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Alkene, Bromide, and ROH – How To Achieve Selectivity? Electrochemical Synthesis of Bromohydrins and Their Ethers

Oleg V. Bityukov,^{a, b} Vera A. Vil',^{a, b} Gennady I. Nikishin,^a and Alexander O. Terent'ev^{a, b,*}

 ^a N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 47 Leninsky prosp., 119991 Moscow, Russian Federation

 ^b All-Russian Research Institute for Phytopathology, B. Vyazyomy, Moscow Region, 143050, Russian Federation Phone: (+7)-91638540
 E-mail: terentev@ioc.ac.ru

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Abstract: Bromohydrins and their ethers were electrochemically synthesized *via* hydroxy- and alkoxybromination of alkenes using potassium bromide and water or alcohols. High selectivity of bromohydrins formation was achieved only with the use of DMSO as the solvent and an acid as the additive. The proposed combination of starting reagents, additives, and solvents allowed to form bromohydrins or their ethers selectively despite the variety of side-products (epoxides, dibromides, diols). Bromohydrins were obtained in high yields, up to 96%, with a broad substrate scope in an undivided electrochemical cell equipped with glassy carbon and platinum electrodes at high current density.

Keywords: Alkene difunctionalization; Potassium bromide; Electrosynthesis; Bromohydrins; C-O bond

Introduction

The importance of halohydrins in organic chemistry^[1] is illustrated by their utility in the synthesis of epoxides,^[2] ketones,^[3] α -alkenyl ketones,^[4] amino acids,^[5] cyclic carbonates,^[6] 2-oxazolidinones,^[7] and Oalkylated oximes^[8] as well as in cross-coupling processes.^[9] Potentially, the simplest approach to bromohydrins starts from alkenes and requires stoichiometric amount of *N*-bromoimides,^[10] [bmim]BF₄-water/NBS,^[11] KBr/I₂O₅,^[12] HBr/DMSO,^[13] tribromoi-socyanuric acid,^[14] chloramine-T trihydrate,^[15] *N*,*N*-dibromo-p-toluenesulfonamide,^[16] HBr/H₂O₂,^[17] and Br_2 (or Br_2/Br^-)/H₂O.^[18] The two-step protocols from alkenes to halohydrins via the reaction of the intermediate epoxides with halides^[19] are also known. However, most of these processes are associated with the formation of side products such as vicinal dihalides and diols,[15,20] require several synthetic steps and produce huge amount of waste. One of the main ideas of our work lies in the replacement of stoichiometric chemical reagents by an electric current, mostly with the involvement of anodic processes, for the transformation of alkenes into halohydrins.

In the electroorganic experiment, electric current can serve both as an oxidant and as a reductant, the "reactivity" of which can be finely tuned by the nature of electrodes, electrolyte, solvent, cell type, and electrolysis mode (potentiostatic or galvanostatic).^[21] Solving the problem of selective synthesis under variability of the experimental options and many possible side processes determines the high level of scientific novelty in the development of selective electroorganic reactions.^[21a,22]

Alkenes offer an excellent starting point for the electrochemical organic synthesis due to their abundance.^[23] Electrochemical oxidative difunctionalization of alkenes has proven to be one of the most promising approaches to increasing molecular complexity.^[24] A lot of transformations of alkenes in alcohol media proceed in an electrochemical cell: α , β -dialkoxylation,^[25] α -alkoxy- β -hydroxylation,^[26] α , α -dialkoxylation,^[27] allylic oxidation,^[25b] dimerization with various regioselectivity,^[25d,28] and oxidative cleavage of C=C bonds.^[26,29]

The addition of bromide salts into the alkene/ROH system increases the variability of the electrochemical transformation of alkenes. Alkene electrolysis in the

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presence of Br⁻/ROH leads to the mixture of bromohydrins ethers with different regioselectivity, α,β -dibromides, and α,β -dialkoxylated products^[30] or α,α -dialkoxy- β -bromide^[31] under CCE (constant current electrolysis) mode, and to the mixture of α,β -dibromides, α,β -dialkoxylated products, and bromohydrins ethers under CPE (controlled potential electrolysis) mode^[32] (Scheme 1, a). Also, bromohydrins in an electrochemical cell undergo cyclization to form epoxides.^[33]

