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Electrooxidation of activated α,ω-diols to cyclic tetramethylene acetals of the corresponding dials

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Abstract—Activated α,ω-diols such as ethylene glycol **1a**, 1,3-propanediol **1b**, but-2-ene-1,4-diol **1c** and hexa-2,4-diyne-1,6-diol **1d** can be converted into cyclic tetramethylene acetals of the corresponding α,ω-dials (**2a–d**) in 70% yield by a simple anodic oxidation in dry tetrahydrofuran on a glassy carbon anode. Glycerol **3** when subjected to similar anodic oxidation gave a structure **4** containing three seven-membered 1,3-dioxepane rings.
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The electrooxidative preparation of masked α,ω-dials for further synthetic application in situ is an attractive prospect, especially in the context of the alkyne chemistry. The mildness of the anodic oxidation at low temperature in a suitable solvent with supporting electrolyte system and anhydrous conditions suggested that a successful procedure could be developed. We chose tetrahydrofuran (THF) as a solvent, since it can be prepared dry and dissolves both α,ω-diols and quaternary supporting electrolytes. Glassy carbon (GC) was selected for the electrodes due to its inertness. The behaviour of THF in anodic oxidation was studied by Wermeckes et al.[1] in an acidic aqueous solution on a smooth platinum, 2-hydroxytetrahydrofuran being formed in 60% yield at 70% current efficiency. Wolf[2] studied the electrooxidation of 2-butyne-1,4-diol and hexadiyne-1,6-diol **1d** in a solution of aqueous sulfuric acid in a divided cell at a PbO$_2$ anode, obtaining the corresponding α,ω-diacids in 75% and 11% yields, respectively. When an anodic oxidation of propargyl alcohol was studied under similar conditions,[2] propynal was formed in 16% yield. We were concerned that following the cathode reaction, the dials formed, or indeed the unsaturated chain from **1c** and **1d** would also be oxidised. Therefore, an electrolytic assembly containing a quasi stationary auxiliary cathode[3] was selected, since there is evidence that an

auxiliary cathode, having essentially less surface area than those of the working anode, can suppress the course of undesired cathodic reduction.

The course of the anodic oxidation of the α,ω-diols is illustrated in Scheme 1 and the results are summarised in Table 1.

The volume of the electrolyte was 200 ml, composed of the starting substance (**1a–d**), Bu$_4$NBF$_4$ as the supporting electrolyte and THF (dried over 4 Å molecular sieves). The electrolysis was performed in an all glass undivided double jacketed cell at 3 °C with magnetic stirring, the temperature being maintained at 3 °C. The anodes were two glassy carbon plates of 55 × 55 mm size located parallel, and the auxiliary cathode was a thin glassy carbon rod 3 mm in diameter (quasi stationary cathode[3]), concentrically placed in the cell, and nitrogen was bubbled into the cell. The electrooxidation proceeded in a galvanostatic way (at constant current) and was manually controlled. The charge passed was recorded using a coulometer constructed in the Heyrovský Institute. The electrooxidation was judged to be complete by a current drop and the conversion of the starting substance was monitored by means of the TLC (thin layer chromatography). The starting current amounted in average to 400 mA (25 V) and this dropped finally to 30 mA (35 V). We consider that the anodic oxidation requires 4e/mol, for the conversion of two alcohol groups into aldehydes. This electron transfer is subsequently followed by a chemical reaction of the reactive
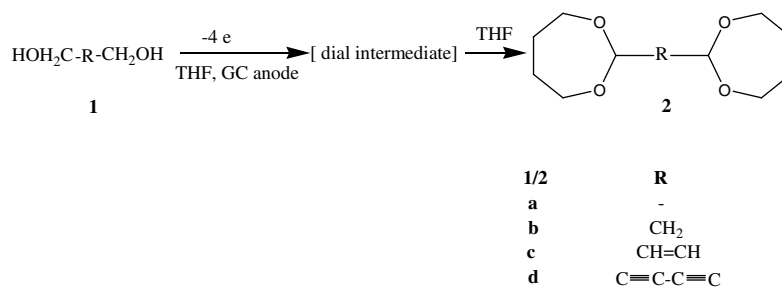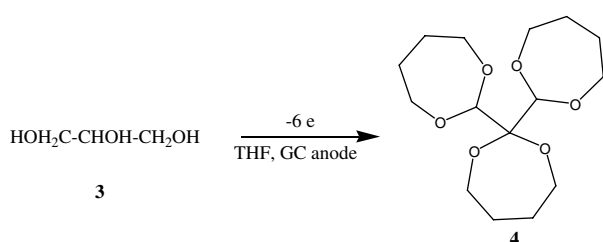
Scheme 1.

