ELECTROCHEMICAL OXIDATION OF BUT-2-YNE-1,4-DIOL
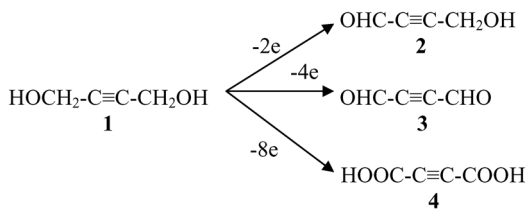
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But-2-yne-1,4-diol (**1**) was electrochemically oxidized on glassy carbon anode in a dry THF solution containing a quaternary ammonium salt, in an undivided cell giving di(1,3-dioxepan-2-yl)ethyne (**5**) in 80% yield. The electrochemically generated dialdehyde intermediate is assumely acetalized in a fast reaction with THF. Dimerized product **6** was isolated in 85% yield after electrooxidation of diol **1** in dry 1,2-dimethoxyethane under similar conditions.

Keywords: Anhydrous electrolytes; But-2-yne-1,4-dial diacetal; But-2-yne-1,4-diol; Galvanostatic preparative electrooxidation; Di(1,3-dioxepan-2-yl)ethyne.

But-2-yne-1,4-diol (**1**) is a commercially available substance, which can serve as a starting material for preparation of alkynes. It has been used by Jäger et al.[1] and Wolf[2] for electrolytic preparation of butynedioic acid (**4**). This procedure was implemented in sulfuric acid solution in a divided cell on PbO_2 anode. Polarographic, electrolytic and chemical investigation[3–5] of **1** can be found in the literature, focused rather on its triple bond reduction. There has been no other attempt of electrochemical oxidation of butynediol **1**, which would yield other alkyne products. The butynediol **1** is theoretically a starting substance for preparation of other compounds, depending on oxidative transformation of one or both alcoholic groups (cf. Scheme 1). But-2-ynedial (**3**) and 4-hydroxybut-2-ynal (**2**) are the most attractive. They would be very good precursors for preparation of polyynes. For butynedial **3** a strong tendency to polymerization can be expected. This feature indicates that an effective protection during its preparation would be reasonable. On the other hand, this protection should be removable for further synthetic applications. That is why acetal protection was chosen. In electrolytic oxidation in an anhydrous solvent, diol **1** could form a cation

radical, which could dimerize, giving in favourable case some interesting products.

$$\text{HOCH}_2\text{-C}\equiv\text{C-CH}_2\text{OH} \quad \xrightarrow{\begin{array}{c}-2e\\ -4e\\ -8e\end{array}} \quad \begin{array}{l}\text{OHC-C}\equiv\text{C-CH}_2\text{OH} \quad \mathbf{2}\\ \text{OHC-C}\equiv\text{C-CHO} \quad \mathbf{3}\\ \text{HOOC-C}\equiv\text{C-COOH} \quad \mathbf{4}\end{array}$$

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SCHEME 1

For electrooxidative preparation of butynedial diacetal we tried to use just butynediol **1**. The isolation of the product and the expected limited thermal stability made us to decide for electrolysis at low temperature in an anhydrous solvent. This paper describes the results of the outlined electro-chemical preparative procedures (cf. Scheme 2) without detailed explana-tion of the reaction mechanism, which would require a special study.

EXPERIMENTAL

But-2-yne-1,4-diol (**1**), THF, 1,2-dimethoxyethane (DME), methanol and supporting electro-lytes (Bu$_4$NClO$_4$, Bu$_4$NBF$_4$, LiClO$_4$, p-CH$_3$C$_6$H$_4$SO$_3$H·H$_2$O and its sodium salt) were of analyt-ical or pure quality, supplied by Sigma–Aldrich. Petroleum ether and diethyl ether were of analytical grade (Lach-Ner, Czech Republic). THF and DME were dried over molecular sieves 4Å (Aldrich).

