Efficient Protocol for Synthesis of β-Hydroxy(alkoxy) selenides via Electrochemical Iodide-Catalyzed Oxyselenation of Styrene Derivatives with Dialkyl(aryl) diselenides

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An efficient protocol for the synthesis of β-hydroxy(alkoxy) selenides was developed through the electrochemical iodide-catalyzed oxyselenation of styrene derivatives with dialkyl(aryl) diselenides under mild reaction conditions. Mechanistic studies showed that the cation I$^+$ is involved during the whole process, and accelerates the formation of seleniranium ion via substitution and addition reaction with dialkyl(aryl)diselenides and styrene derivatives. The corresponding products are formed in good to excellent yields. This electrochemical oxyselenation provides an efficient strategy for difunctionalization of alkenes.

Organoselenium compounds are attractive synthetic targets in organic chemistry,[1] because of their useful biological activities (eg. as antioxidants, enzyme inhibitors, antitumor and anti-infective agents and immunomodulators),[2] fluorescence properties,[3] and their regio-, chemo-selectivity in organic synthesis.[4] In addition, olefins are useful building blocks in organic synthesis and fundamental structure unit in numerous natural products.[5] The difunctionalization of readily available olefins is the common method for the synthesis of vicinal difunctional alkanes, including oxyalkylation,[6] oxysulfuration,[7] and Sharpless dihydroxylation.[8] Among these vicinal difunctional alkanes, β-hydroxy(alkoxy) selenides containing two different functional groups (α-OH or β-OR and β-SeR) at the same single bond could be used as important intermediates for the synthesis of bioactive molecules (such as ephedrine and

selegiline) *via* the selecitve cleage of the C—O and C—Se bonds.[9]

Although various methods for construction of β-hydroxy (alkoxy)selenides have been reported,[10] challenges still exist in developing more efficient methods for their generation. The most direct and useful method for β-hydroxy(alkoxy)selenides is the oxidative difunctionalization of alkenes with arylseleno derivatives (such as diaryldiselenide,[11] arylselenohalide[12] or arylselenophthalimide[13]). However, these methods always need stoichimetric oxidants (such as I$_2$,[14] Ce(NH$_4$)$_2$(NO$_3$)$_6$,[15] (NH$_4$)$_2$S$_2$O$_8$,[16] DDQ[17] or oxone[18]) or a large amount of Lewis acid,[19] which may also generate undesirable and toxic by-products.

Electrochemical synthesis has been recognized as an environmental friendly synthesis tool and attract increasingly interest in organic synthesis,[20] which employs electrons as the "reagent", avoiding the use of a large amount of chemical oxidants or reductants.[21] Furthermore, it is easy to avoid the over oxidation of substrates by precisely controlling the cell potential or constant current. Inspired by the electrochemical iodide-catalyzed C—H selenation of indole reported by Sun's group,[22] we envisioned that a similar mechanism for the formation of seleniranium ion (Scheme 1, **C**) may be involved through the electrochemical iodide-catalyzed oxyselenation. In order to verify this hypothesis, styrene (**1a**) was treated with diphenyldiselenide (**2a**) by the use of platinum-plate anode and graphite cathode, and 0.5 equiv. of potassium iodide (KI) as electrolyte and catalyst, at an undivided cell in co-solvent (CH$_3$CN/H$_2$O) at room temperature for 12 h. We were pleased to discover that the desired product 1-phenyl-2-(phenylselanyl) ethan-1-ol (**3a**) was obtained in the yield of 92%. On the occasion of the completion of our work, Lei's group reported another electrochemical oxyselenation for synthesis of β-

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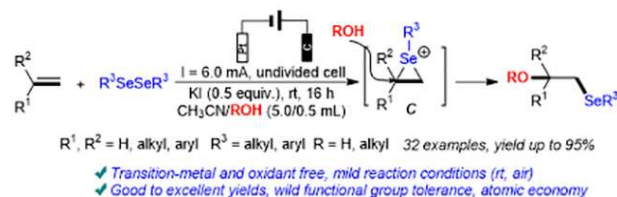
Scheme 1. Electrochemical iodide-catalyzed oxyselenation of styrene derivatives with dialkyl(aryl)diselenides.

hydroxy(alkoxy)selenides, which went through a radical mechanism.[23] Though various functional groups was compatible, low to moderate yields were obtained, when water or alcohols were used as nucleophilic sources, and only styrene and diphenyldiselenide were reported. By using KI as electrolyte and catalyst, highly active intermediate I$^+$ should be formed as a practical catalyst by losing two electrons, which accelerates the formation of seleniranium ion (**C**), which then reacts with nucleophiles to generate difunctional products with good to excellent yields. Herein, we reported our work on developing a mild and highly efficient strategy to β-hydroxy(alkoxy) selenides *via* electrochemical iodide-catalyzed oxyselenation of alkenes with diaryl(alkyl)diselenides and nucleophilic oxygen sources (water or alcohols) (Scheme 1).

