Electrochemical Cleavage of Double Bonds in Conjugated Cycloalkenyl- and 1,2-Alkenobenzenes

Yuri N. Ogibin,* Alexey I. Ilovaisky, and Gennady I. Nikishin

N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, Moscow 117913, Russia

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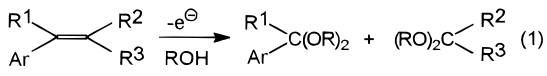
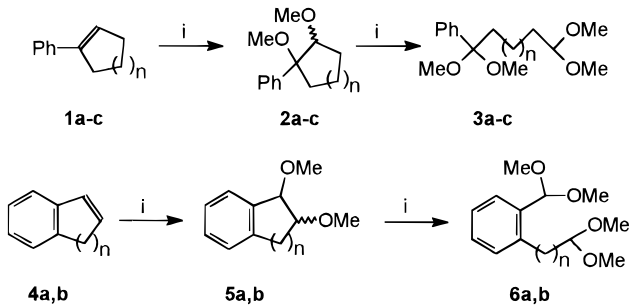
The electrochemical cleavage of olefinic bonds in conjugated C_5−C_7-cycloalkenylbenzenes **1**, indene **4a**, and 1,2-dihydronaphthalene (**4b**) results from anodic oxidation of these compounds in MeOH in an undivided cell. The process includes the formation of (1,2-dimethoxycycloalkyl)benzenes **2a**−**c**, 1,2-dimethoxyindan (**5a**), and 1,2-dimethoxytetralin (**5b**) as intermediates and leads to ω,ω-dimethoxy-ω-phenyl-*n*-C_5−C_7-alkanal dimethyl acetals **3a**−**c**, [2-(dimethoxymethyl)phenyl]ethanal dimethyl acetal (**6a**), and 3-[2-(dimethoxymethyl)phenyl]propanal dimethyl acetal (**6b**) as major products, respectively. The best yields of **3a**−**c** and **6a,b** (58−76%) were obtained when the electrolysis was carried out at 60 °C and 6 F/mol of electricity based on **1**, **4a**, and **4b** was passed using C-anode and Bu_4NBF_4 as a supporting electrolyte. Compounds **2a**−**c** and **5a,b** as mixtures of *cis* and *trans* diastereomers were obtained as major products in 81−90% yield when the electrolysis was terminated after 2 F/mol of electricity based on **1**, **4a**, and **4b** had been passed. The *cis*/*trans* ratio in **2a**−**c** was increased with the increasing the size of cycloalkane rings in **1**, **4a**, and **4b** and the obvious stereoselective effect of the anode nature (C or Pt) being observed in the case of dimethoxylation of **4a**.

Electrooxidation of conjugated arylalkenes in alcohols is a convenient and efficient method for the electrochemical cleavage of a double bond and for the conversion of the compounds to acetals of aromatic aldehydes (eq 1)[1] which are versatile starting materials in organic synthesis.[2]



Now we report a new approach based on this methodology to acetal and ketal derivatives with acetal and ketal groups in one molecule, namely, to the respective derivatives of aromatic 1,5-, 1,6-, and 1,7- dicarbonyl compounds which could be of interest as precursors for a wide variety of carbocycles and heterocycles.[3] The derivatives are still fairly unaccessible since they cannot be derived from the respective dicarbonyl compounds by their acetalization and ketalization because of faster conversion into oxacycloalkanes. 1,3-Dimethoxyisochroman was formed by the reaction of homophthalic aldehyde with MeOH,[4] and 4-benzoylbutanal was found to give 2,6-dimethoxy-2-phenyltetrahydropyran under these reaction conditions. Presuming that the derivatives could be prepared from the readily available conjugated cycloalkenyl- and 1,2-alkenobenzenes, we undertook the present investigation and report here the results of our work.

Scheme 1



We have found that conjugated phenylcycloalkenes **1a**−**c** and 1,2-alkenobenzenes—indene **4a** and 1,2-dihydronaphthalene **4b** being electrolyzed in MeOH under galvanostatic conditions using an undivided cell—undergo a consecutive electrochemical cleavage of benzylic π- and σ-carbon−carbon bonds to give at first (1,2-dimethoxycycloalkyl)benzenes **2a**−**c**, 1,2-dimethoxyindan (**5a**), and 1,2-dimethoxytetralin (**5b**) and then ω,ω-dimethoxy-ω-phenylalkanal acetals **3a**−**c** and 2-(ω,ω-dimethoxyalkyl)-benzaldehyde acetals **6a**,**b** (Scheme 1).