The earlier discussed studies^[25-33] could make one think that investigation of the "alkene, bromide, ROH, electric current" system is hopeless from the novelty point of view and that the chances of creating a selective process are slim. The problem of low selectivity in the synthesis of bromohydrins or their ethers^[30-32] is determined by the fact that using only the obvious reaction components, which form the target products, does not allow to achieve high selectivity. The idea of the present study is to change the reactivity of the starting system using "switching" components. Keeping in mind the potential of electroorganic chemistry, we discovered that the appropriate cosolvent and the acid greatly change the transformation way of "alkene, bromide, ROH, electric current" system. In our study, bromohydrins and their ethers were selectively obtained despite the numerous possible transformations of alkenes in an undivided electrochemical cell in the presence of alcohols and halides (Scheme 1, b).

It is known that halogen cations stabilized by DMSO (Hal⁺/DMSO) can be generated by electrochemical oxidation of corresponding anions (Hal⁻).^[34] These pre-synthesized halogen cation pools were used for the synthesis of α -haloketones and halohydrins from alkenes.^[34] However, there are no known methods for electrochemical difunctionalization of alkenes with such species, generated directly in the process of



Scheme 1. Electrochemical transformations of alkenes in Br^{-/} ROH system - old guard reagents for modern electrosynthesis.

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difunctionalization. Herein, we describe the synthetic approach to bromohydrins and their ethers *via* electrochemical alkene hydroxy- or alkoxybromination. The selectivity is achieved by applying DMSO or CH₃CN as the solvent and an acid as the additive.

Results and Discussion

As the first step, we explored the electrolysis of styrene **1** a using potassium bromide as the supporting electrolyte in water (Scheme 2). At the first glance, it seems that the system alkene / bromine-containing electrolyte / H_2O is sufficient for electrochemical synthesis of bromohydrins. However, this reaction led to a mixture of the following products: 2-bromo-1-phenylethanol **2** a, styrene oxide **3**, (1,2-dibromoethyl)benzene **4**, 1-phenylethane-1,2-diol **5** (Scheme 2). Conversion of the starting styrene **1** a and the composition of the mixture did not change when electric current amount passed per 1 mole **1** a increased from 4 F/mol to 8 F/mol (Scheme 2).

Surprisingly, the addition of acetic acid as the first "switching" component into the reaction mixture resulted in increased yield of bromohydrin 2a (42%) and decreased yield of (1,2-dibromoethyl)benzene 4 (6%) (Table 1, entry 1). In this case, we did not observe the formation of styrene oxide 3 and 1-phenylethane-1,2-diol 5.

This result inspired us to explore another "switching" additive, the solvent,^[35] to increase the yield of 2bromo-1-phenylethan-1-ol 2a (Table 1).

It was found that using the 1:1 DMSO:H₂O system led to a 85% yield of bromohydrin 2a (Table 1, entry 5). H₂O, THF:H₂O, CH₃OH:H₂O and CH₃CN: H₂O solvent systems were less effective (entries 1–4). The DMSO:H₂O ratio had a great influence on 2ayield (entries 6, 7).

It was shown that the most important parameters, which determined the selectivity of the electrochemical reaction, were the use of DMSO as the co-solvent and the addition of an acid into the reaction mixture. Due to a great number of experiments, the full details of the influence of acid nature, electrolyte type, the amount of electricity passed, solvent system, reaction temper-



Scheme 2. Electrochemical transformations of styrene 1 a in KBr/H₂O system.



Table 1.	The	influence	of the	reaction	media	on 2 a	yield.[a]
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Entry	Solvent	Yield of 2 a , %
1	H ₂ O	42 ^[b]
2	$THF:H_2O(1:1)$	44
3	CH ₃ OH:H ₂ O (1:1)	34
4	CH ₃ CN:H ₂ O (1:1)	76
5	DMSO:H ₂ O (1:1)	85
6	DMSO:H ₂ O (4:1)	48
7	DMSO:H ₂ O (1:4)	49

^[a] Reaction conditions: undivided cell, glassy carbon plate anode (GC) (15 mm×25 mm×2 mm), platinum plate cathode (15 mm×25 mm×0.4 mm), constant current=200 mA (*j*=53.3 mA/cm²), 1a (1 mmol, 104 mg), AcOH (10 mmol, 600 mg), KBr (5 mmol, 595 mg), solvent system (10 mL).
^[b] 6% (1,2-dibromoethyl)benzene 4 as by-product.

