

Electrochemical Reduction of a Bromo Propargyloxy Ester at Silver Cathodes in Dimethylformamide

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Cyclic voltammograms for the reduction of ethyl 2-bromo-3-(3',4'-dimethoxyphenyl)-3-(propargyloxy)propanoate (1) at a silver cathode in dimethylformamide (DMF) containing 0.10 M tetraethylammonium tetrafluoroborate (TEABF₄) exhibit several cathodic peaks, the first of which is attributed to reductive cleavage of the carbon–bromine bond. Controlled-potential (bulk) electrolyses of 1 at silver gauze electrodes in DMF–0.10 M TEABF₄ give rise to four products: *cis-* and *trans*-isomers of ethyl 3-(3',4'-dimethoxyphenyl)-prop-2-enoate (4), ethyl 3-(3',4'-dimethoxyphenyl)propiolate (7), and ethyl 3-(3',4'-dimethoxyphenyl)-3-(prop-2-yn-1-yloxy)propanoate (8). These products have been identified with the aid of mass spectrometry and nuclear magnetic resonance spectroscopy. We propose that reduction of 1 involves two-electron cleavage of the carbon–bromine bond to form a carbonion. Then the latter species eliminates $^{-}OCH_2C\equiv CH$ to afford 4. In addition, $^{-}OCH_2C\equiv CH$ can deprotonate 1 to yield (*Z*)-ethyl 2-bromo-3-(3',4'-dimethoxyphenyl)acrylate (5), which is further deprotonated by $^{-}OCH_2C\equiv CH$ to give 7. Alternatively, the carbonion resulting from the original two-electron reduction of 1 can gain a proton from the medium to form 8.

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In two previous projects^{1,2} involving collaboration with our laboratory, electrochemical methods were probed as an avenue to the synthesis of building blocks for lignans, which comprise a class of phenylalanine-derived compounds that have attracted considerable attention due to their pharmacological activity and abundance in nature. In the first of those investigations,¹ we examined the reductive intramolecular cyclization of ethyl 2-bromo-3-(3',4'-dimethoxyphenyl)-3-(propargyloxy)propanoate (1), catalyzed by electrogenerated nickel(I) tetramethylcyclam, to afford 2-(3',4'-dimethoxyphenyl)-3-(ethoxycarbonyl)-4-methylenetetrahydrofuran (2) in good yield (72– 85%); the latter species is a desired precursor for the formation of isogmelinol (a furofuran lignan). In addition, a second product, 2-(3',4'dimethoxyphenyl)-3-ethoxycarbonyl-4-methyl-2,5-dihydrofuran (3), was obtained in significant yield (22–30%).



A second paper² was concerned with the direct reduction of 1 at both glassy carbon and reticulated vitreous carbon cathodes in dimethylformamide (DMF) containing various tetraalkylammonium salts. Interestingly, although 2 was not obtained, 3 (which

3

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arises via base-promoted rearrangement of **2**) was found in modest yield (18–26%). More importantly, the principal product was ethyl *trans*-3-(3',4'-dimethoxyphenyl)acrylate (**4**), although small amounts of (*Z*)-ethyl 2-bromo-3-(3',4'-dimethoxyphenyl)acrylate (**5**) and ethyl 3-(3',4'-dimethoxyphenyl)-2,3-bis(prop-2-yn-1-yloxy)propanoate (**6**)were detected.



Recent publications from our laboratory³⁻⁸ and by other research groups9-24 have dealt with the electrochemistry of halogenated organic compounds at silver cathodes and have revealed the catalytic effect of silver on the reductive cleavage of carbon-halogen bonds; the cited references lead the way to other earlier papers on this topic. For example, our laboratory discovered quite recently⁸ that cleavage of the carbon-chlorine bond of 2-chloro-N-phenylacetamides at a silver cathode occurs at potentials which are 500-600 mV more positive than those seen with a glassy carbon electrode. In an earlier paper, Isse and co-workers¹⁴ found that cyclic voltammograms for reduction of benzyl bromide at a silver electrode in an acetonitrile medium exhibit two cathodic peaks, whereas only one stage of reduction is observed when a glassy carbon cathode is employed. Using silver cathodes, these authors demonstrated that bulk electrolyses of benzyl bromide at a potential corresponding to the first voltammetric peak afford mainly bibenzyl via coupling of benzyl radicals produced by one-electron reduction of the starting material. On the other hand, electrolyses of benzyl bromide at a potential corresponding to the second voltammetric peak resulted in a mixture of bibenzyl and toluene; although toluene was the

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anticipated product, the formation of bibenzyl was attributed to an efficient solution-phase $S_N 2$ reaction between the starting material and the electrogenerated benzyl carbanion, the latter species arising from a two-electron process.