The best yields of acetals **3** (58−76%) and **6** (61−75%) were obtained when electrolysis was carried out at 60 °C using a graphite anode, tetrabutylammonium tetrafluoroborate as a supporting electrolyte, current density of 100 mA/cm^2, and 6 F/mol of electricity based on the starting substrate (Table 1). The optimization of the electrochemical process was performed for **1b** testing C- and Pt-anodes, Bu_4NBF_4, KF, CF_3COONa, and TsONa as electrolytes, room and elevated (60 °C) temperature,

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Table 1. Electrooxidation of Cycloalkenylbenzenes 1a−c and 1,2-Alkenobenzenes 4a,b[a]

substr	electricity passed (F/mol)	conversn (%), C-anode (Pt-anode)	products, yield (%),[b] C-anode (Pt-anode)	*cis*/*trans* ratio,[c] C-anode (Pt-anode)
1a	2	85 (78)	**2a**, 81 (75)	1.3 (0.8)
1a	4	100	**2a**, 58; **3a**, 33	
1a	6	100	**2a**, 3; **3a**, 62	
1b	2	80 (75)	**2b**, 76 (70)	3.2 (2.5)
1b	4	100	**2b**, 56; **3b**, 34	
1b	6	100	**2b**, 4; **3b**, 58	
1c	2	93 (90)	**2c**, 90 (85)	6.1 (5.1)
1c	6	100	**2c**, 13; **3c**, 76	
4a	2	95 (83)	**5a**, 88 (74)	1.4 (1.05)
4a	6	100	**5a**, 17; **6a**, 75	
4b	2	95 (80)	**5b**, 90 (76)	1.8 (1.9)
4b	6	100	**5b**, 11; **6b**, 61	

[a] 60 °C, Bu_4NBF_4. [b] Isolated yields based on the substrate. [c] Determined by GLC and ^{1}H NMR.

Table 2. Electrooxidation of Cyclohex-1-enylbenzene (1b) Using Different Electrolytes, Anodic Materials, and Temperature[a]

anode	electrolyte	temperature, °C	yield of **2b**, %[b]	yield of **3b**, %[b]
C	Bu_4NBF_4	20	34	38
	Bu_4NBF_4	60	6	62
	KF	60	8	54
	CF_3COONa	60	83	15
	TsONa	60	45	37
Pt	Bu_4NBF_4	60	21	53
	KF	60	23	54
	CF_3COONa	60	32	48
	TsONa	60	28	53

[a] 6 F/mol, conversion of **1b** 100%. [b] GLC data.

and 2, 4 and 6 F/mol of electricity passed (Tables 1 and 2). The data obtained give evidence to faster anodic oxidation of intermediate **2b** on the C-anode in the presence of Bu_4NBF_4 or KF than on the Pt-anode using the same electrolytes. With CF_3COONa and TsONa as electrolytes, an opposite result is observed.

The formation of acetals **3** and **6** in substantial amounts has been observed only after the exhaustion of substrates **1** and **4**; this occurred when a little more than 2 F/mol was passed. When the electrolysis was discontinued at this moment, compounds **2** and **5** were isolated as major products in 81−90% yield. They were formed as mixtures of *cis* and *trans* diastereomers, the *cis*/*trans* ratio of the isomers being increased with increasing the size of the cycloalkane ring in **2** and **5** whether the anode was graphite or platinum and the obvious stereoselective effect of the anode nature (C or Pt) being observed in the case of dimethoxylation of **1a** (Table 1). The same effect of the anode material was reported for dimethoxylation of acenaphthylene.[5] The stereochemistry observed for the electrochemical conversion of **1** and **4** into **2** and **5** confirmes that the process proceeds mainly at the anode surface and it is affected essentially by the starting material structure. The latter seems to control the adsorbing ability of the substrate at the anode surface, which results in the attack at the side of the molecule not protected by the electrode. This is supported by the fact that no stereoselective effect took place for chemical dimethoxylation of **4a**.[6]

Theoretically, 2 F/mol of electricity are required for transforming intermediates **2a**−**c** and **5a**,**b** to products of type **3a**−**c** and **6a**,**b**. However, higher oxidative potentials for the intermediates (e.g., 1.80 V vs Ag/Ag^+ for (1,2,3-trimethoxypropyl)benzene[7]) in comparison with those for conjugated alkenylbenzenes (1.42 V vs Ag/Ag^+ for (3-methoxypropenyl)benzene[7]) essentially increase the consumption of electricity by the side anodic oxidation of methanol (solvent)[8] and consequently decrease the conversion of **2** and **5** and the yields of **3** and **6** on the basis of **1** and **4** when the theoretical amount of electricity was passed (4 F/mol based on the starting materials) (see Table 1). To provide higher yields of **3** and **6** based on starting **1** and **4**, we increased the electricity passed to 6 F/mol.