Table 2. The influence of the reaction conditions on 2 a yield.^[a]

GC(+) | Pt(-) 200 mA, 4 F/mol, 50 °C KBr (5 equiv.) AcOH (5 equiv.) 1a 2a DMSO/H₂O (5 mL/5 mL) air atmosphere Entry Deviation from the standard conditions Yield of 2a, % 1 none 86 2 without AcOH n.d. 3 H₂SO₄ instead of AcOH 54 4 TFA instead of AcOH 90 5 without current n.d. 400 mA instead of 200 mA 6 75 7 100 mA instead of 200 mA 86 8 GC(+) | GC(-) instead of GC(+) | Pt(-)61 9 GC(+) | Cu(-) instead of GC(+) | Pt(-)65 10 12 F/mol instead of 4 F/mol 76 11 TFA and 12 F/mol instead of AcOH 91 and 4 F/mol

^[a] **Reaction conditions**: undivided cell, glassy carbon plate anode (15 mm × 25 mm × 2 mm), platinum plate cathode (15 mm × 25 mm × 0.4 mm), constant current = 200 mA (j = 53.3 mA/cm²), **1a** (1 mmol, 104 mg), AcOH (5 mmol, 300 mg), KBr (5 mmol, 595 mg), solvent system (DMSO/ H₂O = 5 mL/5 mL). n.d. = not determined. TFA = trifluoroacetic acid.

ature on the yield of **2***a* are presented in SI (Tables S1–S7).

Table 2 presents an impact of key parameters on the transformation of styrene **1a** into 2-bromo-1-phenyl-

ethan-1-ol **2a** in an undivided electrochemical cell under constant current electrolysis (Table 2).

In the standard conditions, the yield of **2 a** was 86% (entry 1, Table 1). An attempt to carry out the target process without AcOH was unsuccessful - the bromohydrin 2a was not detected (entry 2). Yield of 2a decreased to 54% when H₂SO₄ was used instead of AcOH (entry 3). However, the use of CF₃COOH increased the yield of 2 a to 90% (entry 4). The reaction did not occur in the absence of electric current (entry 5). Yield of 2a remained good (75%) under the constant current of 400 mA ($j = 106.7 \text{ mA/cm}^2$, entry 6) and 100 mA ($j = 26.7 \text{ mA/cm}^2$, 86%, entry 7). Changing the cathode material did not improved the yield of 2a (entries 8, 9). Increasing the amount of passed electricity from 4 to 12 F/mol led to a significantly lower yield of 2 a (76%) (entry 10). It was found that increasing the amount of passed electricity and the use of TFA afforded the target bromohydrines **2 a** in a high 91% yield (entry 11).

In order to investigate the scope of the discovered process and to evaluate the differences in reactivity of various alkenes 1 a-s, the following three slightly modified methods were used: method A – standard condition (Table 2, entry 1), method B – conditions of entry 10, Table 2, method C – conditions of entry 11, Table 2 (Table 3).

Various substituted aryl alkenes 1 a-p possessing both electron-donating and electron-withdrawing groups successfully entered the developed process leading to the target bromohydrins 2 a-p in yields from good to high (Table 3). The exceptions were bromohydrins 2m, 2n with N-heterocyclic core, which were formed in 16-31% yields, probably due to protonation of the nitrogen atom, resulting in a decrease in the electron density at the C=C bond. Bromohydrins 2q, 2r from aliphatic alkenes cyclohexene and cyclopentene were synthesized in moderate yields. Allylbenzene 1s was transformed into a mixture of regioisomeric bromohydrins 2s and 2s' in a total yield 45% using method B. In most cases, method C led to better yields of bromohydrins than methods A and B. Bromohydrins 21, 2m, 2o, and 2s (with 2s') were prepared in higher yields through method B.

