Electrooxidative rearrangement of 5,(*n* + 6)-dimethoxy-1-oxabicyclo[*n*.4.0]alkanes (*n* = 4, 10) into -(2-methoxytetrahydrofur-2-yl)alkanoic esters

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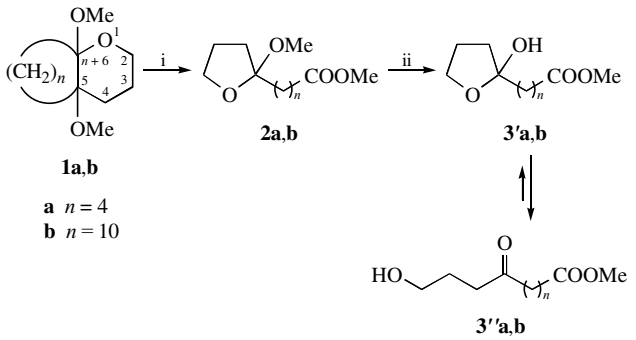
5,(*n* + 6)-Dimethoxy-1-oxabicyclo[*n*.4.0]alkanes undergo a previously unknown oxidative rearrangement into -(2-methoxytetrahydrofur-2-yl)alkanoic esters during electrolysis in methanol.

Rearrangement of 5,(*n* + 6)-dimethoxy-1-oxabicyclo[*n*.4.0]alkanes **1a**,**b**† into -(2-methoxytetrahydrofur-2-yl)alkanoic esters **2a**,**b** occurred when compounds **1a**,**b** were electrolysed in methanol in the presence of Bu_4NBF_4 as an electrolyte, in an undivided cell with a platinum anode and a stainless steel cathode, at room temperature with the passage of 7 F mol^{-1} of electric current. Products **2a**,**b** were formed in yields of 65–75% (Scheme 1).‡

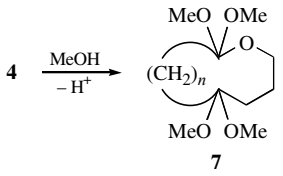
The structures of products **2a**,**b** were assigned based on their spectral data.§ Thus, there were signals (δ_H 1.76–2.13, 3.14, 3.85 and δ_C 47.5–47.8, 66.9–67.1, 108.8–109.1) common to the protons and ^{13}C-nuclei of the 2-methoxytetrahydrofuryl group.[7] In addition, their structures were confirmed by acidic hydrolysis into a mixture of tautomers: methyl -hydroxy-(2-methoxytetrahydrofur-2-yl)alkanoates (**3′a**,**b**) (minor) and -hydroxy-(-3)-oxoalkanoates (**3′′a**,**b**) (major).‡ Evidence for the fact that the hydrolysis products constitute a tautomer mixture is provided by an infrared absorption characteristic of the ketone and ester carbonyl groups (1715 and 1735 cm^{-1}) and 20 lines in the ^{13}C NMR spectrum of **3a**.

The electrochemical transformation of compound **1a** into ester **2a** seems to result from a transannular rearrangement of the cationic intermediate **4a** into a more stable carbocation **6a** *via* the oxonium ion **5a** and subsequent conversion of **6a** into **2a** (Scheme 2).¶

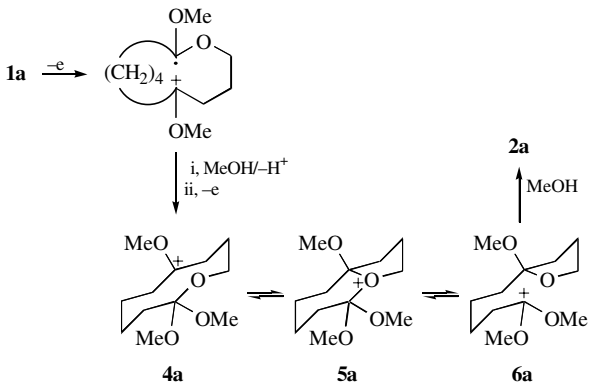
In a similar manner ester **2b** is formed from compound **2a**. Judging by the absence of orthoesters among the electrolysis products,†† the formation of which might be expected as a result of solvolysis of the cationic intermediates **4**, the reaction either



Scheme 1 *Reagents and conditions*: i, Bu_4NBF_4, MeOH, 20 °C, 2.5 h (7 F mol^{-1}); ii, 10% HCl, 20 °C, 20 min.



does not proceed at all, or occurs substantially more slowly than the rearrangement of intermediates **4** into **6**.



