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Cleavage of alkenes by anodic oxidation

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Abstract

Oxidative cleavage of olefinic double bonds to carboxylic acids, aldehydes or ketones is one of the important reactions in organic synthesis. Ozonolysis is mostly applied for this purpose, however, high costs for safety precautions in technical scale conversions demand alternatives. For this purpose different electrochemical methods are investigated. In the direct oxidation of cyclohexene at a platinum or graphite anode no cleavage occurs, but substituted and rearranged products are obtained. At the boron doped diamond electrode (BDDE) aliphatic olefins with high oxidation potential are not converted. Electrochemical ozonolysis by oxidation of water to ozone at the lead dioxide electrode leads to carboxylic acids as cleavage products in high material yield but low current yield. Anodic bromo-formyloxylation followed by an anodic cleavage provides a two step conversion of cyclohexene to hexane-1,6-dial derivatives. Thereby anodic discharge of bromide in formic acid leads to (2-bromocyclohexyl)-formate, which is converted to cyclohexane-1,2-diol and the major part of potassium bromide is recovered for the next cycle. This electrochemical conversion appears to be an attractive alternative to chemical oxidations with oxygen and catalysts or with hydrogen peroxide. The diol is cleaved in high yield to hexane-1,6-dial or its acetal either directly or indirectly with periodate as mediator.

1. Introduction

Oxidative cleavage of alkenes is a significant and frequently applied reaction in organic synthesis. It leads to carboxylic acids and aldehydes or ketones, which provide starting materials for a large variety of functional group interconversions and C,C-bond forming reactions. In the laboratory the method of choice is ozonolysis [1–5], in a few cases it is also applied on a technical scale [6–8], which, however, requires costly safety precautions. Other methods are the conversion to 1,2-diols followed by a glycol cleavage [9–13]. With transition metals and cooxidants this cleavage can be performed as one-pot reaction [14–19]. We have developed an indirect anodic process [20], based on the chemical cleavage with stoichiometric amounts of periodate and $RuCl_3$ as catalyst [14]. With anodic *in cell*- and *ex cell*- periodate regeneration and a chemical reactor employing sonication or an immobilized alkene, we were able to oxidize a number of alkenes with chemical and current yields between 50 and 80% and to decrease the amount of periodate, that is needed in the chemical oxidation, down to 5% [20]. To explore whether this electrochemical approach to cleave alkenes is unique, or whether there are other efficient electrochemical alternatives, we investigated for alkenes the direct anodic oxidation, the anodic ozonolysis and the anodic haloformyloxylation combined with an electrochemical glycol cleavage.

2. Experimental

2.1. *General remarks*

All chemicals were commercially available (Aldrich, Merck, Avocado, Fluka) and were used without further purification, if not specified otherwise. The solvents were destilled and if necessary further purified. All products were identified by ^{1}H-, ^{13}C-NMR, GC-MS, ESI-MS, IR. Gas chromatography was performed on a Hewlett-Packard HP 6860 plus with a quartz capillary column HP 5 (30 m, 0.32 mm inner diameter, 0.25 μm film). The current source for electrolysis was a LD 50/10 GB (Zentro Elektronik, Pforzheim, Germany) or a potentiostat Wenking LB 75L (Bank, Elektronik, Clausthal-Zellerfeld, Germany). The charge was determined with a calibrated DC-integrator. Electrode materials: Graphite P127 und glassy carbon sigradur®-G (Sigri, Meitingen, Germany), titanium foil (0.25 mm) (Strem Chemicals, Newburyport, U.S.A), BDD/Si-electrode (CSEM, Neuchatel, Suisse. To contact the electrode with the current feeder a spot on the silicon side was treated with SiC-paper and then with a conducting varnish), Ru/Ir-oxide electrode on titanium (Metakem, Usingen, Germany). The lead dioxide electrode on titanium was prepared according to [21].

2.2. *Anodic in situ ozonolysis*

2.2.1. *1- Decene(**1**) in a divided cell in water/dichloromethane*

1-Decene (**1**, 1.0 ml, 0.74 g, 5 mmol) in dichloromethane (30 ml) and phosphate buffer (50 ml of 90.0 g l^{-1} disodium hydrogen phosphate, 30.0 g l^{-1} sodium dihydrogen phosphate and 0.12 g l^{-1} sodium fluoride) was electrolyzed in a divided cell with a lead dioxide anode (6 cm^2) and a platinum cathode (catholyte: 10% sulfuric acid) at 20 °C and 150 mA cm^{-2} until after 50.000 C no **1** could be detected by glc in the electrolyte. The aqueous phase was extracted with dichloromethane (3×20 ml), the combined organic phases were dried ($MgSO_4$) and the solvent rotaevaporated. Distillation of the residue yielded nonanoic acid (**3a**, 0.38 g, 2.4 mmol, 48%) and nonanal (2, 0.31 g, 2.2 mmol, 44%).

Nonanal (**2**): FT-IR (film): $\tilde{\nu}$ (cm^{-1}) = 2954 (s, CH), 2852 (s, CH), 1726 (s, C=O), 1463 (m, CH, def.), 1420 (m, CH, def.), 1373 (m), 1139 (w), 976 (br, w), 722 (w, CH_2, rocking). ^{1}H-NMR ($CDCl_3$): δ (ppm) = 0.89 (t, $^3J = 6.4$ Hz, 3H, CH_3), 1.20–1.40 (m, 10H, 5 CH_2), 1.64 (m, 2H, $C\mathit{H}_2CH_2CHO$), 2.38–2.48 (dt, $^3J = 7.6$ Hz, $^3J = 2.0$ Hz, 2H, $C\mathit{H}_2CHO$), 9.77 (t, ^{3}J = 2.0 Hz, 1H, $C\mathit{H}O$). ^{13}C-NMR ($CDCl_3$): δ (ppm) = 14.1 (q, CH_3), 22.2, 22.7, 29.3, 29.0, 29.2, 29.3 (all t, 6CH_2), 32.0 (t, $\mathit{C}H_2CHO$), 204.2 (d, CHO). MS (GC/MS-coupling, EI): *m/z* (%) = 142 (2) [M^+], 124 (9) [M^+–H_2O], 114 (13) [M^+–CO], 99 (5) [M^+–C_3H_7], 98 (43) [M^+–C_2H_4O, *McLafferty*], 85 (4) [M^+–C_4H_9], 71 (14) [M^+–C_5H_{11}], 70 (39) [$C_5H_{10}^+$], 57 (74) [M^+–C_6H_{13}], 44 (32) [$C_2H_4O^+$, *McLafferty*], 43 (78) [$C_3H_7^+$]. The spectroscopic data correspond to those in the literature [22].

2.2.2. *1- Decene (**1**) with oxidative work-up*

1-Decene (**1**, 1.0 ml, 0.74 g, 5 mmol) was electrolyzed according to section 2.2.1. After treating the crude product with 20% hydrogen peroxide (3 ml) and conc. formic acid (6 ml) [4], followed by extraction with dichloromethane (3 ×20 ml) and an otherwise usual work-up led to nonanal (**2**, 0.04 g, 0.3 mmol, 6%) and nonanoic acid (**3a**, 0.62 g, 3.9 mmol, 78%).

