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Visible light-promoted, iodine-catalyzed selenoalkoxylation of olefins with diselenides and alcohols in the presence of hydrogen peroxide/air oxidant: an efficient access to *α*-alkoxyl selenides

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Under iodine-catalyzed and visible light-irradiated aerobic conditions, selenoalkoxylation of olefins with diselenides and alcohols can be efficiently achieved to afford the useful *α*-alkoxyl selenides in the presence of only 0.5 equiv. of H_2O_2. Controlling the sub-stoichiometric H_2O_2 amount is crucial to avoid the non-selective over-oxidation of the diselenides that leads to the ineffective hyper-valent selenium compounds. Meanwhile, under visible light irradiation, the green, safe, and low-cost air can work as a supplemental mild oxidant in the reaction to ensure selective oxidation of the diselenides, full conversion of the reactants, and ultimately good yield of the products.

selenium, alkoxyl selenide, aerobic oxidation, visible light, iodine catalysis

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1 Introduction

Organoselenium compounds have been widely used in biochemistry, medicinal chemistry, organic synthesis, and material science [1,2]. Recently, the eco-friendly aspects of organoselenium chemistry began to draw much attention [3]. Among reported works, organoselenium catalysis [3–5] is an important subject with good industrial application potential because of the clean procedures, transition-metal-free conditions and the metabolizable catalytic element, which is safe to the environment [6]. During the last three years, our group [5] has been taking great effort in organoselenium-catalyzed reactions to develop the green synthetic methods. We were also very interested in screenings of organoselenium compounds that might serve as the starting materials for selenium catalyst development. Recently, *α*-alkoxylselenides came into our sight because of their unique chemical structures. The selenium-containing moieties of these compounds might have catalytic activities, while the adjacent alkoxyl group might allow fixing these molecules onto solid phase carriers to develop the recyclable heterogeneous catalysts [5b,7]. In addition, the adjacent oxygen and selenium groups might well coordinate with transition metals to prepare novel metal complexes with potential unique catalytic activity [8].

Currently, *α*-alkoxyl selenides can be directly synthesized through the selenoalkoxylation reaction of alkenes with electrophilic organoselenium compounds (e.g., RSeBr, RSeCl, etc.) and alcohols, which employs the sensitive organoselenium halides, resulting in the undesirable side reactions

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that leads to the carcinogenic organohalide by-products [9]. The reaction of diselenides with chemical oxidants can generate the electrophilic organoselenium cations *in situ* as well, which avoids the formation of organohalides, but produces mass wastes in the procedures and limits the further large-scale applications [10]. Braga *et. al.* [11] have reported a nice method to prepare α-alkoxyl selenides through a solvent-free selenoalkoxylation reaction of alkenes with diselenides and alcohols, but the reaction employed dimethyl sulphoxide (DMSO) as the oxidant that inevitably led to the smelly by-product Me_2S. Moreover, this protocol used micro-wave as the driven force, which was highly effective in laboratory but required specialized equipment and might result in the high energy consumption in large-scale preparation. Therefore, novel methods that are free of waste generations and employ renewable energy are still required from the practical viewpoint.

Yet, reactions driven by visible light have attracted chemists because of their clean procedures, mild conditions and simple equipments for industrial production [12,13]. These methods afforded additional opportunities to utilize sunlight as the abundant, renewable, and clean energy as well. Recently, we developed an efficient protocol to prepare α-alkoxyl selenides through the visible light-promoted selenoalkoxylation reaction of alkenes with alcohols and diselenides. The reactions were catalyzed by low-loading I_2 and employed H_2O_2/air as the clean oxidant that generated no wastes. Moreover, compared with the reported visible light-promoted reactions [12,13], the method is free of the expensive metal complex catalysts or photosensitizers. Herein, we wish to report our findings.