Table 1. Preparative electrooxidation of α,ω-diols in THF with 100 mmol Bu_4NBF_4 on a GC anode

Starting substance 100 mmol	Charge passed (Ah)	Product			
		Weight (g)	bp (°C)/0.5 mmHg	Structure	Material yield (%)
Ethylene glycol	11.5	14.2	81.5–82.0	**2a**	70
1,3-Propanediol	11.1	14.8	102.0–104.0	**2b**	68
cis-But-2-en-1,4-diol	10.8	14.5	110.0–112.0	**2c**	63.5
[a]Hexa-2,4-diyne-1,6-diol	12.2	8.1	152.0–154.0	**2d**	65
[a]Hexa-2,4-diyne-1,6-diol	10.6	9.8	152.0–154.0	**2d**	78.5[b]

[a] Starting substance (50 mmol).
[b] Undivided cell.

α,ω-dial intermediate with THF. This mechanistic assumption is substantiated by the FTIR analysis, which demonstrated a sequence of very small bands corresponding to dial in the crude product and by our experience of the reaction of THF with propynal. These two components react together at RT giving the 1,3-dioxepyl derivative of ethyne. The charge consumption in all the preparative electrolyses was much higher than the theoretical 4 F/mol. The reason for this is due to the complete conversion of the starting material in the chief product due to the comfortable product isolation. The consequence is that when the product yield is about 70%, the current efficiency is lower, about 60%.

After completion of the anodic oxidation, the reaction mixture (electrolyte) was concentrated at −30 °C at 0.5 mmHg. The viscous residue was extracted with several portions of *n*-pentane and then ether. The combined extracts were dried over anhydrous $CaCl_2$ and concentrated, again at low temperature, under vacuum. The resulting oil was fractionally distilled under vacuum (Table 1). The products were characterised spectroscopically including mass spectra using chemical ionisation with MeOH and with electron ionisation for the structures containing 1,3-dioxepane rings.

Di-(2,7-dioxoepan-1-yl) **2a** was obtained[4] from the electrooxidation of ethylene glycol **1a**.

When 1,3-propanediol **1b** was similarly treated, 1,1-bis-(2,7-dioxepan-1-yl)methane[5] **2b** was isolated. The electrolytic oxidation of *cis*-but-2-ene-1,4-diol **1c** under similar conditions gave[6] the di(tetramethylene)acetal of but-2-ene-1,4-dial **2c**. When hexa-2,4-diyne-1,6-diol **1d** was anodically oxidised in THF, the bis(tetramethylene)acetal of hexa-2,4-diyne-1,6-dial **2d** was obtained.[7] Similarly when glycerol **3** (4.6 g, 50 mmol) was subjected to electrolytic oxidation in THF containing the same supporting electrolyte, electrolysis was completed when 8.3 Ah had passed (i.e. 6.2 F/mol, 60 mA final current). We assumed the elimination of 6e, that is, the consumption of 6 F/mol. The work-up produced a yellow oily product (5 g) which was distilled at 148.0–150 °C/0.5 mmHg to give a colourless oil. The spectral analysis[8] confirmed the oxidative conversion of all the alcoholic groups and the subsequent reaction with THF, to form 1,1-bis(2,7-dioxepan-1-yl)-2,7-dioxepane **4** (Scheme 2).

Scheme 2.