We also found that the addition of co-solvent and acid had a great impact on bromohydrin ether 6a synthesis from styrene 1a (Table 4).

Electrolysis of 1a with KBr as the electrolyte (5 eq.), in the CH₃CN/CH₃OH system in the presence of AcOH (5 eq.) at constant current of 200 mA (the total of 4 F/mol electric current amount passed per mol 1a) gave 6a in a high 87% yield (entry 1, Table 4). The experiment without AcOH led to a 21% yield of 6a (entry 2). The reaction did not occur without an electric current (entry 3). Surprisingly, yield of 6a in neat methanol was lower in comparison with the CH₃CN/CH₃OH mixture (entry 4). Replacement of

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 Table 3. Electrochemical synthesis of bromohydrins 2 a-s from alkenes 1 a-s.

^[a] **Reaction conditions for Method A**: undivided cell, glassy carbon plate anode (15 mm×25 mm×2 mm), platinum plate cathode (15 mm×25 mm×0.4 mm), constant current = 200 mA (j=53.3 mA/cm²), 4 F/mol, **1 a–s** (1 mmol,

68–197 mg), AcOH (5 mmol, 300 mg), KBr (5 mmol, 595 mg), solvent system (DMSO/H₂O = 5 mL/5 mL), 50 °C, air atmosphere.

- [b] Reaction conditions for Method B: 12 F/mol instead of 4 F/ mol.
- ^[c] **Reaction conditions for Method C**: CF₃COOH (5 mmol, 570 mg) and 12 F/mol instead of AcOH (5 mmol, 300 mg) and 4 F/mol.

 Table 4. The influence of the reaction conditions on bromohydrin ether 6 a synthesis.^[a]



Entry	Deviation from the standard conditions	Yield of 6 a , %
1	none	87
2	without AcOH	21
3	without current	n.d.
4	CH_3OH (10 mL) as the solvent	82
5	DMSO/CH ₃ OH (5 mL/5 mL)	29
	as the solvent	
6	12 F/mol instead of 4 F/mol	89
7	TFA instead of AcOH	76

^[a] **Reaction conditions**: undivided cell, glassy carbon plate anode (15 mm \times 25 mm \times 2 mm), platinum plate cathode (15 mm \times 25 mm \times 0.4 mm), constant current = 200 mA, **1a** (1 mmol, 104 mg), AcOH (5 mmol, 300 mg), KBr (5 mmol, 595 mg), solvent system (CH₃CN/CH₃OH = 5 mL/5 mL). n. d. = not determined

CH₃CN by DMSO (entry 5, Table 4) provided the target ether **6a** in a low yield. A possible reason is oxidation of alcohols into ketones in the presence of dimethyl sulfoxide and bromine,^[36] or the formation of alkoxysulfonium ion intermediates, which are not hydrolyzed by CH₃OH into product **6a**.^[37] The increase in the amount of passed electricity to 12 F/mol had a positive effect on **6a** yield (entry 6, Table 4). The use of TFA instead of AcOH led to lower 76% yield of bromohydrin ether **6a** (entry 7, Table 4).

When electrooxidation of styrenes 1 with various alcohols was carried out in the conditions of entry 6, Table 3, bromohydrins ethers 6-8 were formed selectively in 49–89% yields (Table 5).

The results in Table 5 show that the electrochemical alkoxybromination successfully proceeds with styrenes bearing both a halogen substituent in the aromatic ring (6d, 85%) and electron-donating methyl group (6b, 85%). The reaction with α -methyl styrene 1h gave product 6h in a high 86% yield. Using ethanol and *iso*-propanol, bromohydrins ethers 7a and 8a were obtained from styrene 1a in 72% and 49% yields respectively (Table 5).

The proposed pathway of bromohydrins 2 formation *via* alkene 1 difunctionalization includes both electrochemical and chemical stages. Scheme 3 illustrates the mechanism using the transformation of 1ainto 2a.