As part of our ongoing interest in the reduction of halogenated organic compounds at silver cathodes, we have employed cyclic voltammetry and controlled-potential (bulk) electrolysis in the present work to investigate the electrochemical reduction of **1** in dimethyl-formamide (DMF) containing 0.10 M tetraethylammonium tetrafluoroborate (TEABF₄). To the best of our knowledge, reduction of **1** at a silver electrode has not been previously explored. Identities and yields of the various products, none of which is a carbocyclic compound, have been established with the aid of ¹H and ¹³C NMR spectroscopy, gas chromatography (GC) and gas chromatography–mass spectrometry (GC–MS), and high-resolution mass spectrometry (HRMS). Effects of added proton donors (1,1,1,3,3,3-hexafluoro-2-propanol and deuterium oxide) on the coulometric *n* value and product distribution have been examined, and a set of mechanistic pathways is proposed to account for the formation of the various products.

Experimental

Reagents.— Each of the following chemicals was used, as received, without further purification: 1,1,1,3,3,3hexafluoro-2-propanol (HFIP, Sigma Aldrich, 98%), 3,4dimethoxyphenylacetylene (Aldrich, 98%), anhydrous diethyl ether (EMD Millipore Co., 99%), anhydrous ethanol (Pharmco-AAPER), anhydrous sodium sulfate (BDH, ACS grade), n-butyllithium (Aldrich, 2.0 M in cyclohexane), ethyl acetate (Macron, ACS grade), ethyl chloroformate (Aldrich, 97%), n-hexane (BDH, ACS grade), hydrochloric acid (Macron, ACS grade), methanol (Macron, ACS grade), n-undecane (EMD Millipore Co., 99.9+%), ammonium chloride (Macron, 99.5%), tetrahydrofuran (THF, Macron, ACS grade), deuterium oxide (D₂O, Aldrich, 99.9%), and trans-3,4dimethoxycinnamic acid (Aldrich, 99%, as a 19:1 mixture of the trans and cis compounds).

Dimethylformamide (DMF, EMD Millipore Co., 99.9%) was employed, without further purification, as the solvent for all electrochemical experiments. Tetraethylammonium tetrafluoroborate (TEABF₄, GFS Chemicals, 98%) served as the supporting electrolyte; prior to being used, it was recrystallized from methanol–water and stored in a vacuum oven at 90°C to remove traces of water. Deoxygenation of all solutions for cyclic voltammetry and controlled-potential electrolyses was accomplished with zero-grade argon (Air Products). Ethyl 2-bromo-3-(3',4'-dimethoxyphenyl)-3-(propargyloxy)propanoate (1) was prepared according to a published procedure;²⁵ mass and ¹H NMR spectra were in accord with previously reported data.

Electrodes, cells, and instrumentation.— For cyclic voltammetry, we fabricated circular, planar glassy carbon and silver working electrodes (with geometric areas of 0.071 cm^2) by fitting short lengths of either a glassy carbon rod (Grade GC-20, 3.0-mm-diameter, Tokai Electrode Manufacturing Company, Tokyo, Japan) or a silver rod (3.0-mm-diameter, 99.9% purity, Alfa Aesar) into a machined teflon tube. A stainless-steel pole (3.0-mm-diameter), pressed into the opposite end of the machined teflon tube, provided electrical connection to these working electrodes. Before each cyclic voltammogram was recorded, the working electrodes were cleaned on a Master-Tex (Buehler) polishing pad with an aqueous suspension of 0.050-µm alumina, followed by rinsing with deionized water and ultrasonication in DMF. A coil of platinum wire served as the auxiliary (counter) electrode. All potentials reported in this paper are given with respect to a reference electrode consisting of a cadmium-saturated mercury amalgam in DMF saturated with both cadmium chloride and sodium chloride; this electrode has a potential of -0.76 V versus the aqueous saturated calomel electrode (SCE) at 25°C.²⁶⁻²⁸ Cells, instrumentation, and procedural details for cyclic voltammetry are described in previous publications.6,29,30