2.2.3. *1-Decene (**1**) in water/ethyl acetate in an undivided cell*

1-Decene (**1**, 1.0 ml, 0.74 g, 5 mmol), ethyl acetate (30 ml) and phosphate – buffer (50 ml) were electrolyzed in an undivided cell at a lead dioxide anode (14 cm^2) until 55.000 C were consumed. Work-up, according to section 2.2.2, yielded nonanoic acid (**3a**, 0.68 g, 4.3 mmol, 86%).

2.2.4. *(Z)-9-Octadecenoic acid (**4**) in water/ethyl acetate in an undivided cell*

(Z)-9-octadecenoic acid (**4**, 1.77 g, 5 mmol) was electrolyzed according to section 2.2.3. In the work-up the acids were converted to their methyl esters. The crude product was evaporated to dryness, treated with abs. methanol (200 ml), 2,2-dimethoxypropane (10 ml, 82 mmol), conc. hydrochloric acid (p.a., 2 ml) and stirred for 24 h. The solvent was removed under reduced pressure and the product separated by flash chromatography(silica gel) to afford methyl nonanoate (**3b**, 0.65 g, 3.8 mmol, 76%) and dimethyl nonanedioate (**5**, 0.78 g, 3.6 mmol, 72%).

2.2.5. *Cyclododecene (**6**) in water/ethyl acetate in an undivided cell*

Cyclododecene (**6**, 1.0 ml, 0.86 g, 5 mmol) was electrolyzed according to 2.2.3 and the crude product converted into the diester according to 2.2.4 to afford dimethyl dodecanedioate (**7**, 0.95 g, 3.7 mmol, 74%).

2.3. *Two step cleavage of cyclohexene (**8**) by way of its bromo-formyloxylation to cyclohexane-1,2-diol (**10**) and cleavage of the diol.*

2.3.1. *Preparation of trans-(2-bromocyclohexyl)-ethanoate (**9**)*

1-Bromo-2-methoxycyclohexane (0.97 g, 5.0 mmol) [23] in acetic anhydride (0.61 g, 6.0 mmol) and one drop of conc. sulfuric acid were heated at reflux for 2 h. Then the solvent was distilled off and the crude product purified by flash chromatography to afford **9** (0.91 g, 4.1 mmol, 82%).

Trans-(2-bromocyclohexyl)-ethanoate (**9**): R_f-value; 0.28 (*n*-pentane/diethyl ether = 15/1). FT-IR (film): $\tilde{\nu}$ (cm^{-1}) = 3465 (w), 2942 and 2864 (s, CH), 1744 (s, C=O), 1449 and 1438 (m, CH, def.), 1375 (s), 1363 (s), 1245 (m), 1193 (m, C–O, def.), 1152 (m, C–O, Def.), 1098 (m), 1052 (s), 1039 (s), 1015 (m), 894 (w), 843 (w), 774 (w, CH_2, rocking), 674 and 603 (m, asym. and sym. C–Br), 455 (s, br). ^{1}H-NMR ($CDCl_3$): δ (ppm) = 1.21–1.47 (m, 3 H, 3-C*H*H, 4-C*H*H, 5-C*H*H), 1.64–1.87 (m, 3H, 4-CH*H*, 5-CH*H*, 6-C*H*H), 2.01–2.12 (m, 1H, 3-CH*H*), 2.04 (s, 3H, $COCH_3$), 2.25–2.68 (m, 1H, 6-CH*H*), 3.92 (ddd, $^3J_{1,2} = 14$ *Hz*, $^3J_{2,3ax} = 9.4$ Hz, $^3J_{2,3eq} = 4.4$ Hz, 1H, CHBr), 4.84 (ddd, $^3J_{1,6ax} = 9.3$ Hz, $^3J_{1,6eq} = 4.6$ Hz, 1H, CHOAc). ^{13}C-NMR ($CDCl_3$): δ (ppm) = 21.0 (q, $CO\mathit{C}H_3$), 23.3 (t, 4-CH_2), 25.5 (t, 5-CH_2), 31.2 (t, 3-CH_2), 35.6 (t, 6-CH_2), 52.8 (d, CHBr), 75.8 (d, CHOAc), 169.1 (s, $\mathit{C}OCH_3$). MS (GC/MS-coupling, EI): *m/z* (%) = 178, 180 (1, 1) [M^+–$COCH_3$, cluster], 160, 162 (10, 10) [$C_6H_8Br^+$, cluster], 141 (2) [M^+–Br], 99 (12), 98 (3) [$C_6H_{10}O^+$], 81 (72) [$C_6H_9^+$], 80 (82) [$C_6H_8^+$], 67 (4) [$C_5H_7^+$], 53 (4) [$C_4H_5^+$], 43 (100) [$C_3H_7^+$], 39 (6) [$C_3H_3^+$]. The spectroscopic data coincide with those in [24].

2.3.2. *Preparation of cyclohexane-1,2-diol (**10**) from **9***

Bromide **9** (0.99 g, 4.5 mmol) was stirred for 12 h in 2 M sodium hydroxide (30 ml) and then heated under reflux for 1 h. Thereafter the water was evaporated and the residue extracted several times with hot ethyl acetate (4×15 ml). The turbid hot extract was filtered and from the clear, light yellow filtrate the solvent was removed and the residue recrystallized from ethyl acetate to obtain *trans*-cyclohexane-1,2-diol (**10**, 0.49 g, 4.2 mmol, 94%). Mp.101–103 °C (103 °C [25]).

2.3.3. *Dioxygenation of cyclohexene (**8**) by way of anodic bromo-acetoxylation*

2.3.3.1. Tetrabutylammonium bromide as supporting electrolyte. Cyclohexene (**8**, 2.97 ml, 2.41 g, 30 mmol) and tetrabutylammonium bromide (10.6 g, 33 mmol) in acetic acid (18 ml) were electrolyzed in an undivided cell at room temperature at graphite electrodes (each 6 cm^2) at 35 mA cm^{-2} until 3.4 *F* were consumed. Thereafter the solvent was rotaevaporated, the residue stirred for 12 h at room temperature in 2 M sodium hydroxide (30 ml) and then heated under reflux for 1 h. Work-up according to 2.3.2 afforded **10** (2.68 g, 23 mmol, 77%). Mp. 102–103 °C.

2.3.3.2. Potassium bromide as supporting electrolyte. **8** (2.97 ml, 2.41 g, 30 mmol) and potassium bromide (6.0 g, 50 mmol) in 84% acetic acid (60 ml) were electrolyzed in an undivided cell at graphite electrodes (each 6 cm^2) at room temperature and 35 mA cm^{-2} until 3.0 *F* (conversion of **1**:56%) were consumed. For work-up the solvent was rotaevaporated, water (20 ml) was added and then the organic phase was extracted with diethyl ether (4×20 ml). The ether was rotaevaporated and the residue separated by flash chromatography at silica gel to get **9** (0.46 g, 2.1 mmol, 13%), 1,2-dibromocyclohexane (**11**, 10.5 mmol, 63%) and 2-bromocyclohexanol (**12**, 0.32 g, 1.8 mmol, 11%).

