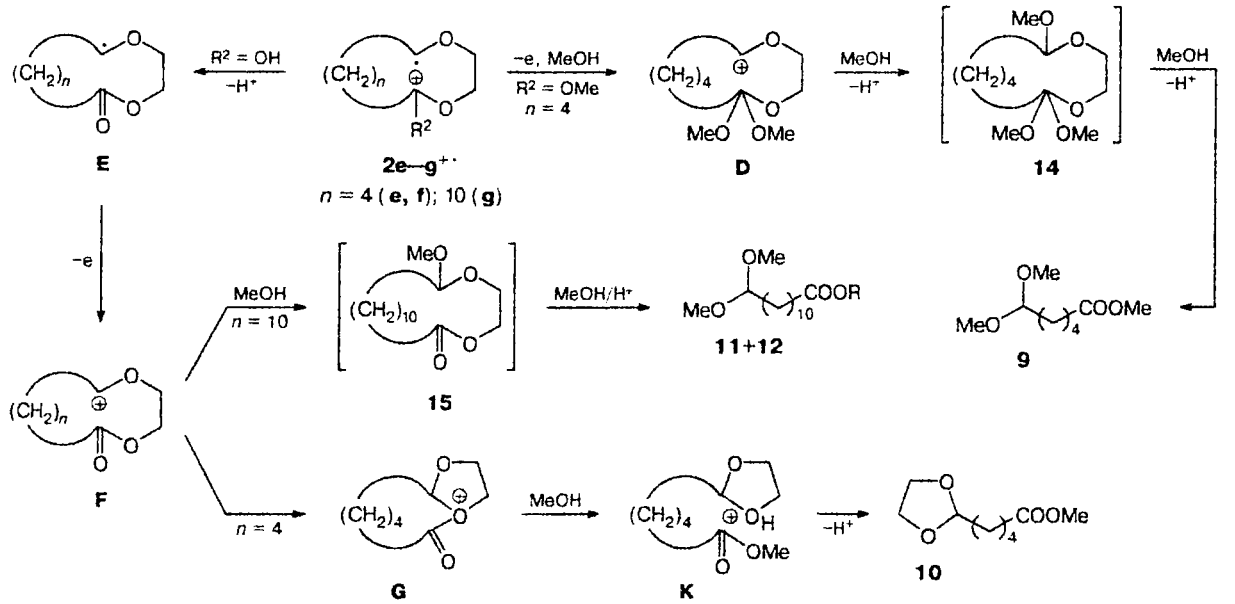
* * *

A new and the most important result of our study of the electrochemical cleavage of bridging carbon—carbon bonds in 2-oxa- and 2,5-dioxabicyclo[n.4.0]alk-1(6)-enes (**1a—d**) and the corresponding 2-oxa- and 2,5-dioxabicycloalkanes (**2a—g**) and the subsequent electrically induced transformation of the resulting intermediates is elucidation of the main characteristics and peculiar features of these processes under conditions of undivided electrolysis in methanol as well as discovery of previously unknown electrooxidative rearrangements

Scheme 6



Scheme 7



R = Me (**11**), CH_2CH_2OH (**12**)

of oxabicycloalkanes of type **2a,b** and dioxabicyclodecane **2f** to give methyl ω-(2-methoxytetrahydrofur-2-yl)- (**6**) and ω-(1,3-dioxolan-2-yl)alkanoates (**10**). The elucidated features of the electrochemical behavior of 2-oxa- and 2,5-dioxabicycloalkenes and the corresponding substituted bicycloalkanes and the discovered rearrangements provided the basis for new synthetic approaches to esters of ω-substituted alkanoic acids such as ω-(2-methoxytetrahydrofuryl)- (**6**), ω-(1,3-dioxolan-2-yl)- (**10**), and ω-(dimethoxymethyl)alkanoic (**9**, **11**, **12**) acids and tautomeric esters 7 ⇌ **8**, which can find application in the synthesis of prostaglandins, pheromones, and other valuable organic compounds.[18] However, due to these features, electrolysis of the monooxa- and dioxabicycloalkenes and bicycloalkanes studied here cannot be used for electrochemical transformation into macrocyclic compounds.