2 Experimental

2.1 General methods

All solvents employed were analytical pure (AR) and were directly used. Reagents were purchased from the reagent merchant and their purities were more than 98% and were directly used. Styrene is distilled by vacuum distillation before using. IR spectra were measured on Bruker Tensor 27 Infrared spectrometer (Germany). ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance 600/400 instrument (600 or 400 MHz for ^{1}H NMR and 150 or 100 MHz for ^{13}C NMR) using $CDCl_3$ as the solvent and Me_4Si as the internal standard. Chemical shifts for ^{1}H and ^{13}C NMR were reported in parts per million (ppm). Mass spectra were measured on a Shimadzu GCMS-QP2010 Ultra spectrometer (EI) and maxis (ESI) (Japan).

2.2 General procedure for the preparation of 4

1 mmol of olefin **1**, 0.5 mmol of selenide **2**, 1 mL of alcohol **3**, 0.5 mmol of 30 *w*/*w*% H_2O_2 and 0.1 mmol of iodine were initially added into a reaction tube. Air was then introduced at the rate of 0.88 cm^3/s into the system and at room temperature under the irradiation of a 200 W incandescent light. The reaction was monitored by thin-layer chromatography (TLC). When the reaction terminated, the solvent was evaporated under reduced pressure. The residue was purified by column chromatography (EtOAc/petroleum ether: 1/20) to give the corresponding compounds **4**. For the reaction with $PhCH_2OH$ (Table 2, vide infra, entry 8 in text), 1 mmol of $PhCH_2OH$ was employed and the reaction was performed in 1 mL of MeCN solvent. The characterization data and NMR spectra of the compounds were given in Supporting Information online.

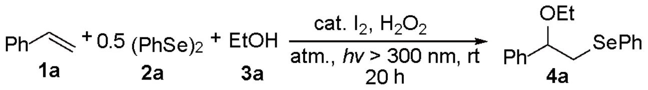
2.3 Detailed procedure for the outdoor reaction under sunlight

1 mmol of styrene **1a**, 0.5 mmol of diphenyl diselenide **2a**, 1 mL of ethanol **3a**, 0.5 mmol of 30 *w*/*w*% H_2O_2 and 0.1 mmol of iodine were initially added into a reaction tube. Air was then introduced into the system at the rate of 0.88 cm^3/s and at room temperature under sunlight for 20 h, totally. The reaction was performed in sunny days in the summer of 2016. It spent two days and the reaction time was from 7 a.m. to 5 p.m. for each day. When the reaction terminated, the solvent was evaporated under reduced pressure. The residue was purified by column chromatography (EtOAc/petroleum ether: 1/20) to give the corresponding compound **4a** in 95% yield.

3 Results and discussion

The selenoalkoxylation reaction of styrene **1a** with $(PhSe)_2$ and EtOH was initially employed to optimize the reaction conditions. Irradiating the solution of styrene **1a** (1 M) and $(PhSe)_2$ **2a** (0.5 M) in EtOH **3a** with sub-stoichiometric H_2O_2 oxidant (50 mol%) by a 200 W incandescent lamp for 20 h afforded the desired adduct **4a** in 45% yield (Table 1, entry 1). Further screenings demonstrated that addition of catalytic I_2 obviously improved the reaction (Table 1, entries 2–5) and the product **4a** could be obtained in almost quantitative yield by using 10 mol% of I_2, (Table 1, entry 5). Experiment performed under N_2 protection decreased the product yield, indicating that air might participate as an additional oxidant in the process (Table 1, entry 6). Nevertheless, the reactions were retarded without H_2O_2 even when performed in pure O_2 atmosphere (Table 1, entries 7, 8); Extending the reaction time only slightly enhanced the product yield in the absence of H_2O_2 (Table 1, entry 9). The effect of H_2O_2 amount was also examined and using 50 mol% of H_2O_2 was found to be the preferable condition (Table 1, entries 5 vs. 10–12). Increased H_2O_2 amount contrarily reduced the product yield, probably due to the over-oxidation of $(PhSe)_2$ into $PhSeO_3H$, which was ineffective for the reaction (Table 1, entries 11–12) [5].