1,2-Dibromocyclohexane (**11**): R_f-value: 0.85 (*n*-pentane/diethyl ether = 20/1). FT-IR (film): $\tilde{\nu}$ (cm^{-1}) = 2941 and 2861 (s, CH), 2158 (w, br), 1642 (m, br), 1445 (s, CH, def.), 1433 (s, CH, def.), 1358 (m), 1339 (m), 1268 (m), 1178 (s), 1119 (w), 1032 (w), 998 (m), 972 (m), 903 (m), 861 (w), 841 (m), 811 (w), 686 and 664 (m, asym. and sym. C–Br), 539 (m), 437 (s, br). ^{1}H-NMR (CDCl$_3$): δ (ppm) = 1.38–1.44 (m, 2H, 2 C*H*HCH$_2$CHBr), 1.72–1.94 (m, 4H, 2 CH*H*C*H*HCHBr), 2.38–2.51 (m, 2H, 2CH*H*CHBr), 4.44 (m, 2H, 2 CHBr). ^{13}C-NMR (CDCl$_3$): δ (ppm) = 22.4 (t, 2 *C*H$_2$CH$_2$CHBr), 34.2 (t, 2 *C*H$_2$CHBr), 55.1 (d, 2 CHBr). MS (GC/MS-coupling, EI): *m*/*z* (%) = 244, 242, 240 (3, 6, 3) [M$^+$, cluster], 162, 160 (3, 3) [M$^+$–Br], 163, 161 (61, 63) [M$^+$–HBr], 135, 133 (2, 2) [C$_4$H$_5$Br$^+$], 121, 119 (5, 5) [$C_3H_5^+$], 82 (39) [$C_6H_{10}^+$], 81 (100) [$C_6H_9^+$], 80 (10) [$C_6H_8^+$], 79 (78) [$C_6H_7^+$], 77 (18) [$C_6H_5^+$], 67 (23) [$C_5H_7^+$], 55 (12) [$C_4H_7^+$], 54 (21) [$C_4H_6^+$], 53 (43) [$C_4H_5^+$], 41 (42) [$C_3H_5^+$], 39 (37) [$C_3H_3^+$]. The data of the spectra agree with those in ref. [26].

2-Bromocyclohexanol (**12**): Bp. 96–98 °C (20 mbar); 73 –75 °C (6 mbar) [27]. FT-IR (film): $\tilde{\nu}$ (cm^{-1}) = 3401 (s, br, OH), 2939 and 2861 (s, CH), 2664 (w, br), 1710 (m), 1449 (s, CH, def.), 1361 (m, OH, def), 1254 (m), 1229 (m), 1186 (s), 1122 (m), 1073 (s, C = O), 1036 (m), 690 and 654 (m, asym. and sym. C–Br), 448 (s, br). ^{1}H-NMR (CDCl$_3$): δ (ppm) = 1.19–1.39 (m, 3H, 3-C*H*H, 4-C*H*H, 5-C*H*H), 1.63–1.85 (m, 3H, 4-CH*H*, 5-CH*H*, 6-C*H*H), 2.07–2.13 (m, 1H, 3-CH*H*), 2.28–2.34 (m, 1H, 6-CH*H*), 2.49 (s, br, 1H, OH), 3.57 (ddd, $^3J_{1,2}$ = 12 Hz, $^3J_{1,6ax}$ = 9.8 Hz, $^3J_{1,6eq}$ = 4.6 Hz, 1H, 1-C*H*OH), 3.86 (ddd, $^3J_{1,2}$ = 12 Hz, $^3J_{2,3ax}$ = 9.4 Hz, $^3J_{2,3eq}$ = 4.3 Hz, 1H, 2-CHBr). ^{13}C-NMR (CDCl$_3$): δ (ppm) = 24.1 (t, *C*H$_2$CH$_2$CHBr), 26.6 (t, *C*H$_2$CH$_2$CHOH), 35.5 (t, *C*H$_2$CHBr), 36.2 (*C*H$_2$CHOH), 61.7 (d, CHBr), 75.3 (d, CHOH). MS (GC/MS-coupling, EI): *m*/*z* (%) = 180, 178 (1, 1) [M$^+$, cluster], 162, 160 (1, 1) [M$^+$ - H$_2$O], 134, 132 (3, 3) [C$_4$H$_5$Br$^+$, cluster], 99 (31) [M$^+$–Br], 98 (3) [M$^+$–HBr], 81 (100) [$C_6H_9^+$], 79 (8) [$C_6H_7^+$], 67 (8), 57 (60) [C$_3$H$_5$O$^+$], 55 (10) [C$_3$H$_3$O$^+$], 41 (19) [$C_3H_5^+$], 39 (10) [$C_3H_3^+$]. The spectroscopic data correspond with those in ref. [27].

2.3.4. *Anodic bromo-formyloxylation*

*2.3.4.1. Preparation of (2-bromocyclohexyl)-methanoate (**13**) with potassium bromide as supporting electrolyte.* **8** (0.99 ml, 0.82 g, 10 mmol) and potassium bromide (1.25 g, 10.5 mmol) were electrolyzed in formic acid (18 ml) in an undivided cell at graphite electrodes (each 6 cm^2) at 35 °C with 35 mA cm^{-2} until 3.0 *F* were consumed. Work-up according to 2.3.3.2 yielded **11** (0.34 g, 1.4 mmol, 14%) and (2-bromcyclohexyl)-methanoate (**13**, 1.68 g, 8.1 mmol, 81%).