The dryness of these solvents and electrolytes was checked with a 756 KF Coulometer (Metrohm). The water content was lower than 80 ppm H$_2$O. The preparative electrolysis was performed mostly in an undivided cell. It was all glass, double jacketed and the temperature of the electrolyte was controlled with a cooling bath Polystat (Cole Parmer). Glassy carbon (GC) plates of 55 × 55 mm size (Carbon Lorraine, France) were mainly used as working anodes. Auxiliary electrode (cathode) was a narrow rod of glassy carbon, 3 mm in diameter. It operated as a quasistationary auxiliary electrode[6] in an undivided cell, causing minimal cathodic reaction during the procedure. This method should strongly limit reduction of tri-ple bond in **1**. This preparative electrolytic oxidation proceeded in the galvanostatic mode and was manually controlled. Saturated mercurosulfate electrode served as reference. The consumed charge was measured with a coulometer constructed in the Heyrovský Institute.

Di(1,3-dioxepan-2-yl)ethyne (**5**)

The general procedure of the galvanostatic preparative electrolysis was as follows: butyne-diol **1** (50 mmol, 4.3 g) was dissolved in dried THF (200 ml), which contained Bu$_4$NBF$_4$ (100 mmol, 33 g). This electrolyte was stirred in undivided cell at 0–1 °C. Two GC plates served as anode and the narrow GC rod was auxiliary electrode, which was placed in a stream of nitrogen. The intensity of electrolytic current was 400 mA (overall voltage 33–36 V). The passed charge amounted to 7.15 F/mol (9.6 A h). The cathode was cleaned (wiped with etha-

nol) in order to remove a thin polymer layer. The initially slightly yellow electrolyte of neutral pH turned to yellow. After passage of a higher than theoretical (4 F/mol) anodic charge, when only a small current was passing, the electrolysis was stopped. The course of electrolysis (conversion of starting substance) was checked by TLC. The electrolyte was worked-up by evaporation at low temperature (–30 °C) and 67 Pa. The viscous residue was extracted several times with 40 ml of petroleum ether and subsequently with ether in several 30 ml portions. The separated petroleum ether and ether extracts were collected and dried over anhydrous $CaCl_2$ and then evaporated under the same conditions as above. TLC analysis confirmed that both petroleum ether and ether concentrates contained the same product. Total 8.8 g of slightly yellow oil was obtained. The product was fractionally distilled at 118–120 °C and 80 Pa. The yield of compound **5** (colourless oil) was 8.6 g (76%). FTIR spectrum (liquid film) indicated the absence of alcoholic bands (corresponding to the starting compound) and no carbonyl band was present. For $C_{12}H_{18}O_4$ (226.5) calculated: 63.73% C, 8.01% H; found: 63.69% C, 8.21% H. ^1H NMR (CDCl$_3$, 400 MHz, δ in ppm): 5.3 s, 1 H (O-CH-O); 4.2 s, 2 H (CH$_2$); 3.8 s, 2 H (CH$_2$); 1.9 s, 4 H (CH$_2$-CH$_2$). ^{13}C NMR (CDCl$_3$, 400 MHz, δ in ppm): 102.0, 81.7, 67.1, 53.9, 32.2, 23.4. GCMS: 226 (M$^+$), 155, 125, 113, 97, 87, 71.

4-Hydroxy-4-methoxybut-2-ynyl 4-Hydroxybut-2-ynoate (6)

Details of preparative electrolysis of diol **1** (8.6 g) in DME, which was performed similarly as in THF, are given in the Table I (cf. Scheme 2). The isolation of the product from this neutral slightly yellow electrolyte included again concentration at –30 °C and 67 Pa, and subsequent extraction with petroleum ether similarly to the case of the THF electrolyte work-up. An amount of 8.4 g of oil product **6** was obtained. FTIR (liquid film, cm^{-1}): 1727 (m), 2000 (w), 3410 (broad). For $C_9H_{10}O_5$ (198.2) calculated: 54.56% C, 5.08% H; found: 54.41% C, 5.4% H. ^1H NMR (CDCl$_3$, 400 MHz, δ in ppm): 4.7 s, 1 H (OCHO); 4.2 s, 2 H (CH$_2$OH); 3.6 s, 2 H (OCH$_2$); 3.3 s, 3 H (OCH$_3$). ^{13}C NMR (CDCl$_3$, 400 MHz, δ in ppm): 94.5, 93.8, 71.5, 67, 58.7, 56.0, 54.5, 54.1, 50.4.