To obtain the optimal conditions, some parameters influencing the iodide-catalyzed electrochemical oxyselenation were explored carefully by using the reaction of styrene (**1a**) with diphenyldiselenide (**2a**) as model reaction. First, the influence of different electrolytes on the electrochemical oxyselenation was studied systematically (Table 1, entries 1–6), and results showed that KI was the most suitable electrolyte for giving the desired product (**3a**) in the highest yield of 92% (Table 1, entry 1). During this oxyselenation, KI was not only used as electrolyte, but also as catalyst. Then, a constant current electrolysis was explored, and results obtained from entries 7–10 indicated that no decrease in yield was observed when the constant current was decreased to 6.0 mA (Table 1, entry 9, 92%). To further optimize the conditions, a series of solvents (such as CH$_3$CN, DMF, THF and DMSO) were examined (Table 1, entries 11–13), and results showed that the co-solvent of CH$_3$CN and H$_2$O as the ratio of 10/1 was the best solvent, affording the desired product 1-phenyl-2-(phenylselanyl)ethan-1-ol (**3a**) in

the yield of 92% (Table 1, entry 9). The amount of electrolyte (KI) was also examined, and desired product was obtained in the yield of 95% by using 0.5 equiv. KI as electrolyte, when the reaction time was extended to 16 hours (Table 1, entry 16). In addition, the yields of desired product (**3a**) was decreased to 76% and 70% respectively, when the graphite anode was replaced by a platinum plate or the platinum plate cathode was replaced by a nickel plate (Table 1, entries 18 and 19). And no increase in yield was observed by increasing the amount of styrene to 4.0 equivalent (Table 1, entry 20). After extensive screening, the optimal conditions were obtained as follows: styrene (**1a**, 2.0 equiv.), diphenyldiselenide (**2a**), electrolyte (KI, 0.5 equiv.), co-solvent of CH$_3$CN and H$_2$O (5.0/0.5 mL), platinum-plate cathode and graphite anode, constant current (6.0 mA), room temperature, and 16 hours.
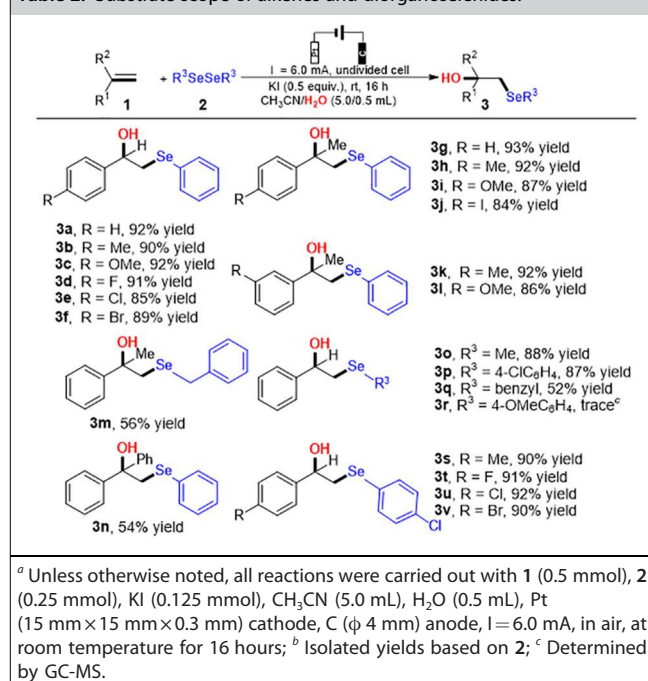
With the optimized conditions in hand, the scope of substrates for the iodide-catalyzed electrochemical oxyselenation was then studied. As shown in Table 2, we see that a variety of styrenes could efficiently undergo oxyselenation to afford coresponding products in good to excellent yields (**3a**–**3f**, 85–92%). Electron-donating groups (eg. Me, OMe) or electron-withdrawing groups (eg. F, Cl, Br) presenting at the *para*- position the benzene ring of the styrene derivatives affected the oxyselenation slightly, giving the corresponding products in excellent yields. This procedure was also suitable for α-methyl styrenes, and the influence of functional groups presenting at the *meta*- or *ortho*- (such as 3-Me, 3-Ome, 4-Me and 4-OMe) can be ignored, giving all corresponding products in the yields of 86%–93% (**3g**–**3l**). As for diorganodiselenides, either diaryl diselenides (diphenyl diselenide, dibenzyl diselenide and di(4-chlorophenyl) diselenide) or dialkyldiselenide (dimethyl diselenide) could undergo oxyselenation efficiently, and good to excellent yields were obtained (**3o**–**3q**, 52%–