Experimental Section

The electrochemical undivided cell was described previously.[1d] The anodes were a 15-mm-diameter graphite rod or a platinum plate (ca. 10 cm^2); the cathode was a stainless steel plate. ^{1}H NMR spectra were recorded in $CDCl_3$ at 300 MHz using TMS as the internal standard; ^{13}C NMR spectra were recorded at 75 MHz. Mass spectra were determined at 70 eV. Gas chromatography was performed using 5% Carbowax 20M on Inerton AW and 5% XE-60 on Chromaton N-AW columns (200 × 0.3 cm). For flash column chromatography silica gel (40−100 mesh) was used. Compounds **1a** and **1c** were prepared by the reaction of the corresponding cycloalkanones with PhMgBr followed by dehydratation with HCOOH;[9] **4b** was synthesized from α-tetralone.[10] Solvents were distilled by using the usual procedures. All other materials were commercially available and used as received.

Electrolysis of Cycloalkenylbenzenes 1a−c and 1,2-Alkenobenzenes 4a,b (Typical Procedure). A stirred 0.1 M solution (30 mL) of Bu_4NBF_4 or another electrolyte in MeOH containing 15 mmol of **1** or **4** was electrolyzed at 60 °C in the undivided cell at a constant current with a current density of 100 mA/cm^2. The solvent was then removed, the residue was extracted with hexane (2 × 30 mL), the combined extracts were concentrated, and the products were isolated by vacuum distillation and purified by flash chromatography with hexane−ethyl acetate (0−2%) as eluent (Table 1). The stereochemistry of **2** and **5** was determined by comparison of ^{1}H NMR signals for the methine protons of *cis* and *trans* **2** with those for the authentic sample of *cis*-**2b** prepared from *cis*-1-phenylcyclohexane-1,2-diol[11,12] and for *cis* and *trans* dimethoxyindans.[13]

1,2-Dimethoxy-1-phenylcyclopentane (2a): mixture of *cis* and *trans* isomers (1:1.3); bp 128−30 °C/10 mmHg; n_D^{20} 1.5276; MS, *m*/*z* (relative intensity) 206 (33, M^+), 175 (14), 174 (79), 173 (15), 160 (12), 159 (17), 148 (13), 147 (100), 143 (51), 142 (34), 131 (47), 121 (26), 117 (53). Anal. Calcd for $C_{13}H_{18}O_2$: C, 75.69; H, 8.79. Found: C, 75.33; H, 8.57. ***cis*-2a**: 1H NMR δ 1.65−2.05 (m, 2H), 2.07−2.30 (m, 4H), 3.02 (m, 1H), 3.10 (s, 3H), 3.32 (s, 3H), 7.25−7.52 (m, 5H); ^{13}C NMR δ 19.01, 27.30, 30.18, 51.33, 57.97, 79.95, 90.00, 126.95, 128.08, 128.53, 141.53. ***trans*-2a**: ^{1}H NMR δ 1.65−2.05 (m, 2H), 2.07−2.30 (m, 4H), 2.97 (s, 3H), 3.02 (s, 3H), 3.65 (m, 1H), 7.25−7.52 (m, 5H); ^{13}C NMR δ 20.10, 28.26, 29.24, 49.78, 57.21, 86.54, 88.74, 127.45, 127.83, 128.08, 139.51.

1,2-Dimethoxy-1-phenylcyclohexane (2b): mixture of *cis* and *trans* isomers (2.5:1); bp 110−3 °C/0.7 mmHg; n_D^{20}

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1.5282; MS, *m/z* (relative intensity) 220 (27, M^+), 188 (9), 184 (5), 154 (18), 147 (61), 84 (100). Anal. Calcd for $C_{14}H_{20}O_2$: C, 76.32; H, 9.15. Found: C, 76.39; H, 9.35. ***cis*-2b**: ^{1}H NMR δ 1.25−2.15 (m, 8H), 2.99 (s, 3H), 3.06 (m, 1H), 3.15 (s, 3H), 7.20−7.50 (m, 5H); ^{13}C NMR δ 20.90, 24.68, 26.56, 31.58, 50.13, 57.91, 80.09, 85.99, 126.71, 127.22, 127.79, 142.45. The same spectra were obtained for the authentic sample of *cis*-**2b**. ***trans*-2b**: ^{1}H NMR δ 1.25−2.15 (m, 8H), 2.86 (s, 3H), 2.93 (s, 3H), 3.27 (m, 1H), 7.20−7.50 (m, 5H); ^{13}C NMR δ 19.31, 20.59, 24.89, 25.00, 48.93, 57.49, 78.92, 83.16, 126.85, 127.08, 127.79, 143.68.