4-Hydroxy-4-methoxybut-2-ynal (8)

A 0.5 M *p*-toluenesulfonic acid in 200 ml methanolic electrolyte was used for the anodic oxidation of diol **1**, the concentration of which being 0.5 mol/l. As this supporting electrolyte contained crystalline water (*p*-CH$_3$C$_6$H$_4$SO$_3$H·H$_2$O), the complete acidic electrolyte contained 4350 ppm of water. This preparative electrolysis proceeded under similar conditions as mentioned for experiments in THF or DME. The electrolyte was worked-up similarly as above, i.e. methanol was evaporated at –30 °C and 80 Pa. Obtained viscous oil was several times extracted in ether and combined extracts were dried over anhydrous $CaCl_2$. The yellow oil (4.5 g) was obtained after their concentration at –30 °C and 80 Pa. TLC analysis indicated the mixture of substances. Small amount of major product **8** was isolated by the column chromatography on silica (50 g) using solvent mixture ether/hexane 1:1 as eluent. FTIR (liquid film, cm^{-1}): 1750 (l), 1950 (w), 2250 (w), 2860 (m), 3450 (l, broad). For $C_5H_6O_3$ (114.1) calculated: 52.63% C, 5.3% H; found: 52.82% C, 5.44% H. ^1H NMR (CDCl$_3$, 400 MHz, δ in ppm): 9.2 s, 1 H (CHO); 5.2 s, 1 H (OCHO); 3.4 s, 3 H (OCH$_3$). ^{13}C NMR (CDCl$_3$, 400 MHz, δ in ppm): 111.5, 94.6, 92.9, 79.9, 52.5.

4,4-Dimethoxybut-2-ynal (**9**)

When 0.5 M sodium *p*-toluenesulfonate was used as a supporting electrolyte in MeOH (200 ml) in the anodic oxidation of diol **1** (0.5 mol/l) under the same conditions of preparative electrolysis as above, another product mixture was obtained. Neutral electrolyte was worked-up similarly to the methanol/*p*-toluenesulfonic acid case by concentration and subsequent extraction with several portions of ether. Finally 4.5 g of yellow oil were obtained after the extract concentration. TLC analysis indicated the mixture of products, which was separated again by column chromatography on silica (the same conditions as above). Small amount of major product **9** was isolated[7]. FTIR (liquid film, cm^{-1}): 1750 (l), 2000 (w), 2110 (w), 2866 (m). For $C_6H_8O_3$ (128.1) calculated: 56.24% C, 6.29% H; found: 56.20% C, 6.55% H. ^{1}H NMR (CDCl$_3$, 400 MHz, δ in ppm): 9.2 s, 1 H (CHO); 5.2 s, 1 H (OCHO); 3.3 s, 6 H (2 × OCH$_3$). ^{13}C NMR (CDCl$_3$, 400 MHz, δ in ppm): 107.0, 92.5, 72.6, 54.2, 52.9.

RESULTS AND DISCUSSION

As aprotic solvents for butynediol **1**, tetrahydrofuran (THF) and 1,2-dimethoxyethane (DME) were chosen as they allowed to use neutral quaternary ammonium salts or LiClO$_4$. The behavior of THF in anodic oxidation was studied by Wermeckes[8] in acidic aqueous solution on smooth platinum; 2-hydroxytetrahydrofuran was formed in 60% yield at 70% current efficiency.

The supporting electrolytes were used in the 0.5 M concentration and diol **1** as 0.25 M solution in electrolyte (200 ml). The increase of diol **1** concentration (to 0.5 mol/l) causes more intensive polymer coverage on the cathode during the preparative electrolysis. The results of the preparative anodic oxidation are summarized in Table I and Scheme 2.
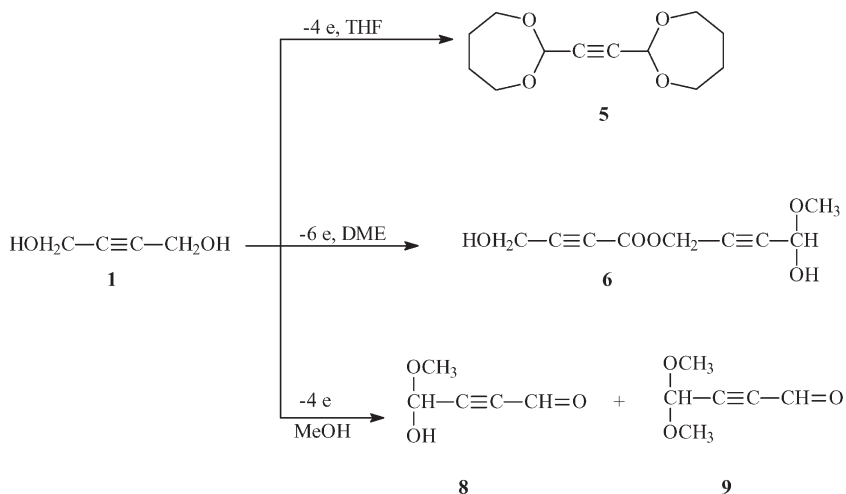
SCHEME 2