(2-Bromcyclohexyl)-methanoate (**13**): n_D^{20}: 1.487, 1.4996 [28]. R_f-value: 0.33 (*n*-pentane /diethyl ether = 20/1).; FT-IR (Film): $\tilde{\nu}$ (cm^{-1}) = 3431 (w), 2942 and 2864 (s, CH), 1733 (s, C = O), 1450 (m, CH, def.), 1367 (m), 1333 (s), 1290 (m), 1171 (s, br, C = O, def.), 1109 (m, C = O, def.), 1058 (m), 1034 (s), 1005 (s), 930 (m), 909 (m), 888 (m), 858 (w), 765 (m), 692 and 588 (m, asym. and sym. C–Br), 461 (s, br). ^{1}H-NMR (CDCl$_3$): δ (ppm) = 1.26–1.46 (m, 3H, 3-C*H*H, 4-C*H*H, 5-C*H*H), 1.65–1.88 (m, 3H, 4-CH*H*, 5-CH*H*, 6-CH*H*), 2.05–2.17 (m, 1H, 3-CH*H*), 2.29–2.36 (m, 1H, 6-CH*H*), 3.94 (ddd, $^3J_{1,2}$ = 10.9 Hz, $^3J_{2,3ax}$ = 9.2 Hz, $^3J_{2,3eq}$ = 4.5 Hz, 1H, CHBr), 4.84 (ddd, $^3J_{1,6ax}$ = 9.2 Hz, $^3J_{1,6eq}$ = 4.5 Hz, 1H, 1-C*H*OCHO), 8.05 (s, 1H, CHO). ^{13}C-NMR (CDCl$_3$): δ (ppm) = 23.1 (t, 4-CH$_2$), 25.3 (t, 5-CH$_2$), 31.1 (t, 3-CH$_2$), 35.5 (t, 6-CH$_2$), 52.1 (d, CHBr), 75.6 (d, 1-*C*HOCHO), 160.0 (s, OCOH). MS (GC/MS-coupling, EI): *m*/*z* (%) = 163, 161 (1, 1) [M$^+$–HCOO, cluster], 162, 160 (14, 14), [M$^+$–HCOOH, cluster], 134, 132 (2, 2) [C$_4$H$_5$Br$^+$, cluster], 121, 119 (1, 1) [C$_3$H$_4$Br$^+$, cluster], 127 (3) [M$^+$–Br], 99 (4) [C$_6$H$_{11}$O$^+$], 98 (1) [C$_6$H$_{10}$O$^+$], 82 (12) [$C_6H_{10}^+$], 81 (100) [$C_6H_9^+$], 79 (10) [$C_6H_7^+$], 77 (3) [$C_6H_5^+$], 67 (4) [$C_5H_7^+$], 57 (13) [C$_3$H$_5$O$^+$], 53 (3) [$C_4H_5^+$], 41 (6) [$C_3H_5^+$], 39 (2) [$C_3H_3^+$]. The spectroscopic data agree with those in ref. [29].

2.3.4.2. Continual addition of potassium bromide. **8** (0.99 ml, 0.8 g, 10 mmol) and potassium bromide (0.64 g, 5.4 mmol) were electrolyzed in formic acid

(18 ml) in an undivided cell as in 2.3.4.1. During the electrolysis potassium bromide (0.64 g, 5.4 mmol) was added continually. The work-up as in 2.3.4.1 afforded **13** (1.76 g (8.5 mmol, 85%)) and **11** (0.22 g) (0.9 mmol, 9%).

*2.3.4.3. Preparation of cyclohexane-1,2-diol (**10**) from (2-bromcyclohexyl)-methanoate (**13**).* **13** (0.93 g, 4.5 mmol) was reacted as in 2.3.2 to afford **10** (0.49 g, 4.2 mmol, 94%) as white powder.

2.3.4.4. Scale-up in the beaker-type cell. **8** (14.84 ml, 12.0 g, 0.15 mol) and potassium bromide (9.6 g, 0.081 mol) in formic acid (270 ml) were electrolyzed at 35 °C at graphite electrodes (each 21 cm^2) with 35 mA cm^{-2} under continual addition of potassium bromide (9.6 g, 0.081 mol) until no further **8** could be detected by glc. Work-up according to 2.3.3.2 afforded **13** (25.8 g, 0.125 mol, 83%) and **11** (5.1 g, 0.021 mol, 14%).

2.3.4.5. Scale-up in the capillary gap-cell. The capillary gap cell contained a stack of 13 graphite discs (thickness 10 mm, area: 19 cm^2, distance maintained with PTFE-stripes was about 0.5 mm). The electrolyte was pumped through holes in the centre of the discs, flowed down on the outside of the stack and was cooled in a heat exchanger.

First run: The system was charged with formic acid (400 ml), **8** (14.84 ml, 12.0 g, 0.15 mol) and potassium bromide (9.6 g, 0.081 mol). With continual addition of further **8** (99.0 ml, 80.0 g, 0.85 mol) and potassium bromide (142.2 g, 1.119 mol), the electrolysis was conducted at 35 °C and 35 mA cm^{-2} until **8** was converted to 95% which needed 0.28 *F* at a cell voltage of 28 V. Thereafter formic acid was distilled off, sodium formiate (68 g, 1 mol), isopropanol (30 ml) and water (400 ml) were added and the mixture heated for two days under reflux. Then the solvent was totally removed under vacuum and the residue extracted with hot ethyl acetate (3×80 ml) and the hot extract was filtered. The solid (185 g) was partially used in the second run. From the combined extracts, recrystallized **10** (79.3 g , 0.68 mol, 72% based on converted **8**) was isolated.

Second run: **8** (0.5 mol), residual solid from first run (93 g) and potassium bromide (11.9 g, 0.1 mol) were electrolyzed in formic acid (250 ml) and worked up as in the first run to afford **10** (44.6 g, 0.384 mol, 81% based on converted **8**) and 90 g of salt.

Third run: Under conditions as in the second run **10** (42.9 g, 0.369 mol, 78% based on converted **8**) and 89 g salt were isolated.

2.3.5. *Cleavage of cyclohexane-1,2-diol (**10**)*

*2.3.5.1. Cleavage of cyclohexane-1,2-diol(**10**) with tetraethylammonium tetrafluoroborate as supporting electrolyte in a beaker type cell.* **10** (1.28 g, 11 mmol) were electrolyzed according to [30, 31] until after 2.9 *F* no further **10** was detectable by glc. For work-up the solvent was rotaevaporated, water (20 ml) added and extracted with diethyl ether (4×20 ml). The combined ethereal extracts were dried ($MgSO_4$), the ether removed and the crude product subjected to flash chromatography at silica gel to afford 6,6-dimethoxyhexanal (**14**, 0.30 g 1.9 mmol, 17%) and 1,1,6,6-tetramethoxyhexane (**15**, 1.40 g, 6.8 mmol, 62%).

6,6-Dimethoxyhexanal (**14**): R_f-value: 0.22 (petroleum ether/diethyl ether = 7/1). FT-IR (film): $\tilde{\nu}$ (cm^{-1}) = 3522 (w, br), 3005 (m), 2947 and 2831 (s, CH), 2722 (m, O-CH_3), 1725 (s, C = O), 1462 and 1389 (m, CH, def), 1369 (m), 1192 (m), 1167 (m) 1130 (s, br, C = O) 1053 (s), 1042 (s), 967 (m), 915 (m), 808 (w), 728 (w), 459 (s, br). ^{1}H-NMR ($CDCl_3$): δ (ppm) = 1.28–1.66 (m, 6H, 3-CH_2, 4-CH_2, 5-CH_2), 2.31–2.48 (m, 2H, 2-CH_2), 3.24 (s, br, 6 H, 2 OCH_3), 4.28 (t, ^3J = 5.6 Hz, 1H, C*H*(OCH_3)$_2$), 9.70 (t, ^3J = 1.6 Hz, 1H, CHO). ^{13}C-NMR ($CDCl_3$): δ (ppm) = 21.8, 24.4, 32.2, 43.7 (je t, 4CH_2), 52.5 (q, 2 OCH_3), 104.4 (d, *C*H(OCH_3)$_2$), 202.2 (d, CHO). MS (GC/MS-coupling, EI): *m*/*z* (%) = 160 (1) [M^+], 159 (2) [M^+–H], 131 (1) [M^+–HCO, α-cleavage], 129 (43) [M^+–OCH_3], 111 (13) [$C_7H_{11}O^+$], 98 (8) [$C_6H_{10}O^+$], 97 (56) [$C_6H_9O^+$], 79 (31) [$C_6H_7^+$], 75 (100) [$CH(OCH_3)_2^+$], 71 (40) [$C_4H_7O^+$], 69 (62) [$C_5H_9^+$], 67 (24), 55 (16) [$C_4H_7^+$], 47 (48), 45 (43) [$C_2H_5O^+$], 41 (45) [$C_3H_5^+$]. The spectral data agree with those in ref. [32].