1,2-Dimethoxy-1-phenylcycloheptane (2c): mixture of *cis* and *trans* isomers (5.1:1); bp 154−7 °C/8 mmHg; n_D^{20} 1.5319; MS, *m/z* (relative intensity) 234 (23, M^+), 203 (10), 202 (45), 172 (20), 170 (25), 147 (100), 121 (28), 105 (26), 91 (30). Anal. Calcd for $C_{15}H_{22}O_2$: C, 76.88; H, 9.47. Found: C, 76.69; H, 9.37. ***cis*-2c**: ^{1}H NMR δ 1.40−1.97 (m, 8H), 2.07 (m, 2H), 3.01 (s, 3H), 3.05 (m, 1H), 3.17 (s, 3H), 7.23-7−47 (m, 5H); ^{13}C NMR δ 20.36, 23.60, 26.11, 26.93, 33.69, 50.83, 57.70, 82.11, 89.51, 126.46, 127.25, 127.54, 144.05. ***trans*-2c**: ^{1}H NMR δ 1.40−1.97 (m, 8H), 2.07 (m, 2H), 2.89 (s, 3H), 3.02 (s, 3H), 3.30 (m, 1H), 7.23-7.47 (m, 5H); ^{13}C NMR δ 19.51, 24.64, 26.73, 29.15, 32.83, 49.82, 57.35, 82.30, 86.90, 127.07, 128.02, 128.68, 145.15.

1,2-Dimethoxyindan (5a): mixture of *cis* and *trans* isomers (1.4:1); bp 125-8 °C/12 mmHg (lit.[6] bp 134−6 °C/22 mmHg); n_D^{20} 1.5358; MS, *m/z* (relative intensity) 178 (100, M^+), 147 (85), 146 (74), 131 (90), 117 (81), 116 (93), 115 (57), 105 (69), 104 (53), 103 (78), 91 (60). ***cis*-5a**: ^{1}H NMR δ 2.75−3.38 (m, 2H), 3.43 (s, 3H), 3.52 (s, 3H), 4.09 (m, 1H), 4.62 (d, 1H, J = 4.97 Hz), 7.20−7.42 (m, 4H); ^{13}C NMR δ 35.31, 56.95, 57.24, 82.05, 86.95, 124.89, 125.23, 127.75, 128.45, 139.49, 140.12. ***trans*-5a**: ^{1}H NMR δ 2.75−3.38 (m, 2H), 3.47 (s, 3H), 3.57 (s, 3H), 4.09 (m, 1H), 4.77 (d, 1H, J = 4.18 Hz), 7.20−7.42 (m, 4H); ^{13}C NMR δ 35.86, 56.05, 56.95, 81.54, 88.02, 124.89, 126.22, 126.67, 128.89, 139.80, 140.75.

1,2-Dimethoxy-1,2,3,4-tetrahydronaphthalene (5b): mixture of *cis* and *trans* isomers (1.8:1); bp 130−5 °C/10 mmHg; n_D^{20} 1.5345; MS, *m/z* (relative intensity) 192 (7, M^+), 160 (40), 134 (100), 119 (55), 91 (31). Anal. Calcd for $C_{12}H_{16}O_2$: C, 74.96; H, 8.39. Found: C, 74.88; H, 8.27. ***cis*-5b**: ^{1}H NMR δ 2.08 (m, 2H), 2.70−3.15 (m, 2H), 3.49 (s, 3H), 3.56 (s, 3H), 3.77 (m, 1H), 4.29 (d, 1H, J = 4.98 Hz); ^{13}C NMR δ 23.47, 25.38, 56.59, 57.50, 77.63, 79.69, 125.90, 127.67, 128.51, 129.81, 134.60, 136.65. ***trans*-5b**: ^{1}H NMR δ 2.08 (m, 2H), 2.70−3.15 (m, 2H), 3.51 (s, 3H), 3.53 (s, 3H), 3.67 (m, 1H), 4.39 (d, 1H, J = 2.84 Hz), 7.12−7.42 (m, 4H); ^{13}C NMR δ 22.36, 27.22, 56.43, 57.19, 77.67, 78.26, 125.41, 128.19, 128.86, 129.92, 133.90, 135.85.