Experimental

^1H and ^{13}C NMR spectra were recorded on Bruker AC-200, Bruker WM-250 (200 and 250 MHz for ^1H), and Bruker AM-300 (75.4 MHz for ^{13}C) spectrometers using Me_4Si as the internal standard and $CDCl_3$ as the solvent. IR spectra were recorded on a Specord-80 spectrometer in thin films and in CCl_4 solutions. GLC analysis was carried out using a Varian-3700 chromatograph (flame ionization detector, glass columns, 5% Carbowax 20M on Inerton and 5% XE-60 on Chromaton N-AW). TLC analysis was carried out using Silufol UV-254 chromatographic plates. Flash chromatography was performed using silica gel L 40/100 mm and a hexane–ethyl acetate mixture (1–5%) as the eluent. Methanol was dehydrated by distillation from magnesium methoxide. The other solvents were purified by standard methods. Commercial reagents (KOH and Bu_4NBF_4) were used as received.

Starting compounds **1a–d** and **2f,g** were prepared by known two- and three-step procedures[19–21] from cyclohexanone or cyclododecanone in the following yields (% based on the initial cycloalkanone): **1a**, 28; **1b**, 60; **1c**, 60; **1d**, 68; **2f**, 40; and **2g**, 33. Compounds **2a–c** were the products of electrolysis of mono- and dioxabicycloalkenes **1a–c** in methanol. Unsubstituted dioxabicyclodecane **2d** was prepared in 60% yield by treatment of 2-(β-chloroethoxy)cyclohexanol, prepared by acid-catalyzed reaction of epoxycyclohexane with 2-chloroethanol, with an alcoholic solution of KOH. Compounds **2e** and **3a,b** were the products of acid-catalyzed addition of methanol to mono- and dioxabicycloalkenes **1a–c**.

1-Oxabicyclo[4.4.0]dec-1(6)-ene[19] (1a). B.p. 70–75 °C (10 Torr). ^1H NMR, δ: 1.60 (m, 6 H, CH_2); 2.03 (m, 6 H, CH_2C=); 3.98 (t, 2 H, CH_2O, J = 5.8 Hz).

1-Oxabicyclo[4.4.0]hexadec-1(6)-ene[20] (1b). B.p. 138–145 °C (1 Torr), n_D^{20} 1.5060. ^1H NMR, δ: 1.35–2.15 (m, 24 H, CH_2); 2.05 (m, 6 H, CH_2C=); 3.88 (t, 2 H, CH_2O, J = 5.6 Hz). MS, m/z (I_{rel} (%)): 222 $[M]^+$ (15).

2,5-Dioxabicyclo[4.4.0]dec-1(6)-ene[21] (1c). ^1H NMR, δ: 1.62 (m, 4 H, CH_2); 2.05 (m, 4 H, CH_2C=); 4.03 (s, 4 H, OCH_2CH_2O).

2,5-Dioxabicyclo[10.4.0]hexadec-1(6)-ene (1d). ^1H NMR, δ: 1.20–1.40 (m, 12 H, CH_2); 1.53 (m, 4 H, CH_2); 2.10 (t, 4 H, CH_2C=, J = 8 Hz); 3.97 (s, 4 H, CH_2O). ^{13}C NMR, δ: 132.16 (C=C); 64.24 (CH_2O); 26.30, 24.80, 24.39, 24.30, 22.36 (CH_2). Found (%) C, 74.92; H, 10.38. $C_{14}H_{24}O_2$. Calculated (%): C, 74.95; H, 10.78. This bicycloalkene, unlike its stable analog **1c**, remained unchanged only for 1–2 days.

***trans*-2,5-Dioxabicyclo[4.4.0]decane[22] (*trans*-2d).** ^1H NMR, δ: 1.20–1.83 (m, 8 H, CH_2); 3.14 (m, 2 H, OCHCHO); 3.76 (s, 4 H, OCH_2CH_2O).