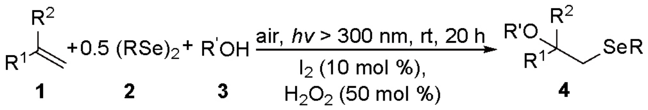
Table 1 Condition optimizations[a)]

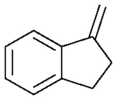


Entry	I_2 (mol%)	H_2O_2 (mol%)	Atm.	**4a** (%)[b)]
1	–	50	air	45
2	2	50	air	75
3	6	50	air	82
4	8	50	air	90
5	10	50	air	99
6	10	50	N_2	50
7	10	–	air	60
8	10	–	O_2	65
9	10	–	O_2	69[c)]
10	10	40	air	91
11	10	80	air	88
12	10	160	air	53

a) 1 mmol of **1a** and 0.5 mmol of **2a** in 1 mL of EtOH were irradiated by a 200 W incandescent lamp at room temperature for 20 h; b) isolated yields based on **1a**; c) the reaction time was extended to 60 h.

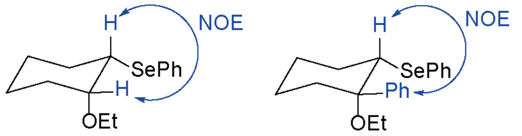
Table 2 Synthesis of α-alkoxyl selenides[a)]



Entry	R^1, R^2	R	R′	**4**: yield (%)[b)]
1	Ph, H	Ph	Et	**4a**: 99, 97[c)]
2	Ph, H	3-FC_6H_4	Et	**4b**: 69 (79)
3	Ph, H	4-FC_6H_4	Et	**4c**: 98
4	Ph, H	4-MeC_6H_4	Et	**4d**: 76
5	Ph, H	4-$MeOC_6H_4$	Et	**4e**: 86
6	Ph, H	*n*-Bu	Et	**4f**: 41 (50)
7	Ph, H	Ph	Me	**4g**: 98
8	Ph, H	Ph	$PhCH_2$	**4h**: 90[d)]
9	Ph, H	Ph	*c*-C_6H_{11}	**4i**: 61
10	Ph, H	Ph	*i*-Pr	**4j**: 47 (70)
11	Ph, H	Ph	*t*-Bu	**4k**: 41 (51)
12	4-BrC_6H_4, H	Ph	Et	**4l**: 86
13	4-ClC_6H_4, H	Ph	Et	**4m**: 90
14	4-MeC_6H_4, H	Ph	Et	**4n**: 99
15	4-ClC_6H_4, Me	Ph	Et	**4o**: 73
16	Ph, *c*-C_6H_{11}	Ph	Et	**4p**: 80
17	Ph, Ph	Ph	Et	**4q**: 40 (51)[e)]
18	4-ClC_6H_4, 4-ClC_6H_4	Ph	Et	**4r**: 40 (53)
19		Ph	Et	**4s**: 70

a) Without special instructions, the reactions were performed under optimized conditions described in Table 1, entry 5; b) isolated yields based on the feed amount of **1** outside the parentheses; isolated yields based on the converted **1** inside the parentheses; c) reaction performed at 10 mmol-scale; d) 1 mmol of benzyl alcohol and 1 mL of MeCN were employed; e) reaction time was extended to 48 h.