For controlled-potential (bulk) electrolyses, working cathodes (with geometric areas of approximately 20 cm²) were constructed from silver gauze (Alfa Aesar, 99.9%, 20-mesh, woven from 0.356mm-diameter wire).^{6,8} Careful pretreatment of these electrodes is crucial to obtain reproducible and complete reduction of a starting material. Therefore, each electrode was cleaned by immersion in a room-temperature aqueous slurry (suspension) of solid sodium bicarbonate that was simultaneously ultrasonicated for 30 min. Then the electrode was thoroughly rinsed with distilled, deionized water to remove the sodium bicarbonate (and any impurities), after which the electrode was placed in an oven at 180°C and atmospheric pressure for 20 min. Finally, a very brief cathodic polarization of the electrode, after being inserted into the electrolysis cell, serves to activate the cathode completely. As indicated in the preceding paragraph, the reference electrode was a saturated cadmium amalgam in DMF;²⁶ the auxiliary anode was a graphite rod separated from the cathode compartment by a medium-porosity sintered-glass disk backed by a methyl cellulose-DMF-0.10 M TEABF₄ plug. Information about the two-compartment (divided) electrolysis cell, as well as details about instrumentation and procedures for bulk electrolyses, can be found in earlier papers.^{6,31}

Separation, identification, and quantitation of electrolysis products.- Prior to the start of each controlled-potential (bulk) electrolysis, a known amount of an internal standard (n-undecane) was added to the solution so that the absolute yield of each product (with respect to the amount of starting material) could be determined; details pertaining to this quantitation procedure have been published elsewhere.³² At the conclusion of a bulk electrolysis, the catholyte (ca. 20-25 mL) was added to approximately 20 mL of diethyl ether and washed three times with brine. Then the ether phase was dried over anhydrous sodium sulfate, filtered to remove the drying agent, and concentrated by means of rotary evaporation. Gas chromatography (GC) and gas chromatography-mass spectrometry (GC-MS) were employed to separate, identify, and quantitate the various electrolysis products in each ether extract. Each of the gas chromatographic systems (Agilent 7890A instrument) included a 60 m \times 0.25 mm i.d. capillary column (Agilent Technologies) with a polyethylene glycol stationary phase; a flame-ionization detector was utilized for the GC measurements, whereas an inert mass-selective detector in electron-ionization mode (70 eV) was used for the GC-MS analyses. As appropriate, gas chromatographic retention times, along with NMR and mass spectral data, for the electrolysis products were compared with those for chemically synthesized authentic samples. Identities of synthesized compounds were established with the aid of ¹H and ¹³C NMR spectroscopy (400- or 500-MHz Varian Inova instrument) and high-resolution GC–MS (Thermo Electron Corporation instrument) coupled to a MAT-95XP magnetic-sector mass spectrometer.

Synthesis of ethyl trans-3-(3',4'-dimethoxyphenyl)acrylate (trans-4).— To 1 mL of concentrated hydrochloric acid in 50 mL of anhydrous ethanol was added trans-3,4-dimethoxycinnamic acid (1.1 g, 4.7 mmol), and this solution was refluxed overnight. Rotary evaporation was used to remove the ethanol, and the resulting solid was recrystallized from a hot methanol–water mixture to afford the desired product (actually a 19:1 mixture of trans and cis species). We confirmed the identity of trans-4 by spectroscopic methods: ¹H NMR (400 MHz, CDCl₃) δ 7.63 (d, J = 15.6 Hz, 1H, CCH=C), 7.11 (dd, J= 2.0, 8.4 Hz, 1H, aromatic H), 7.06 (d, J = 1.6 Hz, 1H, aromatic H), 6.87 (d, J = 8.4 Hz, 1H, aromatic H), 6.32 (d, J = 16.0 Hz, 1H, C= CH–C), 4.19 (q, J = 7.2 Hz, 2H, OCH₂), 3.92 (s, 6H, OCH₃), 1.34 (t, J = 6.8 Hz, 3H, CH₃); MS (70 eV) m/z 236, M⁺ (100%); 191, [M – OCH₂CH₃]⁺ (57%); 164, [M – CO₂CH₂CH₃]⁺ (25%). These results are in agreement with the literature.^{2,33}