***trans*-1-Methoxy-2,5-dioxabicyclo[4.4.0]decane[14] (2e).** ^1H NMR, δ: 1.55–1.80 (m, 8 H, CH_2); 3.23 (s, 3 H, MeO); 3.30 (m, 1 H, CH); 3.46 (m, 2 H, AA′, OCH_e); 3.82 (m,

2 H, BB′, OCH_a). ^{13}C NMR, 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).

1-Hydroxy-2,5-dioxabicyclo[4.4.0]decane[21] (2f) (a mixture of *cis*- and *trans*-isomers). B.p. 130—132 °C (2 Torr). ^1H NMR, δ: 1.26—1.77 (m, 8 H); 2.45 (s, 1 H, HO); 3.37 (dd, 0.3 H, J = 8.7 Hz, 4.1 Hz), 3.45 (dd, 0.7 H, J = 8.2 Hz, 4.1 Hz) (*cis*- and *trans*-CH); 3.98 (m, 4 H, OCH_2CH_2O). ^{13}C NMR, δ: 109.66 and 109.46 (O—C—OH); 80.44 and 78.39 (CH—O); 65.49, 65.37, 65.19, and 64.97 (OCH_2CH_2O); 34.09, 33.90, 30.00, 29.90 (CH_2); 23.36 (2 CH_2); 22.60, 22.22 (CH_2).

1-Hydroxy-2,5-dioxabicyclo[4.4.0]hexadecane[21] (2g). M.p. 90—94 °C. ^1H NMR, δ: 1.20—1.75 (m, 20 H, CH_2); 1.97 (s, 1 H, OH); 3.90—4.10 (m, 5 H, CH—O and OCH_2CH_2O). ^{13}C NMR, δ: 112.59 (O—C—OH); 69.76 (CH—O); 65.44 and 65.53 (CH_2O); 31.36, 27.97, 26.14, 25.96, 23.55, 22.69, 22.43, 22.18, 22.00, 19.85 (CH_2).

***trans*-1-Methoxy-2-oxabicyclo[4.4.0]decane[23] (3a).** B.p. 120—125 °C (20 Torr). ^1H NMR, δ: 1.10—2.00 (m, 13 H, CH_2 and CH); 3.14 (s, 3 H, MeO); 3.50—3.68 (m, 2 H, CH_2O).

***trans*-1-Methoxy-2-oxabicyclo[10.4.0]hexadecane (3b).** Found (%): C, 75.87; H, 12.05. $C_{16}H_{30}O_2$. Calculated (%): C, 75.53; H, 11.87. ^1H NMR, δ: 1.05—2.30 (m, 25 H, CH_2 and CH); 3.20 (s, 3 H, MeO); 3.45—3.58 (m, 2 H, CH_2O).

Electrolysis of 2-oxa- and 2,5-dioxabicyclo[*n*.4.0]alk-1(6)-enes (1a—d) and the corresponding bicycloalkanes (2a—g) (general procedure). ***A. Undivided cell.*** The initial substrate (5 mmol), a solution of the supporting electrolyte (5 mmol), and *n*-decane or *n*-dodecane (3 mmol, internal standard) in 25 mL of MeOH were placed in an undivided cell[2c] with a platinum (3 cm^2) or graphite (4 cm^2) anode and a stainless-steel cathode. The electrolysis was carried out with vigorous stirring at 20—25 °C; electric current (0.5 A) was passed until an 85—95% degree of conversion of the substrate was attained. The solvent was evaporated, the residue was extracted with hexane (2×20 mL), the extracts were concentrated, and the residue was analyzed by GLC. In the preparative experiments, the electrolysis products were isolated from the residue by vacuum distillation or flash chromatography and identified by spectroscopy. For preparative-scale electrolysis, the amount of the solvent and the amounts of the initial compounds and electrolytes were increased four- or fivefold; no internal standard was used in this case.

B. Divided cell. The cell was a cylindrical vessel having a shell for the circulation of water (internal diameter 45 mm), a ceramic chuck (internal diameter 22 mm) with a 2-mm thick wall serving as the diaphragm, and gauze made of stainless-steel wire and fixed on the outer surface of the chuck serving as the cathode. The anode (16×30 mm platinum plate) was mounted in the inner cavity of the ceramic chuck. Prior to electrolysis, a methanolic solution of the electrolyte was divided into two portions, which were poured into the anodic and cathodic areas of the cell. The substrate and the internal standard were added preliminarily to the former portion. The electrolysis and the subsequent workup of the products were carried out by the above-described procedure.