Molecular bromine is electrochemically generated from the bromide anions on the anode surface,^[38] and then can be transformed into $[Br]^{+[39]}$ species. In

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^[a] Reaction conditions: undivided cell, glassy carbon plate anode (15 mm×25 mm×2 mm), platinum plate cathode (15 mm×25 mm×0.4 mm), constant current=200 mA, 12 F/mol, 1a-d, 1h (1 mmol, 104–122 mg), AcOH (5 mmol, 300 mg), KBr (5 mmol, 595 mg), solvent system (CH₃CN/CH₃OH or CH₃CN/EtOH or CH₃CN/*i*-PrOH=5 mL/5 mL).



Scheme 3. Proposed reaction mechanism on the example of the formation of 2 a from styrene 1 a.

addition, DMSO can react with the $[Br]^+$ species to form complex C.^[34] The attack of the electrochemically

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generated bromine or $[Br]^+$ species leads to cyclic bromonium cation **A**. The side dibromide **4** is probably obtained by the reaction of bromide with cyclic bromonium cation **A**.^[40] The reaction of styrene **1 a** with the stabilized cation **C** leads to the sulfonium salt **B**,^[34] which can be also formed from the reaction of **A** with DMSO.^[13]

The water as the nucleophile can attack either the bromonium ion **A** or the sulfonium salt **B**.^[13,37] Both reactions would afford the target product 2a. High concentration of hydroxide ion can result in epoxide 3 formation possibly via cyclization of 2a.^[33] The diol 5 could be formed from the subsequent nucleophilic opening of epoxide **3**.^[41] The use of AcOH or TFA as an additive lowers the hydroxide ion concentration. A control experiment (see SI) confirms that epoxide 3 does not transform into bromohydrin 2a under our optimized reaction conditions. Also, the radical mechanism of target product formation supposing several reaction stages on the surface of the electrodes cannot be completely excluded. The Br anion could be oxidized at the anode into Br radical, which attached to the styrene double bond, followed by anodic oxidation of the benzyl radical to the cation and nucleophile attack. Since we used high current density (j = 53.3 mA/cm^2) and observed the bromine dripping off the electrodes during the reaction the radical pathway seems less likely.

The proposal about the anodic oxidation of bromide is supported by CV data (Figures 1, 2), which demonstrate that bromide anion is the only component of the reaction mixture that undergoes oxidation (Figure 1); styrene 1a is not oxidized under these conditions (Figure 2). Addition of styrene 1a into KBr solution results in decreasing of reverse peak of reduction (Figure 3). It can be explained by the reaction of styrene 1a with the generated bromine species.



Figure 1. CV curve for a 0.1 M solution of KBr in 0.125 M Bu_4NBF_4 in DMSO/H₂O (3/1 vv) on a working glassy-carbon electrode (d=3 mm) under a scan rate of 0.1 V/s (An enlarged image of the section of CV from 0 to 1.6 V is in the center.).

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Figure 2. CV curve for a 0.1 M solution of **1a** in 0.125 M Bu_4NBF_4 in DMSO/H₂O (3/1 vv) on a working glassy-carbon electrode (d = 3 mm) under a scan rate of 0.1 V/s.



Figure 3. CV curve for a solution mixture of 1 a (0.1 M) with KBr (0.1 M) in 0.125 M Bu₄NBF₄ in DMSO/H₂O (3/1 vv) on a working glassy-carbon electrode (d=3 mm) under a scan rate of 0.1 V/s.

The additional evidence of the proposed mechanism (Scheme 3) was received from the experiments with various amounts of added acid and potassium hydroxide (Scheme 4).

In the presence of 5 eq. AcOH, the target bromohydrin 2a was formed in an 86% yield. The formation of epoxide 3 did not occur. Decreasing the acid amount and increasing the hydroxide amount led to inhibition



Scheme 4. Control experiments.

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of 2a formation and growth of 3 yield. The observed result confirms the importance of the acid for slowing down the epoxide formation in the electrochemically induced bromohydrin synthesis from alkenes.

Conclusion

An effect of co-solvent and acid in the indirect electrochemical transformations of alkenes was discovered in this work. The addition of the co-solvent and the acid into the well-known system "alkene, bromide anion, ROH, electric current", which previously led to unselective chemistry, allows to selectively obtain bromohydrins and their ethers. It illustrates the unlimited possibilities of the electroorganic synthesis reopened by the addition of counter-intuitive at first glance reagents. Electrochemical synthesis of bromohydrins and their ethers from alkenes in yields from moderate to high was disclosed. The newly developed electrochemical method is characterized by high efficiency and experimental convenience, as it involves an undivided electrochemical cell, high current densities, and high concentration of starting reagents.