Table 1. Optimization of the reaction conditions[a].					
Entry	I	Electrolyte/equiv.	Solvent	Time	Yield/%[b]
1	18 mA	KI (1.0)	CH$_3$CN	12 h	92
2	18 mA	NH$_4$I (1.0)	CH$_3$CN	12 h	25
3	18 mA	NaI (1.0)	CH$_3$CN	12 h	83
4	18 mA	^{n}Bu$_4$NI (1.0)	CH$_3$CN	12 h	21
5	18 mA	^{n}Bu$_4$NBr (1.0)	CH$_3$CN	12 h	Trace
6	18 mA	^{n}Bu$_4$NBF$_4$ (1.0)	CH$_3$CN	12 h	43
7	10 mA	KI (1.0)	CH$_3$CN	12 h	92
8	8 mA	KI (1.0)	CH$_3$CN	12 h	92
9	6 mA	KI (1.0)	CH$_3$CN	12 h	92
10	4 mA	KI (1.0)	CH$_3$CN	12 h	87
11	6 mA	KI (1.0)	DMF	12 h	68
12	6 mA	KI (1.0)	DMSO	12 h	71
13	6 mA	KI (1.0)	THF	12 h	34
14	6 mA	KI (0.5)	CH$_3$CN	12 h	86
15	6 mA	KI (0.5)	CH$_3$CN	14 h	89
16	6 mA	KI (0.5)	CH$_3$CN	16 h	95(92)[c]
17	6 mA	KI (0.5)	CH$_3$CN	20 h	95
18[d]	6 mA	KI (0.5)	CH$_3$CN	16 h	76
19[e]	6 mA	KI (0.5)	CH$_3$CN	16 h	70
20[f]	6 mA	KI (0.5)	CH$_3$CN	16 h	95

[a] Standard reaction conditions: undivided cell, Pt (15 mm×15 mm×0.3 mm) cathode, Graphite (φ 4 mm) anode, **1a** (0.2 mmol), **2a** (0.1 mmol), H$_2$O (0.5 mL), solvent (5.0 mL), constant current, electrolyte (equiv.), rt, air. [b] GC yields based on **2a**. [c] Isolated yields based on **2a**. [d] Pt(−)IIPt(+) instead of Pt(−)IIC(+). [e] Ni(−)IIC(+) instead of Pt(−)IIC(+). [f] 4.0 equiv. of **1a** was used.

Table 2. Substrate scope of alkenes and diorganoselenides.^{a,b}

3a, R = H, 92% yield
3b, R = Me, 90% yield
3c, R = OMe, 92% yield
3d, R = F, 91% yield
3e, R = Cl, 85% yield
3f, R = Br, 89% yield

3g, R = H, 93% yield
3h, R = Me, 92% yield
3i, R = OMe, 87% yield
3j, R = I, 84% yield

3k, R = Me, 92% yield
3l, R = OMe, 86% yield

3m, 56% yield

3n, 54% yield

3o, R^3 = Me, 88% yield
3p, R^3 = 4-ClC$_6$H$_4$, 87% yield
3q, R^3 = benzyl, 52% yield
3r, R^3 = 4-OMeC$_6$H$_4$, trace^c

3s, R = Me, 90% yield
3t, R = F, 91% yield
3u, R = Cl, 92% yield
3v, R = Br, 90% yield

^{a} Unless otherwise noted, all reactions were carried out with **1** (0.5 mmol), **2** (0.25 mmol), KI (0.125 mmol), CH$_3$CN (5.0 mL), H$_2$O (0.5 mL), Pt (15 mm×15 mm×0.3 mm) cathode, C (φ 4 mm) anode, I = 6.0 mA, in air, at room temperature for 16 hours; ^{b} Isolated yields based on **2**; ^{c} Determined by GC-MS.

91 %). However, when di(4-methylphenyl)diselenide or di(4-methoxyphenyl) diselenide were used as selenide reagents under the optimal conditions, trace yields were obtained, mainly due to the weak eletrophilicity of intermediate ArSe$^+$ substituted by electron-donating groups (eg. Me, OMe) (**3 r**, trace). In addition, the optimal conditions were also suitable for the oxyselenation of ethene-1,1-diyldibenzene with diphenyldiselenide, for giving the desired product **3 n** in the yield of 54 %. The oxyselenation of varieties of styrenes with di(4-chlorophenyl) diselenide was also explored, and all the reactions gave corresponding products in excellent yields (**3 s**–**3 v**, 90 %–92 %).