The following final products of the electrolysis in undivided and divided cells were obtained: 1,6-dimethoxy- (**2a—c**) and 1-methoxy-substituted oxabicycloalkanes (**3a,b**) and ethers **4** and **5** from oxabicycloalkenes **1a—d**; 1-methoxy-2,5-dioxabicyclodecane (**2e**) from unsubstituted dioxabicyclodecane **2d**, and esters **6a,b** and **9—12** from dioxabicycloalkanes **2d—g** (see Table 1).

1,6-Dimethoxy-2-oxabicyclo[4.4.0]decane (2a) (a mixture of *cis*- and *trans*-isomers). B.p. 130—140 °C (20 Torr). ***cis*-2a:** oil. ^1H NMR, δ: 1.22—2.02 (m, 12 H); 3.13, 3.17 (both s, 6 H, MeO); 3.66 (m, 2 H, CH_2O). ^{13}C NMR, δ: 100.3 (O—C—O); 75.3 (C—O); 61.2 (CH_2O); 47.3, 48.0 (MeO); 28.9, 26.4, 24.1, 22.5, 21.6, 20.8. ***trans*-2a:** m.p. 54—55 °C. Found (%): C, 66.25; H, 10.22. $C_{11}H_{20}O_3$. Calculated (%): C, 65.97; H, 10.07 ^1H NMR, δ: 1.25—2.10 (m, 12 H, CH_2); 3.30, 3.33 (both s, 6 H, MeO); 3.68 (m, 2 H, CH_2O). ^{13}C NMR, δ: 100.0 (O—C—O); 75.7 (C—O); 60.6 (CH_2O); 47.8, 48.5 (MeO); 29.3, 26.2, 24.1, 23.1, 21.6, 20.8.

1,6-Dimethoxy-2-oxabicyclo[10.4.0]hexadecane (2b). Found (%): C, 71.80; H, 11.31. $C_{17}H_{32}O_3$. Calculated (%): C, 71.85; H, 11.35. ^1H NMR, δ: 1.10—2.30 (m, 24 H, CH_2); 3.23, 3.27 (both s, 6 H, MeO); 3.46—3.57 (m, 2 H, CH_2O). ^{13}C NMR, δ: 110.7 (O—C—O); 103.1 (C—O); 60.1 (CH_2O); 50.6, 47.7 (MeO). MS (EI, 70 eV, m/z (I_{rel} (%)): 284 (1.1) $[M]^+$, 269 (18.3), 257 (14.3), 253 (18.7), 252 (22.2), 242 (8.5), 127 (14.7), 123 (12.2), 113 (42.4), 111 (21.22), 109 (14.1), 101 (14.7), 100 (12.9), 99 (17.46), 98 (18.9), 97 (39.7), 95 (24.4), 93 (11.4), 86 (15.2), 85 (99), 84 (11.5), 83 (17.6), 81 (25.8), 73 (24.5), 72 (100).

1,6-Dimethoxy-2,5-dioxabicyclo[4.4.0]decane (2c) (a mixture of *cis*- and *trans*-isomers). ***cis*-2c:** oil. ^1H NMR, δ: 1.43—2.03 (m, 8 H, CH_2); 3.25 (s, 6 H, MeO); 3.72 (m, 4 H, OCH_2CH_2O). ^{13}C NMR, δ: 97.48 (O—C—O); 60.32 (CH_2O); 48.00 (MeO); 27.70, 21.83 (CH_2). ***trans*-2c:** m.p. 80—83 °C. Found (%): C, 71.52; H, 11.20. $C_{17}H_{32}O_3$. Calculated (%): C, 71.79; H, 11.34. ^1H NMR, δ: 1.25—1.80 (m, 8 H, CH_2); 3.22 (s, 6 H, MeO); 3.42 (m, 2 H, AA′, OCH_e); 4.04 (m, 2 H, BB′, OCH_a). ^{13}C NMR, δ: 97.45 (O—C—O); 59.22 (CH_2O); 46.97 (MeO); 27.03, 21.39 (CH_2).

1-Methoxy-2,5-dioxabicyclo[4.4.0]decane (2e) was identical to the adduct obtained from bicyclene **1c** and methanol in the presence of a catalytic amount of sulfuric acid.