1,1,6,6-Tetramethoxyhexane (**15**): R_f-value: 0.34 (petroleum ether/diethyl ether = 7/1). FT-IR (film): $\tilde{\nu}$ (cm^{-1}) = 3541 (w, br), 3008 (m), 2948 und 2854 (s, CH), 2830 (m, O-CH_3), 2680 (w, br), 1741 (m), 1462 and 1386 (m, CH, def.), 1365 (m), 1192 (m), 1165 (m) 1129 (s, br, C = O) 1055 (s), 962 (m), 914 (m), 829 (w), 732 (w), 458 (s, br). ^{1}H-NMR ($CDCl_3$): δ (ppm) = 1.28–1.33 (m, 4H, 3-CH_2, 4-CH_2), 1.50–1.57 (m, 4H, 2-CH_2, 5-CH_2), 3.23 (s, br, 12H, 4 OCH_3), 4.28 (t, ^3J = 5.7 Hz, 2H, 2C*H*(OCH_3)$_2$,). ^{13}C-NMR ($CDCl_3$): δ (ppm) = 24.3 (t, 3-CH_2, 4-CH_2), 32.4 (t, 2-CH_2, 5-CH_2), 52.5 (q, 4OCH_3), 104.8 (d, 1-C*H*(OCH_3)$_2$, 6-C*H*(OCH_3)$_2$). MS (GC/MS-coupling, EI): *m*/*z* (%) = 205 (< 1) [M^+–H], 175 (1) [M^+–OCH_3], 173 (1) [$C_9H_{18}O_3^+$], 159 (1) [M^+–$HC(OCH_3)_2$], 144 (3) [$C_8H_{16}O^+$], 143 (31) [$C_8H_{15}O^+$], 127 (1) [$C_7H_{11}O_2^+$], 113 (14) [$C_7H_{13}O^+$], 111 (37) [$C_7H_{11}O^+$], 97 (4) [$C_6H_9O^+$], 84 (15) [$C_5H_8O^+$], 81 (16), 79 (24) [$C_6H_7^+$], 75 (100) [$HC(OCH_3)_2^+$], 69 (4) [$C_5H_9^+$], 55 (9) [$C_4H_7^+$], 47 (35), 45 (34) [$C_2H_5O^+$], 41 (19) [$C_3H_5^+$]. The spectral data agree with those in [33].

*2.3.5.2. Cleavage of cyclohexane-1,2-diol (**10**) with methyltriethylammonium methylsulfate (**16**) as supporting electrolyte in a beaker type cell.* **10** (1.28 g, 11 mmol) and **16** (0.3 g, 1.33 mmol) were electrolyzed and worked up as in 2.3.5.1 to afford **14** (0.32 g, 2.0 mmol, 18%) and **15** (1.59 g, 7.7 mmol, 70%).

*2.3.5.3. Cleavage of cyclohexane-1,2-diol (**10**) with methyltriethylammonium methylsulfate (**16**) as supporting electrolyte in the capillary gap cell.* **10** (34.8 g, 0.3 mol) and **16** (14.7 g, 64 mmol) in methanol (200 ml) were electrolyzed in the capillary gap cell of 2.3.4.5 for 30 h at 20 mA cm^{-2}(per disc) until full conversion of **10** was reached. Thereafter methanol was rotaevaporated, water (100 ml) added and extracted with diethyl ether (1 × 100 ml 2×50 ml). The combined extracts were dried (MgSO$_4$), the ether rotaevaporated to afford 39.6 g crude product, that consisted (according to glc) of **14** (3%), **15** (55%), methyl 6,6-dimethoxyhexanoate (**17**, 27%) and dimethyl adipate (**18**, 9%).

Methyl 6,6-dimethoxyhexanoate (**17**): MS (GC/MS coupling, EI): *m*/*z* (%): 189 (1)[M$^+$–H], 159(9)[M$^+$–OCH$_3$], 128 (3) (M$^+$–C$_2$H$_6$O$_2$), 127 (34) [M$^+$–C$_2$H$_7$O$_2$], 99(9), 95(19), 82(12), 75(100) [CH(OCH$_3$)$_2^+$].The spectrum corresponds to this one in [34].

*2.3.5.4. Cleavage of cyclohexane-1,2-diol (***10***) with periodate as mediator.* **10** (2.32 g, 20 mmol) and sodium periodate (1.06 g, 5 mmol) in phosphate buffer (40 ml, pH 6, Na$_2$HPO$_4$/NaH$_2$PO$_4$) were electrolyzed in a divided cell at a lead dioxide anode (6 cm^2) at room temperature and 35 mA cm^{-2} until 3 *F* were consumed. For work-up the electrolyte was extracted with diethyl ether (4 ×20 ml), the combined extracts were dried (MgSO$_4$), the ether rotaevaporated and the residue separated by flash chromatography to afford hexane-1,6-dial (**19**, 1.78 g, 15.6 mmol, 82%).

Hexane-1,6-dial (**19**): R_f-value: 0.51(ethyl acetate). FT-IR (film): $\tilde{\nu}$ (cm^{-1}) = 3524 (w, br), 2942 and 2869 (s, CH), 2830 (m), 2729 (m), 1721 (s, C = O), 1459 and 1412 (m, CH, def.), 1393 (m), 1244 (w), 1170 (m), 1095 (m) 1014 (m), 940 (m, br), 859 (m), 790 (w), 663 (w), 459 (s, br). ^{1}H-NMR (CDCl$_3$): δ (ppm) = 1.59–1.65 (m, 4H, 3-CH$_2$, 4-CH$_2$), 2.42–2.47 (m, 4H, 2-CH$_2$, 5- CH$_2$), 9.73 (t, ^3J = 1.5 Hz, 2H, 2CHO). ^{13}C-NMR (CDCl$_3$): δ (ppm) = 21.3 (t, 3-CH$_2$, 4-CH$_2$), 43.4 (t, 2-CH$_2$, 5-CH$_2$), 201.9 (d, 2CHO). MS (GC/MS-coupling, EI): *m*/*z* (%) = 114 (1) [M$^+$] 112 (< 1) [M$^+$–2H], 98 (4), 96 (12) [M$^+$–H$_2$O], 95 (4) [C$_6$H$_7$O$^+$], 86 (6) [M$^+$–CO], 71 (18) [M$^+$–C$_2$H$_3$O], 70 (100) [C$_4$H$_6$O$^+$], 58 (9) [C$_4$H$_{10}$O$^+$], 57 (79) [C$_4$H$_9$O$^+$], 55 (9) [C$_3$H$_3$O$^+$], 44 (59) [C$_2$H$_4$O$^+$, *McLafferty*], 43 (30), 41 (63) [C$_3$H$_5^+$], 39 (35) [C$_3$H$_3^+$]. The spectral data are compatible with those in [33].