5,5-Dimethoxy-5-phenylpentanal dimethyl acetal (3a): bp 118−20 °C/0.1 mmHg; n_D^{20} 1.4905; MS, *m/z* (relative intensity) 237 (2, M^+ − OMe), 224 (9), 173 (8), 172 (100), 151 (10), 131 (12), 130 (75), 118 (40); ^{1}H NMR δ 1.05 (m, 2H), 1.48 (m, 2H), 1.91 (m, 2H), 3.16 (s, 6H), 3.22 (s, 6H), 4.22 (t, 1H), 7.27−7.48 (m, 5H); ^{13}C NMR δ 18.59, 32.26, 36.93, 48.60, 52.59, 103.49, 104.28, 126.96, 127.60, 127.96, 141.10. Anal. Calcd for $C_{15}H_{24}O_4$: C, 67.13; H, 9.01. Found: C, 67.09; H, 8.89.

6,6-Dimethoxy-6-phenylhexanal dimethyl acetal (3b): bp 133−5 °C/0.1 mmHg; n_D^{20} 1.4882; MS, *m/z* (relative intensity) 251 (10, M^+ − OMe), 233 (19), 220 (9), 219 (51), 204 (13), 179 (49), 165 (64), 151 (100), 145 (16), 105 (30), 91 (12); ^{1}H NMR δ 1.01 (m, 2H), 1.22 (m, 2H), 1.47 (m, 2H), 1.89 (m, 2H), 3.14 (s, 6H), 3.25 (s, 6H), 4.24 (t, 1H), 7.27−7.48 (m, 5H); ^{13}C NMR δ 23.12, 24.43, 32.18, 37.02, 48.48, 52.47, 103.42, 104.24, 126.82, 127.45, 127.80, 140.80. Anal. Calcd for $C_{16}H_{26}O_4$: C, 64.98; H, 8.39. Found: C, 64.75; H, 8.17.

7,7-Dimethoxy-7-phenylheptanal dimethyl acetal (3c): bp 140−3 °C/0.07 mmHg; n_D^{20} 1.4880; MS, *m/z* (relative intensity) 265 (5, M^+ − OMe), 234 (6), 233 (20), 152 (18), 151 (100), 105 (15); ^{1}H NMR δ 0.97 (m, 2H), 1.19 (m, 4H), 1.48 (m, 2H), 1.87 (m, 2H), 3.13 (s, 6H), 3.25 (s, 6H), 4.27 (t, 1H), 7.22−7.47 (m, 5H); ^{13}C NMR δ 23.29, 24.44, 29.43, 32.36, 37.15, 48.60, 52.55, 103.62, 104.42, 126.95, 127.53, 127.70, 141.01. Anal. Calcd for $C_{17}H_{28}O_4$: C, 68.89; H, 9.52. Found: C, 68.78; H, 9.37.

2-(2,2-Dimethoxyethyl)benzaldehyde dimethyl acetal (6a): bp 81−3 °C/0.07 mmHg (lit.[14] bp 74−6 °C/0.05 mmHg); MS, *m/z* (relative intensity) 209 (3, M^+ − OMe), 208 (2), 207 (3), 193 (5), 178 (7), 177 (56), 146 (10), 134 (17), 115 (15), 91 (16), 75 (100); ^{1}H NMR δ 2.99 (d, 2H), 3.29 (s, 6H), 3.32 (s, 6H), 4.48 (t, 1H), 5.54 (s, 1H), 7.15−7.55 (m, 4H); ^{13}C NMR δ 35.94, 53.05, 53.64, 101.84, 105.58, 125.99, 126.57, 128.17, 130.94, 135.21, 136.09.

2-(3,3-Dimethoxypropyl)benzaldehyde dimethyl acetal (6b): bp 125−8 °C/1 mmHg; n_D^{20} 1.4968; MS, *m/z* (relative intensity) 254 (5, M^+), 252 (22), 242 (21), 241 (25), 191 (15), 190 (18), 176 (17), 175 (18), 164 (19), 156 (25), 149 (37), 141 (30), 117 (85), 89 (92), 75 (100); ^{1}H NMR δ 1.91 (m, 2H), 2.77 (m, 2H), 3.33 (s, 6H), 3.36 (s, 6H), 4.42 (t, 1H), 5.52 (s, 1H), 7.18−7.58 (m, 4H); ^{13}C NMR δ 26.93, 33.85, 52.50, 52.94, 101.39, 103.86, 125.55, 126.71, 128.44, 129.51, 135.29, 139.82. Anal. Calcd for $C_{14}H_{22}O_4$: C, 66.11; H, 8.72. Found: C, 66.02; H, 8.58.

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