Synthesis of ethyl 3-(3',4'-dimethoxyphenyl)propiolate (7).— A solution of 3,4-dimethoxyphenylacetylene (1.0 g, 6.2 mmol) in dry THF (10 mL) was prepared and cooled to -5° C in an ice–salt bath; to this solution, *n*-butyllithium (2.0 M in cyclohexane, 3.3 mL,

6.2 mmol) was added, and the cooled mixture was stirred for 10 min. Then the solution was allowed to warm to room temperature and was stirred for 1 h. A dry ice-acetone bath was used to cool the mixture to -78°C, ethyl chloroformate (0.67 g, 6.2 mmol) was added, and the solution was stirred at this temperature for 30 min. Next, the temperature of the mixture was raised to 0°C and the solution was stirred for an additional 1 h. Saturated aqueous ammonium chloride solution was added to quench the reaction and the mixture was extracted with ethyl acetate, after which the organic phase was washed three times with brine, dried over anhydrous sodium sulfate, concentrated under reduced pressure, and introduced into a silica-gel chromatographic column which was eluted with 20:1 hexane:ethyl acetate to afford the desired product as a colorless oil: ¹H NMR (500 MHz, CDCl₃) & 7.23 (d, J = 9.5 Hz, aromatic H), 7.08 (s, 1H, aromatic H), 6.85 (d, J =8.5 Hz, 1H, aromatic H), 4.30 (q, J = 7.5 Hz, 2H, OCH₂), 3.89 (s, 3H, OCH₃), 3.92 (s, 3H, OCH₃), 1.36 (t, J = 6.8 Hz, 3H, CH₃); ¹³C NMR (125 MHz, CDCl₃) δ 14.1, 56.0, 62.0, 79.9, 87.0, 111.1, 111.5, 115.3, 127.3, 148.8, 151.5; HRMS (ESI, 70 eV) m/z: calculated for C₁₃H₁₄O₄ [M]⁺ 234.0892, found 234.0886.



Identification and characterization of ethyl 3-(3',4'-dimethoxyphenyl)-3-(prop-2-yn-1-yloxy)propanoate (8).— We confirmed one of the electrolysis products as the title compound by means of mass spectrometry: MS (70 eV) *m*/z 292, M⁺ (23%); 253, [M – CH₂C≡CH]⁺ (20%); 236, [M – HOCH₂C≡CH]⁺ (42%); 205, [M – CH₂CO₂CH₂CH₃]⁺ (98%); 191, [M – CH₂CO₂CH₂CH₃]⁻ (22%) 165, [M – CO₂CH₂CH₃ – OCH₂C≡CH]⁺ (100%); HRMS (ESI, 70 eV) *m*/z: calculated for C₁₆H₂₀NaO₅ [M + Na]⁺ 315.1208; found 315.1194.



Results and Discussion

Cyclic voltammetric behavior of ethyl 2-bromo-3-(3',4'dimethoxyphenyl)-3-(propargyloxy)propanoate (1).- Displayed in Figure 1 is a cyclic voltammogram recorded at 100 mV s⁻¹ for the direct reduction of a 2.0 mM solution of 1 at a silver cathode (curve A, solid line) in oxygen-free DMF containing 0.10 M tetraethylammonium tetrafluoroborate (TEABF₄). For comparison, a cyclic voltammogram for reduction of 1 at a glassy carbon electrode under the same conditions is included in this figure (curve B, dashed line). For each electrode, the first peak (-0.67 V for silver and -0.75 V for glassy carbon) is highly reproducible and is assigned to the irreversible twoelectron reductive cleavage of the carbon-bromine bond of 1. It is interesting to note that cleavage of the carbon-bromine bond is easier at silver than at glassy carbon by 80 mV, a finding in accord with the recognized electrocatalytic ability of silver to promote cleavage of carbon-halogen bonds. With respect to curve A, we attribute the peaks at more negative potentials to the reduction of products formed



Figure 1. Cyclic voltammograms recorded at 100 mV s⁻¹ for reduction of 2.0 mM **1** at a silver cathode (curve A, solid line) and a glassy carbon cathode (curve B, dashed line) in oxygen-free DMF containing 0.10 M TEABF₄; each electrode had an area of 0.071 cm^2 . Curve A was scanned from 0 to -1.5 to 0 V, and curve B was scanned from 0 to -2.0 to 0 V. Potentials are given with respect to a reference electrode consisting of a cadmium-saturated mercury amalgam in contact with DMF saturated with both cadmium chloride and sodium chloride; this electrode has a potential of -0.76 V versus an aqueous saturated calomel electrode (SCE) at 25°C.

at potentials corresponding to the first peak, as will be discussed later when we consider mechanistic aspects of the reduction of 1 at silver.