3. Results and discussion

3.1. *Attempted one step cleavage of aliphatic alkenes by direct electrolysis at different anode materials*

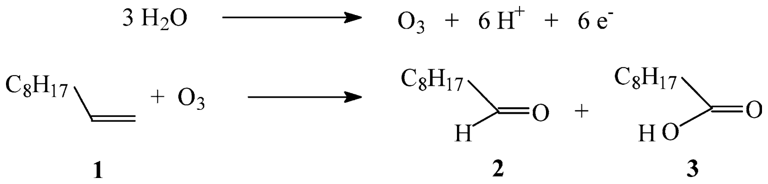
Aryl alkenes, enol ethers or enol acetates can be cleaved in one step by direct electrolysis [30, 31, 35, 36]. The cleavage of aliphatic alkenes with higher oxidation potentials (> 2.0 V vs. sce) needs multi-step methods mostly via chemically prepared 1,2-dioxygenated compounds, that are subsequently anodically cleaved [30, 31, 37–43]. The 1,2-dioxy compounds are frequently synthesized by epoxidation of alkenes with hydroperoxides. As an alternative we explored whether aliphatic alkenes with high oxidation potential can be converted by direct anodic oxidation into 1,2-diols, which subsequently, can be anodically cleaved. Oxidation of cyclohexene in tetrahydrofuran water however, gave mainly allylic substitution products and rearranged products via a radical cation corresponding to those formed in the anodic methoxylation of cyclohexene [44]. The change of the anode material (graphite, glassy carbon, platinum), the supporting electrolyte (Bu$_4$NBF$_4$, NaBF$_4$, HBF$_4$), the temperature 0 °C, 20 °C), the current density (10, 50, 150 mA cm^{-2}) and the solvent (tetrahydrofuran/water, acetonitrile/water, dichloromethane/water, DMF/water) did not lead to detectable amounts of the wanted cyclohexane-1,2-diol.

The boron doped diamond electrode (BDDE) generates reactive hydroxyl radicals from water. These react with organic compounds, which are in most cases oxidized completely to water and carbon dioxide with no detectable intermediates. For that reason the BDDE is used mostly for the disintegration of organic material [45]. Recently however, applications in organic synthesis have appeared as the direct oxidation of alkyl benzenes [46, 47] and furan [48], Kolbe electrolyses of carboxylic acids [46] or indirect oxidations with cerium-, titanium- or copper-ions as mediators [47]. As hydroxyl radicals are strong electrophiles [49] it appeared worthwhile to check whether these react with the electron rich double bonds of alkenes to 1,2-diols, that subsequently can be cleaved. In an undivided cell at a BBD/Ti- or a BBD/Si-anode and a Ti-cathode several olefins (oleic acid, sodium oleate, sodium undecenoate, 1-decene, maleic acid, disodium maleate) were electrolyzed under different conditions: solvent (water/ethyl acetate, water), temperature (20, 30, 70 °C), pH(3, 8.5, 10), current density (5, 20, 100 mA cm^{-2}). In no case was a conversion to diols or products resulting from them found.

Rutheniumoxide electrodes are successfully used in chloralkali electrolysis [50, 51]. We found, however, no reports on their use in the oxidation of organic compounds. For ruthenium tetroxide it is known that it cleaves olefinic double bonds like permanganate or osmium tetroxide via 1,2-diols to carboxylic acids [14, 20]. Possibly at a ruthenium oxide electrode higher oxides are formed, which can act as immobilized mediator for the cleavage of double bonds, like nickel oxide hydroxide does at the nickel hydroxide electrode in the oxidation of alcohols [52]. In an undivided cell cyclohexene (1 M) was electrolyzed with water (1 M) in 0.5 M NaClO$_4$ in THF at a Ru/Ir-oxide anode and a titanium cathode. The same products in a similar distribution but in a lower conversion as on the graphite anode were found. However, no cyclohexane-1,2-diol or cleavage products thereof were detected.

3.2. *Cleavage with anodically generated ozone*

The use of ozone, generated at a lead dioxide anode, could be a further possibility to electrochemically cleave



Scheme 1. Anodic generation of ozone and ozonolysis of 1-decene (1).

the olefinic double bond. The advantage of the electrochemical ozonolysis compared to the ozone generation by the corona method would be the lower stationary concentration of the hazardous ozone and ozonides, because of their *in situ* reaction, which should reduce the costs for safety precautions. Ozone is formed at the lead dioxide electrode by water oxidation (scheme 1) and is used for water disinfection [53]. One mechanism proposes that the PbO_2-lattice is partially hydrated forming gel zones. These slow down the diffusion of anodically generated molecular oxygen and thus allow the combination with atomic oxygen formed in these zones [54, 55]. As electrolyte a fluoride containing phosphate buffer is favourable [53].

An emulsion of 1-decene (**1**) in phosphate buffer: dichloromethane (5:3) was electrolyzed with intense stirring at 20 °C and a current density of 150 mA cm^{-2} until no further alkene could be detected by glc, which needed 17 *F*. After work-up nonanal (**2**, 44%) and nonanoic acid (**3**, 48%) were isolated by distillation (scheme 1). Hydrogen peroxide, which is formed in the hydrolysis of the intermediate ozonide, oxidizes part of the aldehyde **2** to acid **3**. The chemical yield of **2** and **3** is 92%, the current yield of 6%, however, is low.

For the electrochemical ozone generation yields of 15–20% of ozone are reported [56–58]. Possibly the current yield of the electrochemical ozonolysis can be approached to these values by suitable optimization of the cell geometry and the electrolysis conditions. Electrolyses at different temperatures (10, 15, 20, 25, 30 °C) produced the best chemical yields at 15–20 °C (91–92% in the 1-decene oxidation) corresponding to the temperature dependence of the ozone yield at the PbO_2-anode [53]. The current yield, however, remained low at 5%. A simplification of the method would be the use of an undivided cell. 1-Decene (**1**) was electrolyzed under the same conditions as in the divided cell, however with ethyl acetate as cosolvent instead of dichloromethane, which leads in an undivided cell to chloride via cathodic cleavage and unwanted products of chloride via its anodic oxidation. After oxidative work-up the acids or esters were obtained in good chemical yields (Table 1).

Due to the low current yield and the stoichiometric consumption of six electrons /mol of ozone the energy demand is higher than this for the ozonolysis via a corona discharge. Because of the less expensive electrochemical ozone generator this route, however, is favourable for the production of up to 100 g $O_3\ h^{-1}$ corresponding to the cleavage of two moles of alkene h^{-1} (S. Stucki, Personal Communication) . In addition to this there is the advantage of lower costs for safety precautions due to a smaller stationary concentration of ozone and ozonides.