Experimental Section

General Experimental Details

¹H and ¹³C NMR spectra were recorded on Bruker AVANCE II 300 spectrometer (300.13 and 75.48 MHz, respectively) in CDCl₃. Chemical shifts were reported in parts per million (ppm), and the residual solvent peak was used as an internal reference: ¹H (CDCl₃ δ = 7.26 ppm), ¹³C (CDCl₃ δ = 77.16 ppm). Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet).

High resolution mass spectra (HR-MS) were measured on a Bruker micrOTOF II instrument using electrospray ionization (ESI).^[42] The measurements were performed in a positive ion mode (interface capillary voltage – 4500 V); mass range from m/z 50 to m/z 3000 Da; external calibration with Electrospray Calibrant Solution (Fluka). A syringe injection was used for all acetonitrile solutions (flow rate 3 μ L/min). Nitrogen was applied as a dry gas; interface temperature was set at 180 °C.

Cyclic voltammetry (CV) was implemented on an IPC-Pro M computer-assisted potentiostat manufactured by Econix (scan rate error 1.0%; potential setting 0.25 mV; scan rate 100 mV s^{-1}). The experiments were performed in a 2 mL five-neck glass conic electrochemical cell with a water jacket for thermostatting. CV curves were recorded using a three-electrode scheme. The working electrode was a disc glassy-carbon electrode (d=3 mm). A platinum wire served as an auxiliary electrode and was linked to the solution by a porous glass diaphragm. The solutions were kept under thermally controlled conditions at 50 ± 0.5 °C and deaerated by bubbling argon. Electrochemical experiments were performed under an argon atmosphere. The working electrode was polished before record-

The TLC analysis was carried out on standard silica gel chromatography plates (DC-Fertigfolien ALUGRAM^R Xtra SIL G/UV_{254}). Column chromatography was performed using silica gel (0.060-0.200 mm, 60 A, CAS 7631-86-9, Acros).

ing each CV curve. In a typical case, 2 mL of solution was

utilized. The compound concentration was 0.1 M.

Vinylbenzene (1 a), 1-methyl-4-vinylbenzene (1 b), 1-methyl-2vinylbenzene (1 c), 1-fluoro-4-vinylbenzene (1 d), 1-chloro-4vinylbenzene (1 e), 1-(4-vinylphenyl)ethan-1-one (1 f), 1-methyl-3-vinylbenzene (1 g), prop-1-en-2-ylbenzene (1 h), 2-vinylpyridine (1 m), 3-methyl-2-(prop-1-en-1-yl)pyridine (1 n), 1Hindene (1 o), cyclohexene (1 q), cyclopentene (1 r), allylbenzene (1 s), acetic acid, trifluoroacetic acid, HCO_2H , HBr (48% aq), H_2SO_4 , KBr, NH₄Br, Me₄NBr, LiClO₄, Na₂SO₄, CH₃OH, THF, DMSO, CH₃CN, CH₂Cl₂, petroleum ether (PE, 40/70), ethyl acetate (EA) were purchased from commercial sources and was used as is.

Starting alkenes 1i,^[43] 1j,^[44] 1k,^[45] 1l,^[46] 1p,^[47] were prepared accordingly literature procedures.

Experimental Procedure for Scheme 2

An undivided cell was equipped with a glassy carbon anode (15 mm × 25 mm × 2 mm) and a platinum plate cathode (15 mm × 25 mm × 0.4 mm) and connected to a DC regulated power supply. The solution of styrene **1a** (1.0 mmol, 104.1 mg) and supporting electrolyte KBr (5.0 mmol, 595.0 mg) in a H₂O (10 mL) was electrolyzed using constant current conditions (53.3 mA/cm²) at 50 °C under magnetic stirring for 32 or 64 min with I=200 mA. Then electrodes were washed with CH₂Cl₂ (20 mL). The organic phases were washed with water (15 mL) and dried over Na₂SO₄, filtered and concentrated under reduced pressure using a rotary evaporator (15–20 mmHg), (bath temperature, ca. 20–25 °C). Products **2a**, **3**, **4**, **5** were isolated by chromatography on SiO₂.