Shown in Figure 2 is a comparison of the cyclic voltammetric behavior of 2.0 mM solutions of 1 in the absence and presence of a proton donor (1,1,1,3,3,3-hexafluoro-2-propanol, HFIP). Both cyclic voltammograms were recorded at a scan rate of 100 mV s⁻¹ in DMF containing 0.10 M TEABF₄ and either no HFIP (curve A, solid line) or 20 mM HFIP (curve B, dashed line). In the presence of HFIP, all stages in the reduction of 1 are shifted dramatically toward less negative potentials: (a) the first peak shifts from -0.67 to -0.08 V and (b) the second set of cathodic peaks coalesces and shifts from ca. -1.30 to -0.91 V. These large shifts in peak potentials are believed to be the result of protonation of the ester moiety of 1, which draws electron density away from the carbon–bromine bond. A referee suggested an alternate way to view the effect of the added proton donor. Accordingly, the first event in the reduction of 1 involves addition of



Figure 2. Cyclic voltammograms recorded at 100 mV s⁻¹ for reduction of 2.0 mM **1** at a silver cathode (area of 0.071 cm²) in oxygen-free DMF containing 0.10 M TEABF₄ and in the absence of HFIP (curve A, solid line) and in the presence of 20 mM HFIP (curve B, dashed line). Curve A was scanned from 0 to -1.5 to 0 V; curve B was scanned from 0 to -1.2 to 0 V. Potentials are given with respect to a reference electrode consisting of a cadmium-saturated mercury amalgam in contact with DMF saturated with both cadmium chloride; this electrode has a potential of -0.76 V versus an aqueous saturated calomel electrode (SCE) at 25°C.

Table I. Coulometric data and product distributions for direct reduction of ethyl 2-bromo-3-(3',4'-dimethoxyphenyl)-3-(propargyloxy)propanoate (1) at silver gauze cathodes held at -0.80 V in DMF containing 0.10 M TEABF₄.

			Product distribution (%) ^a				
[1] (mM)	HFIP (mM) ^b	n ^c	cis-4	trans-4	7	8	Total
5.0	0	1.0	10	40	49	ND ^d	99
5.0	50.0	2.0	TR ^e	62	ND ^d	35	97

^aYield expressed as the percentage of 1 incorporated into each product; $\mathbf{4} = \text{ethyl } 3-(3',4'-\text{dimethoxyphenyl})\text{acrylate}; \mathbf{7} = \text{ethyl } 3-(3',4'-\text{dimethoxyphenyl})\text{propiolate}; \mathbf{8} = \text{ethyl } 3-(3',4'-\text{dimethoxyphenyl})-3-(\text{prop-2-yn-1-yloxy})\text{propanoate}.$

^bHFIP = 1,1,1,3,3,3-hexafluoro-2-propanol.

^cAverage number of electrons per molecule of **1**.

 $^{d}ND =$ species was not detected.

eTR = a trace (<1%) of the species was detected.

an electron to a LUMO that is a combination of the carbon–bromine σ^* orbital and the carbonyl π^* orbital; protonation of the carbonyl moiety would lower the energy of the π^* orbital as well as the energy of the combined LUMO which, by pulling electron density away from the carbon–bromine bond, would shift its reduction potential to a less negative value.

Controlled-potential electrolysis of ethyl 2-bromo-3-(3',4'dimethoxyphenyl)-3-(propargyloxy)propanoate (1).— Controlledpotential (bulk) electrolyses of 1 were performed at silver gauze cathodes in DMF-0.10 M TEABF₄. To ensure complete electrolysis of 1 and to preclude reduction of any products, the cathode potential was held at -0.80 V, which is consistent with the cyclic voltammogram displayed in Figure 1, curve A. Table I summarizes the coulometric n values and the product distributions obtained from at least two separate experiments. No starting material was detected at the end of any electrolysis, and the total yield of 99% provides evidence that we were able to account for all of the products. As shown by the first entry in Table I, essentially equal yields of an alkene (cis- and trans-4) and an alkyne (7) were found and the coulometric *n* value was 1.0; as explained in the discussion of mechanism below, this *n* value arises because one-half of the starting material engages in a two-electron process, whereas the other half of the starting material undergoes a purely chemical reaction. With respect to 4, the 4:1 trans:cis ratio is not surprising, as the trans-isomer is more stable. In another experiment in which the initial concentration of 1 was raised to 10.0 mM, the n value, the cis-trans ratio, and the ratio of yields of products 4 and 7 were not significantly affected.