3.3. *Two step cleavage of cyclohexene(*8*) by way of its bromo-formyloxylation to cyclohexane-1,2-diol(*10*) and anodic conversion of* 10 *to hexane-1,6-dial (*19*) or its derivatives* 14 *and* 15

3.3.1. *Electrochemical conversion of cyclohexene (*8*) to cyclohexane-1,2-diol (*10*)*

The synthesis of the 1,2-diol **10** was intended by an anodic halo-alkoxylation of cyclohexene to a β-alkoxyalkylhalide [23, 59]. The diol can be anodically cleaved to the dialdehyde [30, 31]. At first cyclohexene (**8**) was electrochemically transformed in NaBr/methanol as electrolyte to 1-bromo-2-methoxycyclohexane [23], which was converted with acetic anhydride into the bromoacetate **9** (82%), that was reacted with 2 M NaOH to afford cyclohexane-1,2-diol (**10**, 94%). This way the diol **10** could be obtained in three steps and 62% overall yield from cyclohexene (**8**).

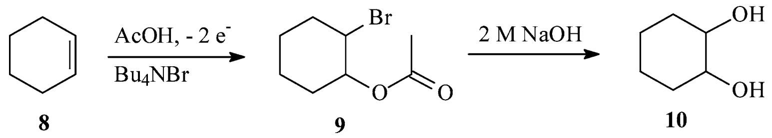
The simplified electrolysis of cyclohexene (**8**) with tetrabutylammonium bromide (TBABr) in acetic acid followed by treatment of the crude bromoacetate **9** with 2 M NaOH [60] led to 77% of diol **10** in a one-pot reaction (scheme 2).

Less favourable in this conversion is the use of the costly TBABr, which additionally is difficult to regenerate. Therefore it was replaced by KBr. Because of the

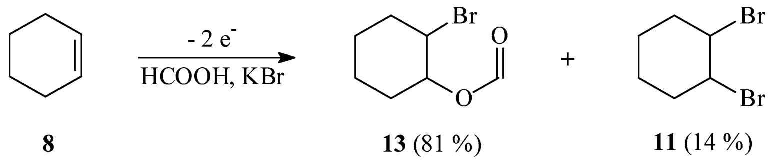
Table 1. Anodic ozonolysis of alkenes in an undivided cell[a]

Alkene	Acid, Ester/%[b]	Current yield/%	Chemical yield/%
1-decene (**1**)	nonanoic acid (**3a**)	5	84
oleic acid (**4**)	methyl nonanoate (**3b**),	4	76
	dimethyl nonanedioate (**5**)		72
cyclododecene(**6**)	dimethyl dodecanedioate (**7**)	4	74

[a]Alkene (62.5 mM), ethyl acetate (30 ml), phosphate buffer (50 ml), undivided cell, PbO_2-anode on titanium (6 cm^2) , Pt-cathode, current density 150 mA cm^{-2}, current consumption 55.000C. [b]The crude product was treated with 20% H_2O_2 /HCO_2H. [c] The crude product was treated with 2,2-dimethoxypropane/HCl in abs. methanol.



Scheme 2. Anodic bromo-acetoxylation of cyclohexene and hydrolysis of the adduct **9** to 1,2-cyclohexanediol (**10**).



Scheme 3. Anodic bromo-formyloxylation of cyclohexene (**8**).

poor solubility of KBr in acetic acid, the electrolysis had to be performed in 84% aqueous acetic acid with 1.68 equivalents of KBr. After a current consumption of 3 *F* a 56% conversion of cyclohexene was found, which, however, gave as main product the unwanted 1,2-dibromide **11** in 63% yield, whose formation is presumably promoted by the presence of water [61], whilst the yield of the needed bromoacetate **9** dropped to 13%. Thus it appeared necessary to electrolyze in a water free solvent. As KBr is readily soluble in formic acid, cyclohexene was electrolyzed in this solvent with 1.05 equivalents of KBr. This gave 81% of the wanted 1-bromo-2-formyloxycyclohexane (**13**) and only 14% of **11** (scheme 3).

To further increase the selectivity for the bromoformate **13**, the KBr-concentration was lowered to 0.5 equivalents and continually further 0.5 equivalents of KBr were added during the electrolysis. Thereby the selectivity could be improved to 85% of bromoformate **13** and 9% of dibromide **11**. With 2 M NaOH the bromoformate **13** was converted into 94% of diol **10**, which this way is accessible in two steps and 80% yield from cyclohexene (**8**). In a 15-fold scale-up cyclohexene and KBr were electrolyzed in formic acid in an undivided beaker type cell at graphite electrodes with continual addition of further KBr until cyclohexene was totally consumed after 2.3 *F* and 83% of bromoformate **13** and 14% of dibromide **11** were obtained.

For a further 6.6-fold scale-up a capillary gap cell was used and the base: 2 M NaOH was replaced by a 2.3 M aqueous sodium formate solution. A solution of cyclohexene (**8**, 0.15 mol) and KBr (0.081 mol) in formic acid

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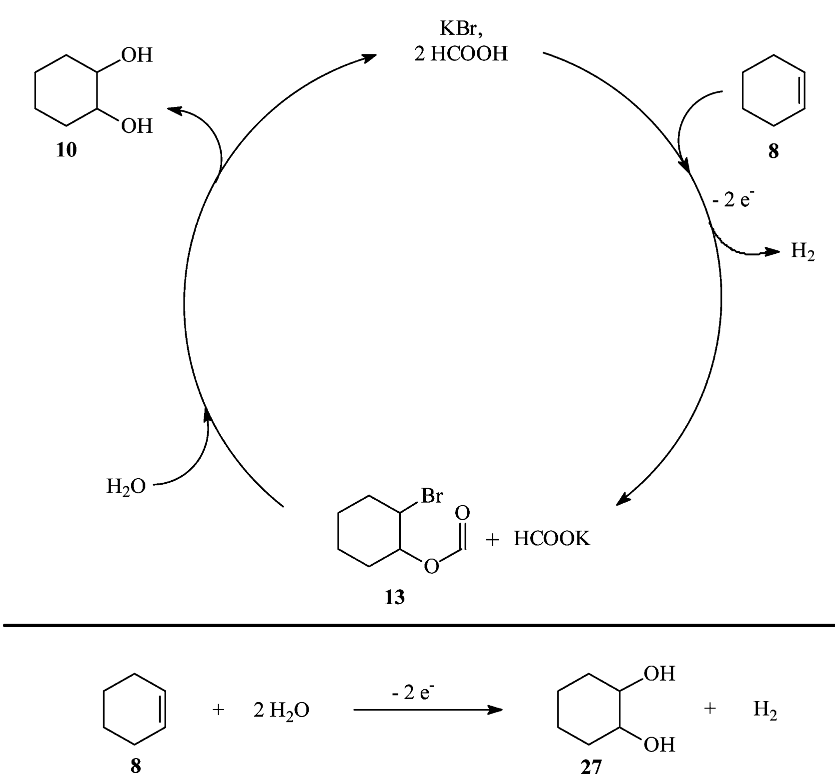
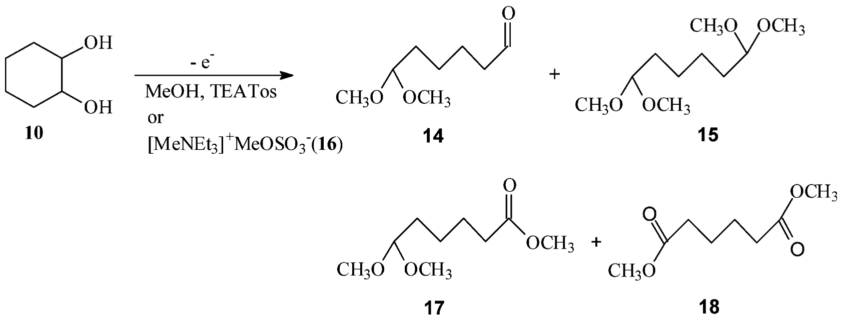
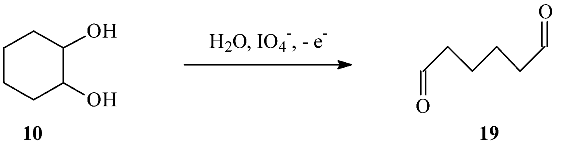