Our efforts then focused on exploring the substrate scope with respect to other nucleophilic oxygen sources, such as alcohols (including primary, secondary and tertiary alcohols) could be also applied in this iodide-catalyzed electrochemical oxyselenation to give the corresponding ether selenides in excellent yields (Table 3). A series of alcohols also undergo the oxyselenation efficiently, and correponding products were obtained in the yields of 84 %–90 %, except for tertiary butanol and adamantanol (**3 ac**, 43 % and **3 ag**, n.d.), mainly due to their large steric hindrance. No obvious decrease in yields was observed, when the chain length of the primary alcohol was extended to nine carbons (**3 ad**, 87 %). The oxyselenation was also suitable for cyclopentanol and cyclohexanol for giving the desired products in the yields of 85 % and 83 % respectively (**3 ae** and **3 af**).

The iodide-catalyzed electrochemical oxyselenation could also be carried out on a larger scale reaction, and desired paroducts **3 a** and **3 x** were obtained in the yields of 76 % and 71 % respectively, when 3.0 mmol of styrene (**1 a**) was treated with diphenyldiselenide (**2 a**) in CH$_3$CN/H$_2$O or CH$_3$CN/EtOH,
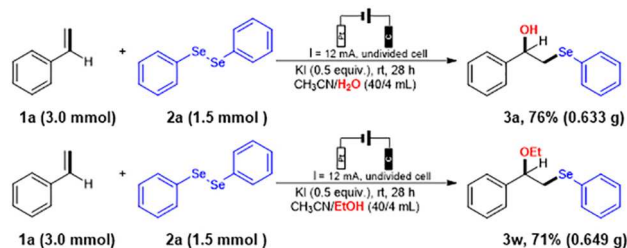
Scheme 2. Larger-scale reactions.
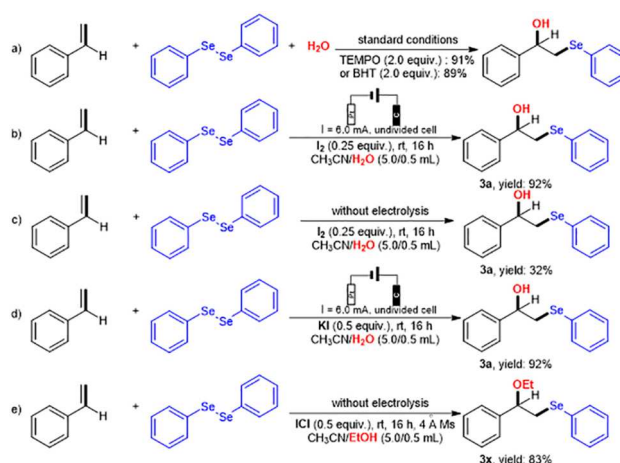
Scheme 3. Control experiments for mechanism study.

under the standard conditions by increasing the constant current to 12 mA, and extending the reaction time to 28 h (Scheme 2).

To shed light on the mechanism of the iodide-catalyzed electrochemical oxyselenation, 2.0 equiv. of TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl) or BHT (butylated hydroxytoluene) was used as radical scavenger under the optimal conditions, and desired product 1-phenyl-2-(phenylselanyl) ethan-1-ol (**3 a**) was obtained in the yield of 91 % and 89 % respectively, indicating no single-electron transfer was involved through the whole reaction process (Scheme 3, a). In addition, the electrochemical oxyselenation could undergo efficiently in the presence of 0.25 equiv. of I$_2$ (Scheme 3, b, 92 %), while low yield (32 %) was observed without electrolysis (Scheme 3, c and d), suggesting that iodine cation I$^+$ should be the practical catalyst during the oxyselenation, which was also consistent with the result of ICl catalyzed oxyselenation (Scheme 3, e, 83 %). Next, the cyclic voltammetry (CV) experiments was carried out to study the oxidation potential of the substrates, and results showed that the oxidation potential of potassium iodide (1.98 V vs Ag/AgCl) was lower than that of styrene (3.51 V vs Ag/AgCl) and diphenyldiselenide (2.67 V vs Ag/AgCl) (Figure 1), which indicated that the oxidation of iodide should occur first under the galvanostatic mode.[22]

On the basis of previous works[22,23] and above experimental results, a possible mechanism has been depicted in Scheme 4. The first step of the oxyselenation is the generation of the I$^+$ by