Scheme 2

† The starting compounds **1a**,**b** were obtained from 1-oxabicyclo[4.4.0]dec-5(10)-ene[1] and 1-oxabicyclo[10.4.0]hexadec-5(16)-ene[2] in 65% yield under the conditions used for the electrochemical dimethoxylation of linear and monocyclic enol ethers.[3–5]

‡ *Electrolysis of* **1** (*typical procedure*). An electrolyte solution (9 mmol), compound **1** (5 mmol) and n-decane (internal standard, 3 mmol) in MeOH (15–25 ml) were placed in an undivided cell described previously[6] and then electrolysed at a constant current (0.5 A) and room temperature with efficient stirring until more than 90% conversion of **1** (2.5 h, 7 F mol^{-1}) had occurred. The solvent was then removed, the residue extracted with hexane (2×20 ml), the combined extracts were concentrated and the products isolated using vacuum distillation or flash chromatography with hexane–ethyl acetate (1%) as eluent.

§ *Spectral data for* **2a**: ^{1}H NMR (200 MHz, $CDCl_3$) δ: 1.20–1.75 (m, 6H, CH_2 of aliphatic chain), 1.76–2.13 (m, 4H, CH_2 of THF ring), 2.31 (t, 2H, CH_2COO), 3.14 (s, 3H, MeO), 3.64 (s, 3H, COOMe), 3.85 (t, 2H, CH_2O). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 173.8 (COO), 109.1 (O-C–O), 67.1 (CH_2O), 51.3, 47.8 (MeO), 35.7, 35.2, 33.8, 24.97, 24.14, 24.07 (CH_2). IR (thin film, ν/cm^{-1}): 1060, 1165 (C–O), 1735 (C=O).

For **2b**: ^{1}H NMR (200 MHz, $CDCl_3$) δ: 1.20–1.75 (m, 18H, CH_2 of aliphatic chain), 1.76–2.13 (m, 4H, CH_2 of THF ring), 2.31 (t, 2H, CH_2COO), 3.17 (s, 3H, MeO), 3.67 (s, 3H, COOMe), 3.85 (t, 2H, CH_2O). ^{13}C NMR (50 MHz, $CDCl_3$) 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).

For **3a**: ^{1}H NMR (250 MHz, $CDCl_3$) δ: 1.55–1.90 (m, 4H, CH_2), 2.10–2.23 (m, 2H, CH_2COO), 2.30–2.63 (m, 4H, CH_2C=O), 3.35 (t, 2H, CH_2OH), 3.68 (s, 3H, MeO), 4.28 (t, 2H, CH_2O of THF ring). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 210.1 (C=O), 174.2, 173.8 (O=C-O), 104.4 (O-C-O), 66.9, 61.8 (CH_2), 51.8, 51.3 (OMe), 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).

For **3b**: ^{1}H NMR (200 MHz, $CDCl_3$) δ: 1.27 (br. s, 12H, CH_2), 1.50–2.00 (m, 6H, CH_2), 2.30 (t, 2H, CH_2COO), 2.43 and 2.56 (t, 4H, CH_2COCH_2), 3.65 (t, 2H, CH_2OH), 3.67 (s, 3H, OMe), 4.87 (br. s, 1H, OH). ^{13}C NMR (50 MHz, $CDCl_3$) 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).

¶ Similar involvement of the tetrahydrofuranyl oxonium ions in the transformation of linear methoxy-substituted aliphatic carbenium ions was discussed in detail in ref. 8.

†† Tests for the content of orthoesters in the electrolysis products were performed using the procedure described in ref. 9.

The rearrangement of **1** into **2** is accompanied by the side process of solvent oxidation and this leads to an increase in the consumption of electricity (7 F mol^{-1}) with respect to the theoretical amount (2 F mol^{-1}) in order to achieve a high degree of conversion of **1**.

In conclusion, it may be noted that the transformation of 5,(*n* + 6)-dimethoxy-1-oxabicyclo[*n*.4.0]alkanes **1a**,**b** into -methoxy- -(tetrahydrofur-2-yl)alkanoic **2a**,**b** and -hydroxy-(-3)-oxoalkanoic **3a**,**b** esters is a new synthetic approach to substituted alkanoic esters of a similar type, which may find application in, *e.g.* the preparation of -(4-oxobutanoyl)alkanoic esters and 2-(-alkoxycarbonylalkyl)cyclopent-2-en-1-ones,[10] synthons for the synthesis of prostaglandins, pheromones and other valuable organic products.

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