Scheme 4. Electrochemical and chemical cycle for the conversion of cyclohexene (**8**) into diol **10**.



Scheme 5. Anodic cleavage of cyclohexane-1,2-diol (**10**).



Scheme 6. Cleavage of cyclohexane-1,2-diol (**10**) by indirect anodic oxidation with $NaIO_4$ as mediator.

was electrolyzed at 35 mA cm^{-2} and further cyclohexene (in total 1.0 mol) and KBr (in total 1.2 mol) were added continually. After conversion of 95% of cyclohexene formic acid was removed from the crude product by distillation. Then sodium formate (1.0 mol) was added, to replace sodium hydroxide used in the preceding experiment, and the solution was refluxed for 2 days in *i*-propanol/water. Work-up yielded diol **10** (72%, 0.68 mol), dibromide **11** (16 mmol) and solid supporting electrolyte (185 g), which was used for the second electrolysis. There cyclohexene (0.5 mol), residual salt from the first electrolysis (93 g) and KBr (0.1 mol, 11.9 g) was electrolyzed as before. After the same work-up as before diol **10** (81% based on converted cyclohexene, 44.6g) and salt (90 g) was isolated. In a third electrolysis cyclohexene (0.5 mol) and recovered salt from the second electrolysis under the same conditions gave diol **10** (78% based on converted cyclohexene, 42.9 g) and salt (89 g).

These results showed: (a) The scale could be increased from the initial experiment with 10 mmol (0.82 g) of cyclohexene (**8**) by the factor 100 to 1 mol (82 g of **8**); (b) The base sodium hydroxide for the conversion of bromoformate **13** into diol **10** could be replaced by sodium formate; (c) In the substitution of bromide in **13** sodium formate is converted into sodium bromide and this way the bromide anion for the next electrolysis is regenerated. This salt could be used in succeeding conversions as supporting electrolyte and bromide source. The yield of diol **10** remained constant in the three electrolyses at about 77%, the yield of dibromide **11** at about 14%. The bromide bound in **11** is compensated by addition of 0.2 equivalents of KBr in the second and third electrolysis.

The conversion of cyclohexene into cyclohexane-1,2-diol (**10**) is shown in the following cycle (scheme 4). After the electrochemical generation of bromoformate **13** formic acid can be removed from the electrolyte by distillation and after the addition of water the diol **10** is obtained by refluxing the solution. Removal of water by rotaevaporation and addition of ethyl acetate allows the separation of salt and diol **10**.

All reagents, except for a small portion of KBr, can be recycled and only electricity is consumed. Thus the electrochemical conversion of cyclohexene to cyclohexane-1,2-diol appears to be an attractive alternative to chemical conversions with oxygen and catalysts or with hydrogen peroxide [17, 62–66].

Cyclohexane-1,2-diol (**10**) can be cleaved with a current consumption of 2 *F* in methanol/ tetraethylammonium tosylate (TEATos) at 20 mA cm^{-2} to 15% of acetal **14** and 51% of diacetal **15** (scheme 5) [30, 31].

By increasing the charge to 2.9 *F* until **10** is totally consumed, an increased yield of 62% **14** and 17% **15** was achieved. In an electrolysis, where TEATos as supporting electrolyte was exchanged for the cheaper methyltriethylammonium methylsulfate (**16**), 18% of **14** and 70% of **15** were isolated. To achieve a 30-fold scale-up diol **10** (0.3 mol) was electrolyzed in a capillary gap cell up to total consumption. Thereby 3% of acetal **14**, 55% of diacetal **15** and due to further oxidation additionally 27% of ester **17** and 9% of diester **18** were obtained. The results show that: (a) Diol **10** can be cleaved in good yield to the dialdehyde and his acetal, respectively; (b) A cheap supporting electrolyte can be applied and thereby the yield of cleavage product improved to 88%; (c) A 30-fold scale-up in the capillary gap cell is possible; however a lower selectivity was observed due to overoxidation.

A further method for the anodic cleavage of 1,2-diols is indirect electrolysis with periodate as mediator [20, 67, 68]. For application of this method the diol **10** was electrolyzed in a divided cell at a lead dioxide anode with 0.25 equivalents of $NaIO_4$ in an aqueous, phosphate buffered electrolyte (pH 6). At 35 mA cm^{-2} after a current consumption of 3 *F* hexanedial (**19**) was isolated in 82% yield (scheme 6).

4. Conclusion

For the cleavage of olefinic double bonds, which is an important reaction in organic synthesis, electrochemical methods which are an alternative to ozonolysis or to indirect electrolysis [20], have been examined. The following results were achieved:

(1) The direct oxidation of cyclohexene at graphite or platinum anodes leads to allylic substitution and rearranged products instead of double bond cleavage.

(2) At the boron doped diamond electrode aliphatic alkenes with oxidation potentials higher than 2.0 V (vs. sce) are not converted.

(3) Ozone, generated anodically from water at the lead dioxide electrode, affords carboxylic acids as cleavage products in high material, but low current yield. This route is favourable for the production of up to 100 g O_3 h^{-1} corresponding to the conversion of two moles of alkene h^{-1}. Moreover, there is the advantage of lower costs for safety precautions due to smaller stationary concentrations of ozone and ozonides.

(4) Anodic bromo-formyloxylation, followed by an anodic 1,2-diol cleavage, gives the double bond cleavage of cyclohexene in two steps to hexane-1,6-dial or its acetals in high yield. The electrochemical conversion of cyclohexene into cyclohexane-1,2-diol is an attractive alternative to chemical oxidations with oxygen and catalysts or with hydrogen peroxide.

Acknowledgements

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