Entry 2 in Table I shows the results of bulk electrolyses of 1 done at -0.80 V in the presence of a tenfold excess of a proton donor (HFIP). For these experiments, the *n* value was 2.0 and the products were *trans*-4 (62%) and 8. Thus, when a proton donor is introduced, no 7 is formed, but 8 (a species undetected in experiments performed in the absence of a proton donor) is produced.

Mechanistic aspects of the reduction of ethyl 2-bromo-3-(3',4'-dimethoxyphenyl)-3-(propargyloxy)propanoate (1).— Scheme 1



Scheme 1. Proposed mechanistic steps for direct electrochemical reduction of bromo propargyloxy ester 1 at a silver cathode. Note that the only hydrogen atoms specifically shown among the various intermediates are those removed as protons via reaction with $^{-}OCH_{2}C=CH$.

Ar = 3,4-dimethoxyphenyl

provides a sequence of mechanistic steps that can account for the electrochemical behavior of 1 at a silver electrode. In the first step, 1 accepts a pair of electrons, accompanied by expulsion of a bromide ion, to give an intermediate carbanion 9 (reaction 1). Once formed, 9 triggers the formation of the observed final products (4, 7, and 8). Interestingly, the absence of carbocyclic products such as 2-(3',4'dimethoxyphenyl)-3-(ethoxycarbonyl)-4-methylenetetrahydrofuran (2) or 2-(3',4'-dimethoxyphenyl)-3-ethoxycarbonyl-4-methyl-2,5dihydrofuran (3) indicates, in contrast to earlier work,^{1,2} that intramolecular cyclization of a radical intermediate (arising from one-electron reduction of 1) is an irrelevant process when 1 is reduced at a silver cathode. Furthermore, if a radical intermediate were to be formed, we suggest that it would be anchored by its acetylenic moiety or by its two oxygen atoms to the surface of the silver electrode and that it would immediately accept another electron to yield 9. When bulk electrolysis of a 5.0 mM solution of 1 was carried out at a silver gauze cathode in DMF-0.10 M TEABF₄ containing 500 mM D₂O, no 8 was detected; this observation implies that 9 is a short-lived intermediate and that a proton donor more potent than water is needed to trap 9. In the absence of a sufficiently strong acid, 9 eliminates the propargyloxy anion to yield 4 (reaction 2). We propose that the released propargyloxy anion, acting as a base, attacks unreduced 1 to afford 5 (reaction 3); it is the occurrence of this latter reaction that is responsible for the coulometric n value of 1 (when bulk electrolysis of 1 is conducted in the absence of a potent proton donor), since essentially half of the starting material is consumed by this reaction. Subsequent base-promoted removal of a proton from 5, followed by immediate loss of bromide, yields 7 (reaction 4). Evidence supporting the occurrence of reactions 3 and 4 was obtained by addition of an excess of NaOH to a 5.0 mM solution of 1 in DMF-0.10 M TEABF₄ that was stirred for 20 min at room temperature. When this solution was subjected to the usual post-electrolysis extraction and analysis protocol, the presence of 7 was confirmed by means of GC-MS. Furthermore, very small amounts of prop-2-yn-1-ol (arising from protonation of $-OCH_2C \equiv CH$ during the diethyl ether-water extraction of the catholyte) were detected in the ether phase by means of GC-MS; however, most of the prop-2-yn-1-ol is lost to the aqueous phase, so we did not attempt to quantitate this species.

When HFIP is added to the system, the electrogenerated bases are protonated and no base-promoted eliminations (reactions 3 and 4) occur, which results in the absence of 7. An acidic environment (containing HFIP) causes protonation of electrogenerated anion 9 to give 8 (reaction 5). Our proposed mechanistic steps, whereby 4 and 8 are produced, both proceed via an overall two-electron process, which is in agreement with the observed n value of 2 when electrolyses of 1 are carried out in the presence of HFIP.

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