General Experimental Procedure for Table 1

An undivided cell was equipped with a glassy carbon anode $(15 \text{ mm} \times 25 \text{ mm} \times 2 \text{ mm})$ and a platinum plate cathode (15 mm×25 mm×0.4 mm) and connected to a DC regulated power supply. The solution of styrene 1a (1.0 mmol, 104.1 mg), acetic acid (5.0 mmol, 300.2 mg) and supporting electrolyte KBr (5.0 mmol, 595.0 mg) in a solvent system $(H_2O = 10 \text{ mL} \text{ or } THF/H_2O, CH_3OH/H_2O, CH_3CN/H_2O,$ $DMSO/H_2O = 5 \text{ mL/5 mL}$) was electrolyzed using constant current conditions (53.3 mA/cm²) at 50 °C under magnetic stirring for 32 min with I = 200 mA. Then electrodes were washed with CH_2Cl_2 (2×20 mL). The combined organic phases were washed with water $(3 \times 15 \text{ mL})$ and dried over Na₂SO₄, filtered and concentrated under reduced pressure using a rotary evaporator (15-20 mmHg), (bath temperature, ca. 20-25 °C). Product 2a was isolated by chromatography on SiO₂ (PE: EtOAc = 10:1).

General Experimental Procedure for Table 2

An undivided cell was equipped with a glassy carbon anode (15 mm \times 25 mm \times 2 mm) and a platinum plate cathode

(15 mm × 25 mm × 0.4 mm) and connected to a DC regulated power supply. The solution of styrene **1a** (1.0 mmol, 104.1 mg), acetic acid (5.0 mmol, 300.2 mg) and supporting electrolyte KBr (5.0 mmol, 595.0 mg) in DMSO/H₂O (5 mL/ 5 mL) was electrolyzed using constant current conditions (53.3 mA/cm²) at 50 °C under magnetic stirring for 32 min with I = 200 mA. Then electrodes were washed with CH₂Cl₂ (2 × 20 mL). The combined organic phases were washed with water (3 × 15 mL) and dried over Na₂SO₄, filtered and concentrated under reduced pressure using a rotary evaporator (15–20 mmHg), (bath temperature, ca. 20–25 °C). Product **2a** was isolated by chromatography on SiO₂ (PE:EtOAc = 10:1).

Experimental Procedures for Table 3

Method A

An undivided cell was equipped with a glassy carbon anode (15 mm × 25 mm × 2 mm) and a platinum plate cathode (15 mm × 25 mm × 0.4 mm) and connected to a DC regulated power supply. The solution of alkene **1 a–s** (1.0 mmol, 68.1–197.1 mg), acetic acid (5.0 mmol, 300.2 mg) and supporting electrolyte KBr (5.0 mmol, 595.0 mg) in solvent system (DMSO/H₂O = 5 mL/5 mL) was electrolyzed using constant current conditions (53.3 mA/cm²) at 50 °C under magnetic stirring for 32 min with I=200 mA. Then electrodes were washed with CH₂Cl₂ (2 × 20 mL). The combined organic phases were washed with water (3 × 15 mL) and dried over Na₂SO₄, filtered and concentrated under reduced pressure using a rotary evaporator (15-20 mmHg), (bath temperature, ca. 20–25 °C). Product **2a-s** was isolated by chromatography on SiO₂ (PE: EtOAc).

Method B

An undivided cell was equipped with a glassy carbon anode (15 mm × 25 mm × 2 mm) and a platinum plate cathode (15 mm × 25 mm × 0.4 mm) and connected to a DC regulated power supply. The solution of alkene **1**a–s (1.0 mmol, 68.1-197.1 mg), acetic acid (5.0 mmol, 300.2 mg) and supporting electrolyte KBr (5.0 mmol, 595.0 mg) in solvent system (DMSO/H₂O = 5 mL/5 mL) was electrolyzed using constant current conditions (53.3 mA/cm²) at 50 °C under magnetic stirring for 96 min with I=200 mA. Then electrodes were washed with CH₂Cl₂ (2 × 20 mL). The combined organic phases were washed with water (3 × 15 mL) and dried over Na₂SO₄, filtered and concentrated under reduced pressure using a rotary evaporator (15–20 mmHg), (bath temperature, ca. 20–25 °C). Product **2**a–s was isolated by chromatography on SiO₂ (PE: EtOAc).