***trans*-1-Methoxy-2-oxabicyclo[4.4.0]decane (3a)** was identical to the adduct obtained from oxabicyclodecane **1a** and methanol in the presence of a catalytic amount of sulfuric acid.

***trans*-1-Methoxy-2-oxabicyclo[10.4.0]hexadecane (3b)** was identical to the adduct obtained from oxabicyclohexadecane **1b** and methanol in the presence of a catalytic amount of sulfuric acid.

1-Methoxy-2,5-dioxabicyclo[10.4.0]hexadec-6-ene (4). Found (%): C, 70.39; H, 10.23. $C_{15}H_{26}O_3$. Calculated (%): C, 70.83; H, 10.30. ^1H NMR, δ: 1.10—1.60 (m, 14 H, CH_2); 1.65—1.90 (m, 3 H); 2.38 (m, 1 H); 3.30 (s, 3 H, OMe); 3.93 (m, 4 H, OCH_2CH_2O); 4.96 (dd, 1 H, CH=, J = 8.0 Hz). ^{13}C NMR, δ: 147.35 (O—C=); 110.96 (CH=); 101.75 (O—C—O); 66.77 and 60.66 (OCH_2); 48.90 (OCH_3); 26.47, 26.36, 25.99, 24.27, 23.83, 23.62, 23.27, 19.80 (CH_2).

Dimethyl adipate (5) was identical to an authentic sample of the corresponding adipate.

Methyl ω-(2-methoxytetrahydrofur-2-yl)pentanoate[1a] (6a). Found (%): C, 59.21; H, 9.13. $C_{10}H_{20}O_4$. Calculated (%): C, 58.80; H, 9.87. ^1H NMR, δ: 1.20—1.75 (m, 6 H, CH_2 in the aliphatic chain); 1.76—2.13 (m, 4 H, CH_2 in the THF ring); 2.31 (t, 2 H, CH_2COO, J = 7 Hz); 3.14 (s, 3 H, MeO); 3.64 (s, 3 H, COOMe); 3.85 (t, 2 H, CH_2O, J = 5 Hz). ^{13}C NMR, δ: 173.8 (COO); 109.1 (O—C—O); 67.1 (CH_2COO); 51.3, 47.8 (MeO); 35.2, 33.8, 24.14, 24.07, 24.00 (CH_2). IR (thin film), ν/cm^{-1}: 1060, 1165 (C—O); 1735 (C=O).

Methyl ω-(2-methoxytetrahydrofur-2-yl)undecanoate[1a] (6b). ^1H NMR, δ: 1.20—1.75 (m, 18 H, CH_2 in the aliphatic chain); 1.76—2.13 (m, 4 H, CH_2 in the tetrahydrofuran ring); 2.31 (t, 2 H, CH_2COO, J = 7 Hz); 3.17 (s, 3 H, MeO); 3.67 (s, 3 H, COOMe); 3.85 (t, 2 H, CH_2O, J = 5 Hz). ^{13}C NMR, δ: 173.5 (COO); 108.8 (O—C—O); 66.9 (CH_2O); 51.0, 47.5

(MeO); 34.0, 29.07, 28.95, 26.25, 24.67, 24.10, 23.85, 23.61 (CH_2). IR (thin film), ν/cm^{-1}: 1070, 1175 (C—O); 1735 (C=O).

Methyl 5-(2-hydroxytetrahydrofur-2-yl)pentanoate (7a) and 9-hydroxy-6-oxononanoate[1a] (8a) (a mixture of tautomers) were obtained by treatment of the electrolyzate from entry 10 with hydrochloric acid (10%, 1 mL, 20 min, 20 °C) and isolated by flash chromatography. ^1H NMR, δ: 1.55—1.90 (m, 4 H, CH_2); 2.10—2.23 (m, 2 H, CH_2COO); 2.30—2.63 (m, 4 H, CH_2C=O); 3.35 (t, 2 H, CH_2OH); 3.68 (s, 3 H, MeO); 4.28 (t, 2 H, CH_2O in the THF ring). ^{13}C NMR, δ: 210.1 (C=O); 174.2, 173.8 (COO); 104.4 (O—C—O); 66.9, 61.8 (CH_2); 51.8, 51.3 (MeO); 43.8, 41.8, 33.92, 32.63, 32.31, 31.30, 30.62, 26.32, 25.70, 25.45, 23.80, 22.67 (CH_2). IR (CCl_4), ν/cm^{-1}: 1060, 1165 (C—O); 1715, 1735 (C=O); 3660 (OH).