**Table 3.** Substrate scope of alcohols.^{a,b}

^{a} Unless otherwise noted, all reactions were carried out with **1** (0.5 mmol), **2** (0.25 mmol), KI (0.125 mmol), CH$_3$CN (5.0 mL), ROH (0.5 mL), Pt (15 mm×15 mm×0.3 mm) cathode, C (ϕ 4 mm) anode, I = 6.0 mA, in air, at room temperature for 16 hours; ^{b} Isolated yields based on **2**; ^{c} N. D. = not detected.
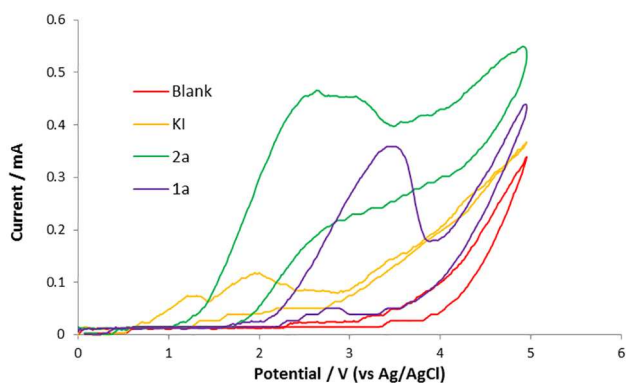
Figure 1. For cyclic voltammetrys of **1a** and **2a** (10^{-2} M): CH$_3$CN with n-Bu$_4$NBF$_4$ (0.005 M); for KI (10^{-2} M): CH$_3$CN without n-Bu$_4$NBF$_4$. Conditions: 3 mm diameter glassy carbon disc working electrode, Pt plate electrode, Ag/AgCl reference electrode, scan rate $= 0.2\ v\,s^{-1}$.
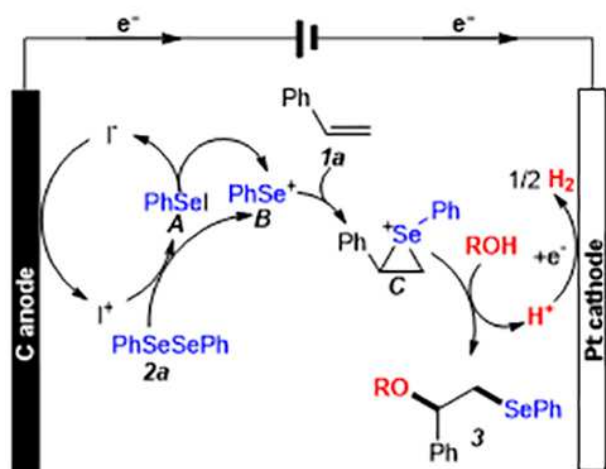
Scheme 4. Proposed mechanism for the iodide-catalyzed electrochemical oxyselenation.

losing two electrons, then the diphenyldiselenide undergoes electrophilic substituion by I$^+$ to give PhSeI (**A**), and release PhSe$^+$ (**B**), which can also be converted from PhSeI (**A**). The coordination of electrophile PhSe$^+$ with styrene forms seleniranium ion **C**, which reacts with ROH to yield final proudcts **3**.

Conclusion

In summary, we have developed an effecient and green protocol for the synthesis of β-hydroxy(alkoxy) selenides via iodide-catalyzed electrochemical oxyselenation of styrene derivatives using 0.5 equiv. of KI as electrolyte and catalyst. A broad range of styrene derivatives, diorganodiselenides and alcholds were tolerated, and all the desired products could be obtained in moderate to excellent yields. Other advantages include transition-metal and oxidant-free, simple operation, mild reaction conditions, atomic economy and less waste, providing a convenient way to β-hydroxy(alkoxy) selenides.

Experimental Section

General procedure for the iodide-catalyzed electrochemical oxy-selenation of styrenes: In an undivided three-necked flask (25 mL) equipped with a stir bar, styrene derivatives (0.5 mmol), dialykl(aryl) diselenides (0.25 mmol), H$_2$O or alcohols (0.5 mL), KI (20.8 mg, 0.125 mmol), CH$_3$CN (5 mL) were combined and added. The flask was equipped with platinum electrodes (15 mm × 15 mm × 0.3 mm) as cathode, graphite rod (Φ 4 mm) as the anode. The reaction mixture was stirred and electrolyzed at a constant current of 6.0 mA under room temperature for 16 h. The solvent was removed with a rotary evaporator. The pure product was obtained by flash chromatography on silica gel using petroleum ether and ethyl acetate as the eluent.

Conflict of Interest

The authors declare no conflict of interest.

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