Method C

An undivided cell was equipped with a glassy carbon anode (15 mm \times 25 mm \times 2 mm) and a platinum plate cathode (15 mm \times 25 mm \times 0.4 mm) and connected to a DC regulated power supply. The solution of alkene **1a-s** (1.0 mmol, 68.1–197.1 mg), trifluoroacetic acid (5.0 mmol, 371.0 µL) and supporting electrolyte KBr (5.0 mmol, 595.0 mg) in solvent system (DMSO/H₂O = 5 mL/5 mL) was electrolyzed using constant current conditions (53.3 mA/cm²) at 50 °C under

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magnetic stirring for 96 min with I=200 mA. Then electrodes were washed with CH_2Cl_2 (2×20 mL). The combined organic phases were washed with water (3×15 mL) and dried over Na₂SO₄, filtered and concentrated under reduced pressure using a rotary evaporator (15-20 mmHg), (bath temperature, ca. 20– 25°C). Product **2 a-s** was isolated by chromatography on SiO₂ (PE:EtOAc).

General Experimental Procedure for Table 4

An undivided cell was equipped with a glassy carbon anode $(15 \text{ mm} \times 25 \text{ mm} \times 2 \text{ mm})$ and a platinum plate cathode $(15 \text{ mm} \times 25 \text{ mm} \times 0.4 \text{ mm})$ and connected to a DC regulated power supply. The solution of styrene 1a (1.0 mmol, 104.1 mg), acetic acid (5.0 mmol, 300.2 mg) or trifluoroacetic acid (5.0 mmol, 570.1 mg) and supporting electrolyte KBr (5.0 mmol, 595.0 mg) in solvent system $(CH_3OH = 10 \text{ mL})$; CH_3CN/CH_3OH or $DMSO/CH_3OH = 5 \text{ mL/5 mL}$) was electrolyzed using constant current conditions (53.3 mA/cm²) at 50 °C under magnetic stirring for 32 min or 96 min with I = 200 mA. The reaction mixture was concentrated down to 3-4 mL volume, and then dissolved in 40 mL CH₂Cl₂ which was washed with water $(2 \times 15 \text{ mL})$ and dried over Na₂SO₄, filtered and concentrated under reduced pressure using a rotary evaporator (15-20 mmHg), (bath temperature, ca. 20-25°C). Product 6a was isolated by chromatography on SiO₂ (PE:EtOAc).

Experimental Procedure for Table 5

An undivided cell was equipped with a glassy carbon anode $(15 \text{ mm} \times 25 \text{ mm} \times 2 \text{ mm})$ and a platinum plate cathode $(15 \text{ mm} \times 25 \text{ mm} \times 0.4 \text{ mm})$ and connected to a DC regulated power supply. The solution of alkene 1a-d, 1h (1.0 mmol, 104.1-122.1 mg), acetic acid (5.0 mmol, 300.2 mg) and supporting electrolyte KBr (5.0 mmol, 595.0 mg) in solvent system (CH₃CN/CH₃OH or CH₃CN/EtOH or CH₃CN/*i*-PrOH = 5 mL/ 5 mL) was electrolyzed using constant current conditions (53.3 mA/cm²) at 50 °C under magnetic stirring for 96 min with I = 200 mA. The reaction mixture was concentrated down to 3– 4 mL volume, and then dissolved in 40 mL CH₂Cl₂ which was washed with water $(2 \times 15 \text{ mL})$ and dried over Na₂SO₄, filtered and concentrated under reduced pressure using a rotary evaporator (15-20 mmHg), (bath temperature, ca. 20-25 °C). Product 6a, 6b, 6d, 6h, 7a, 8a was isolated by chromatography on SiO₂ (PE:EtOAc).

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