Methyl 11-(2-hydroxytetrahydrofur-2-yl)undecanoate (7b) and 15-hydroxy-12-oxopentadecanoate[1a] (8b) (a mixture of tautomers) were obtained by hydrolysis of the electrolyzate from entry 11 similarly to esters **6**. ^1H NMR, δ: 1.27 (m, 12 H, CH_2); 1.50—2.00 (m, 6 H, CH_2); 2.30 (t, 2 H, CH_2COO, J = 7.7 Hz); 2.43 and 2.56 (both t, 4 H, CH_2COCH_2, J = 7.5 Hz); 3.65 (m, 2 H, CH_2OH); 3.67 (s, 3 H, MeO); 4.30 (t, 2 H, CH_2O, J = 5.7 Hz); 4.87 (br.s, 1 H, HO). ^{13}C NMR, δ: 211.9 (C=O); 174.3 (COO); 62.3 (CH_2OH); 51.4 (OMe); 42.9, 39.5, 34.05, 29.29, 29.14, 27.90, 26.43, 24.88, 23.81 (CH_2). IR (CCl_4) ν/cm^{-1}: 1060, 1165 (C—O); 1715, 1735 (C=O); 3660 (OH).

Methyl 5-(dimethoxymethyl)pentanoate[13] (9). ^1H NMR, δ: 1.35 (m, 2 H, CH_2); 1.60 (m, 4 H, CH_2); 2.30 (t, 2 H, CH_2COO, J = 7.5 Hz); 3.28 (s, 6 H, OMe); 3.63 (s, 3 H, MeOOC); 4.31 (t, 1 H, CHOMe, J = 5).

Methyl 5-(1,3-dioxolan-2-yl)pentanoate[24] (10). ^1H NMR, δ: 1.42—1.63 (m, 6 H, CH_2); 2.30 (t, 2 H, CH_2COO, J = 7.5 Hz); 3.63 (s, 3 H, MeO); 3.87 (m, 4 H, OCH_2CH_2O); 4.81 (t, 1 H, OCHO, J = 4.9 Hz).

Methyl (11) and 2-hydroxyethyl (12) 11-(dimethoxymethyl)undecanoate. Esters **11** and **12** were isolated by flash chromatography from the electrolyzate of entry 18 with minor impurities: 5% **12** in **11** and 10% **11** in **12**. **Ester 11.** The ^1H NMR spectrum was identical to that reported in the literature.[9a] ^{13}C NMR, δ: 174.30 (COO); 104.65 (O—C—O); 52.58 (2 MeO); 51.40 (COOMe); 34.12 (CH_2COO); 29.48—29.16 (m, 8 CH_2); 24.97 (CH_2). **Ester 12.** ^1H NMR, δ: 1.26 (br.s, 14 H, CH_2); 1.60 (m, 4 H, CH_2); 2.31 (t, 2 H, CH_2COO, J = 7 Hz); 2.60 (br.s, 1 H, OH); 3.26 (s, 6 H, OMe); 3.78 (t, 2 H, CH_2OH, J = 5.5 Hz); 4.17 (t, 2 H, $COOCH_2$, J = 5.5 Hz); 4.31 (t, 1 H, OCHO, J = 4.9 Hz). ^{13}C NMR, δ: 174.24 (COO); 103.94 (O—C—O); 65.86 ($COOCH_2$); 61.10 (CH_2OH); 52.61 (OMe); 34.20 (CH_2COO); 29.32—29.13 (m, 8 CH_2); 24.91 (CH_2).

Methyl 6-oxohexanoate[25] (13) was prepared by treatment of the electrolyzate from entry 17 with hydrochloric acid (10% HCl, 1 mL, 20 min, 20 °C) and isolated by flash chromatography. Its ^1H NMR spectrum was identical to that reported in the literature.[25]

This work was supported by the Russian Foundation for Basic Research (Project No. 97-03-33159).

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Received April 2, 1999;
in revised form June 4, 1999