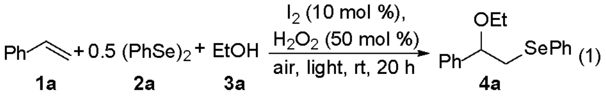
Under the optimized conditions, a series of α-alkoxyl selenides **4** were then synthesized (Table 2). It was found that both of the electron-deficient or -enriched diaryl diselenides led to the corresponding α-alkoxyl selenides **4a**–**4e** smoothly in 69%–99% yields (Table 2, entries 1–5). Dialkyl diselenide ($(n\text{-BuSe})_2$) as substrate was also tested, but the reaction proceeded slowly and gave the desired product **4f** in low yield, while the starting materials were not converted completely (Table 2, entry 6). Primary alcohols, such as EtOH, MeOH, and $PhCH_2OH$, were preferable for the reaction, affording the corresponding product **4a**, **4g,** and **4h** in excellent yields (Table 2, entries 1, 7, 8), while secondary or tertiary alcohols were obviously unfavorable substrates and gave the related products in decreased yields (Table 2, entries 9–11). It was found that both electron-enriched and-deficient styrene derivatives led to the corresponding α-alkoxyl selenides smoothly in good to excellent yields (Table 2, entries 12-14). 1-Alkyl-1-aryl-substituted ethenes afforded the products in good yields (Table 2, entries 15, 16), but the 1,1-*bis*aryl-substituted alkenes were obviously not preferable for the reaction, giving **4q** and **4r** in poor yields even with extended reaction time (Table 2, entries 17, 18). Exocyclic alkene **1s** was also fit for the reaction, affording **4s** in 70% yield (Table 2, entry 19). The reaction of the cyclic alkenes cyclohexene (**1t**) and 1-phenylcyclohexene (**1u**) with diselenide and alcohol led to the α-alkoxyl selenides **4t** and **4u**, which were *syn*-adducts, as confirmed by the nuclear overhauser effect spectroscopy (NOESY) analysis (Figure 1, for details please see Supporting Information online). The reaction of 1,2-disubstited alkene, such as 1,2-diphenylethene, was tested, but was retarded under the mild visible light-irradiation conditions. Benzoic acid, the oxidative C=C cleavage by-product was generated and detected in gas chromatography-mass spectrum (GC-MS) after heating at 80 °C in a sealed tube.



4t, 53% **4u**, 60% (74%)

Figure 1 NOESY study of the products **4t** and **4u** (color online).

Reactions of **1a** with **2a** in EtOH driven by different light sources were also examined. As shown in Eq. (1), the reactions irradiated by LEDs blue or white light both led to very good product yields at 90% and 91%, respectively. An outdoor experiment under sunlight afforded the product **4a** in 95% yield. The results clearly showed the possibility for the utilization of solar energy in this reaction for future industrial-scale production.



90% (LEDs blue light)
91% (LEDs white light)
95% (Sunlight)

Mechanisms of this interesting reaction were our next concern and a series of control experiments were conducted. The reaction was slowed down without light irradiation (Table 3, entry 1) and was further restrained in dark (Table 3, entries 2, 3). Comparison of the results with those in Table 1, entries 5, 6 indicated that the use of air as oxidant required visible light irradiation as the driven force. Without I_2, the product was obtained in very low yield (Table 3, entries 4, 5). No reaction occurred when H_2O_2 was further removed (Table 3, entry 6). But with sufficient I_2 (50–100 mol%), the reaction could occur even without H_2O_2 in dark and under N_2 protection to give **4a** in 48%–89% yields and AgI precipitations could be observed after adding the solutions into aqueous $AgNO_3$

Table 3 Control experiments[a)]

Entry	Conditions[b)]	C_{1a}[c)]	**4a** (%)[d)]
1	Without additional light irradiation (ambient light), I_2 (10%), H_2O_2 (50%), air	73	70
2	In dark, I_2 (10%), H_2O_2 (50%), air	63	58
3	In dark, I_2 (10%), H_2O_2 (50%), N_2	47	43
4	In dark, H_2O_2 (50%), air	14	12
5	In dark, H_2O_2 (50%), N_2	11	10
6	In dark, N_2	0	0
7	In dark, I_2 (50%), N_2	61	48
8	In dark, I_2 (100%), N_2	>99[e)]	89
9	Visible light irradiation, I_2 (10%), H_2O_2 (50%), air hydroquinone (100%)	>99[e)]	91
10	Visible light irradiation, I_2 (10%), H_2O_2 (50%), air TEMPO (100%)	>99[e)]	93
11	Visible light irradiation, I_2 (10%), H_2O_2 (50%), air AIBN (100%)	>99[e)]	45[f)]