When anodic oxidation of diol **1** was carried out with the same composition of the electrolyte, but in the undivided cell containing usual GC cathode (with electrode surface area comparable with that of working anode), the same diacetal product **5** was obtained (Scheme 2). This means that alkyne structure is not damaged on the auxiliary cathode. The arrangement of the preparative electrolysis is improved and simplified by this way. The structure of **5** was confirmed by elemental analysis, FTIR, NMR and GC/MS spectra (cf. Experimental and Table II). The NMR spectrum indicates non-equivalent CH_2 protons in the neighborhood of oxygen in the 1,3-dioxepane rings. The electrooxidation of butynediol **1** in THF with $LiClO_4$ as supporting electrolyte gave the same product, but, due to strong coverage of the auxiliary electrode with a thin polymer layer, the electrolysis was blocked and could not be completed (cf. Table I).

TABLE I
Electrooxidation of butynediol **1** in undivided cell on GC anode

Supporting salt/ Solvent 0.5 mol/l	Water content ppm	Current /Voltage mA/V	Charge passed A h	Temp °C	Product/Yield g/%
Bu_4NClO_4/THF	80	400/36	9.7	1	8.8/78.6
Bu_4NBF_4/THF	76	420/34	9.5	1	9.0/80.7
$LiClO_4$/THF	60	416/38	2.1[a]	1	4.5
Bu_4NClO_4/DME	65	400/33	8.3	5	8.4/84.8

[a] Uncompleted.

The electrolytic oxidation of butynediol **1** in THF with quaternary ammonium salts proceeded under almost anhydrous conditions (cf. Table I), which support stability of the intermediates formed in the primary electrolytic step. The structure and the formation of the cyclic diacetal **5** can be explained by reaction of the but-2-ynedial intermediate with the solvent. The THF ring is opened and the cyclic diacetal **5** is formed in a consecutive fast reaction. It is known that the THF ring opening is initiated by the attack of acidic reagents (and Lewis acids, too). We consider that the primary intermedial alkyne aldehyde structure formed at anodic oxidation initiates the THF opening. But-2-ynedial (**3**) was described by Gorgues[9]. Its preparation is very tedious using deprotection of 1,1,4,4-tetraethoxybut-2-yne with formic acid in dichloromethane. The electrophilic properties of the dialdehyde **3** towards dienes[9] were reported. They indicate extraordinary re-

activity of alkynedial **3**. Ethyl or methyl diacetals of but-2-ynedial have been prepared[7] in a three step synthesis and their partial deprotection to monoacetal, which is not without problems[10], was described. Due to the limited availability of this alkynedial **3** as the probable intermediate, we could not confirm the exact reaction path.

We found the support for the course of the chemical reaction with solvent in our related experiment concerning the interaction of propynal with THF. In a quick chemical reaction similar cyclic acetal of dioxepanyl structure was formed under spectral investigation. The assumed reaction path of the anodic oxidation of diol **1** in THF requires 4 F/mol for the electrochemical reaction. Due to the effective product separation, the total conversion of the starting diol **1** was needed. This is the reason why the passed charge was much higher (7.1 F/mol) than theoretical 4 F/mol. Thus the current yield of compound **5** is about 55% whereas the material yield 76%.