References and notes

1. Wermeckes, B.; Beck, F.; Schulz, H. *Tetrahedron* **1987**, *43*, 577–583.
2. Wolf, V. *Chem. Ber.* **1954**, *87*, 668–676.
3. Wermeckes, B.; Beck, F. *Chem. Ber.* **1985**, *118*, 3771–3773.

4. *Di(2,7-dioxoepan-1-yl)* **2a**: ^{1}H NMR (300 MHz, CDCl$_3$) δ: 5.0 (s, 2H), 3.68 (s, 4H), 3.5 (m, 4H), 1.75 (s, 8H). ^{13}C NMR (75 MHz, CDCl$_3$) δ: 23.30, 30.51, 32.18, 66.53, 103.77. MS (CI): *m/z* (%) 202.9 (32) (MH)$^+$, 132.9 (48), 71 (100). Elemental analysis for C$_{10}$H$_{18}$O$_4$ (202.25): calcd: C, 59.38; H, 8.97; found: C, 59.08; H, 8.73.

5. *1,1-bis(2,7-dioxepan-1-yl)methane* **2b**: ^{1}H NMR (300 MHz, CDCl$_3$) δ: 5.0 (s, 2H), 3.8 (m, 4H), 3.3 (s, 6H), 1.80 (s, 8H). ^{13}C NMR (75 MHz, CDCl$_3$) δ: 23.41, 25.78, 30.11, 32.24, 66.73, 103.60. MS (CI): *m/z* (%) 217 (30) (MH)$^+$, 203 (35), 147 (67), 129 (11), 87 (15), 71 (100). Elemental analysis for C$_{11}$H$_{20}$O$_4$ (216.27) calcd: C, 61.08; H, 9.32; found: C, 60.85; H, 9.38.

6. *1,2-bis(2,7-dioxepan-1-yl)ethylene* **2c**: ^{1}H NMR (300 MHz, CDCl$_3$) δ: 5.65 (s, 2H), 5.08 (s, 2H), 4.15 (s, 4H), 3.82 (s, 4H), 1.85 (s, 8H). ^{13}C NMR (75 MHz, CDCl$_3$) δ: 23.50, 32.20, 62.20, 67.00, 103.50, 129.10. MS (CI): *m/z* (%) 229 (20) (MH)$^+$, 159 (33), 71 (100). Elemental analysis for C$_{12}$H$_{20}$O$_4$ (228.28): calcd: C, 63.18; H, 8.83; found: C, 63.28; H, 8.86.

7. *1,4-bis(2,7-dioxepan-1-yl)buta-1,3-diyne* **2d**: ^{1}H NMR (300 MHz, CDCl$_3$) δ: 5.22 (s, 2H), 4.23 (s, 4H), 3.85 (s, 4H), 1.9 (s, 8H). ^{13}C NMR (75 MHz, CDCl$_3$) δ: 23.21, 32.28, 54.18, 65.10, 67.28, 69.78, 102.33. MS (EI): *m/z* (%) 250 (15) M$^+$, 233 (28), 71 (100), 43 (23); (CI): *m/z* (%) 252 (10) MH$^+$, 231 (10), 217 (8), 181 (10), 161 (20), 147 (10), 107 (8), 71 (100). Elemental analysis for C$_{14}$H$_{18}$O$_4$ (250.29): calcd: C, 67.18; H, 7.24; found: C, 66.95; H, 7.52.

8. *1,1-bis(2,7-dioxepan-1-yl)-2,7-dioxepane* **4**: ^{1}H NMR (300 MHz, CDCl$_3$) δ: 5.1 (s, 2H), 3.8 (s, 6H), 3.6 (s, 6H), 1.83 (s, 12H). ^{13}C NMR (75 MHz, CDCl$_3$) δ: 23.40, 26.51, 30.66, 32.31, 66.89, 103.68. MS (EI): *m/z* (%) 302 (5) M$^+$, 173 (15), 103 (10), 71 (100), 43 (15); (CI): *m/z* (%) 303 (8) MH$^+$, 233 (44), 173 (10), 163 (63), 71 (100). Elemental analysis for C$_{15}$H$_{26}$O$_6$ (302.36) calcd: C, 59.58; H, 8.66; found: C, 59.80; H, 8.85.