The electrooxidation of butyndiol **1** in anhydrous DME on GC anode (cf. Table I and Scheme 2) resulted in hemiacetal **6**, isolated in 85% yield. The structure of this product was established on the basis of NMR and FTIR spectra and elemental analysis (cf. Experimental). FTIR spectrum indicates CO, C_{sp} and CH_2OH groups. ^1H NMR spectrum[11], confirming CH_2OH and $-C\equiv C-$ groups, points to the hemiacetal structure with CH_3 and $-OCH_2-$ groups. Compound **6** was formed from two molecules of the starting substance and from the methoxy group originating from DME as a solvent. We assume a chemical reaction of two primary electrochemical intermediates $HOCH_2-C\equiv C-CHO$ (2×2 e in anodic step) yielding the coupling intermediate $HOCH_2-C\equiv C-CH(OH)-OCH_2-C\equiv C-CHO$, which after another anodic step (2 e oxidation) gives an esteraldehyde intermediate $HOCH_2-C\equiv C-CO-OCH_2-C\equiv C-CHO$. Compound **6** is formed by acetalization with OCH_3 group from DME. This reaction sequence assumes, that 6 e must be withdrawn per one molecule of compound **6** (cf. Scheme 2). The ester bond was confirmed by FTIR spectra and alkaline hydrolysis of compound **6** giving 4-hydroxybutynoic acid (**7**), which was evidenced by comparison of TLC and spectral record of hydrolysate with standard[12] **7**.

$$HOCH_2-C\equiv C-COOH$$

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The elemental composition calculated for $C_9H_{10}O_5$ is in accord with that found (cf. Experimental). The compound **6** is a result of intermediate coupling reaction. Similar coupling reaction occurs in the electrooxidation of propargyl alcohol under analogous conditions as we observed in related ex-

periments. Final hemiacetalization of **6** proceeds at the expense of DME solvent, which participates in chemical reaction. The charge passed in the preparative electrooxidation (cf. Table I) yielding compound **6** amounts 3.1 F/mol of diol **1** (0.1 mol of diol **1** in the electrolyte, 8.3 A h), which corresponds to the theoretical assumption (3 F/mol).

The electrooxidation of diol **1** in MeOH proceeds differently depending on the supporting electrolyte used. Hemiacetal **8** of but-2-ynedial was isolated in a small amount from the resulting product mixture when *p*-toluenesulfonic acid was a supporting electrolyte. Its structure was confirmed by NMR and FTIR spectra (cf. Experimental and Scheme 2). *p*-Toluenesulfonic acid brought strong acidity and water content (crystalline water) in the methanolic electrolyte. Similar product mixture was formed in the anodic oxidation of diol **1** in MeOH containing sodium salt of *p*-toluenesulfonic acid. Monoacetal **9** of but-2-ynedial (cf. Scheme 2) was isolated in a small amount from the product mixture. In this case the methanolic electrolyte was neutral but contained the water as well. The structure of the product mentioned was confirmed from NMR and FTIR spectra, which are in accordance with the literature[7] (cf. Experimental). Due to the tedious separation of particular products after the mentioned anodic oxidation of diol **1** in MeOH, quantitative evaluation of experiments was not feasible (cf. Table II).

TABLE II
Preparative anodic oxidation of butynediol **1**

Solvent	Supporting electrolyte	Product	Yield, %
THF	Bu_4NBF_4	**5**	80.7
DME	Bu_4NClO_4	**6**	84.8
MeOH	*p*-$CH_3C_6H_4SO_3H \cdot H_2O$	**8**	[a]
MeOH	*p*-$CH_3C_6H_4SO_3Na$	**9**	[a]

[a] No quantitative isolation from product mixture.

CONCLUSIONS

The new cyclic diacetal of butynedial, di(1,3-dioxepan-2-yl)ethyne **5**, is formed in high yield by electrolysis of but-2-yne-1,4-diol (**1**) in anhydrous THF. The chemical stabilization of anodically generated highly reactive but-2-ynedial intermediate in fast reaction with THF is assumed (cf. Scheme 2). In anhydrous 1,2-dimethoxyethane (DME), intermediary hydroxyaldehyde

dimerizes and the corresponding dimer is subjected to the next subsequent anodic two-electron oxidation resulting in ester formation. Dimeric hydroxyaldehyde is stabilized by the acetalization with methoxy group (originating from DME) giving final hemiacetal **6**. The anodic oxidations of diol **1** in MeOH solution containing *p*-toluenesulfonic acid or its sodium salt at otherwise similar electrolytic conditions give only mixtures of substances in mild yield. Monoacetal and hemiacetal of but-2-ynedial were separated from these mixtures as pure compounds by column chromatography in small amounts.

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