a) 1 mmol of **1a**, 0.5 mmol of **2a**, and 1 mL of EtOH were employed; the reactions were conducted at room temperature for 20 h; b) molar ratio of I_2, H_2O_2 or additives based on **1a** inside the parentheses; c) conversion ratio of **1a** determined by GC; d) isolated yields of **4a** based on **1a**; e) full conversion of **1a**; f) reaction finished within 4 h

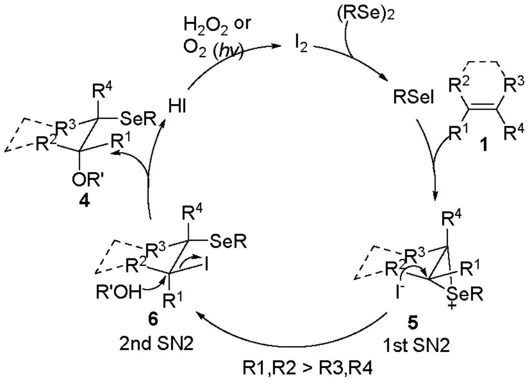
(Table 3, entries 7, 8), showing that the re-oxidation of the generated HI into I_2 by H_2O_2 or air should be a crucial step in the I_2 catalysis circle. Although $(PhSe)_2$ might generate free radicals under the visible light irradiation conditions [1e], the addition of hydroquinone or 2,2,6,6-tetramethylpiperidinooxy (TEMPO) as free radical scavenger did not obviously restrain the reaction (Table 3, entries 9, 10), while the addition of free radical initiator azodiisobutyronitrile (AIBN) resulted in the decreased **4a** yield and the generation of many unidentified by-products on the contrary (Table 3, entry 11), indicating that free-radical mechanisms should be excluded during the processes. In summary, the above experimental results showed that the alkene selenoalkoxylation occurred through an I_2-initiated non-free radical reaction which might release HI. In the process, H_2O_2 and air were crucial oxidants to regenerate I_2 from HI and the aerobic oxidation of HI required visible light irradiation condition.

On the basis of the above experimental results as well as Refs. [14–16], a possible mechanism was supposed. First of all, as supported by the result of our previous ^{77}Se NMR studies [5a], the oxidation of $(PhSe)_2$ with 1 equiv. of H_2O_2 could furnish PhSeOH (Eq. (2)).

$$(PhSe)_2 + \underset{\text{1 equiv.}}{H_2O_2} \xrightarrow{N_2} 2PhSeOH \qquad (2)$$

^{77}Se NMR chemical shift
dtd. at 1056 ppm (Ref. 5a)

In the reaction, the amount of H_2O_2 was controlled to be sub-stoichiometric to avoid the possible non-selective over-oxidation that might lead to the hyper-valent selenium species, which were ineffective for the reaction (Table 1, entries 5 vs. 11, 12) [5]. The reaction of styrene with PhSeOH and ethanol could afford the desired product **4a**, but because of the sub-stoichiometric H_2O_2 amount, styrene and diselenide could not be completely converted (Table 1, entry 1). Addition of I_2 led to PhSeI [14], which was more active than PhSeOH and soon reacted with alkenes [15] to generate the onium **5** (Scheme 1). Nucleophilic attack of I^- at the backside led to the intermediate **6**, in which the bulky selenium groups were at the less steric hindrance carbon. Another nucleophilic substitution of alcohol with **6** afforded the product **4** and HI (Table 3, entries 7, 8), which could be re-oxidized into I_2 by H_2O_2 or air and the oxidation of HI by air was driven by visible light irradiation. As indicated by the results in Table 3, entries 9–11, the reactions of diselenides in the presence of strong oxidants were inclined to occur via electrophilic processes [16], which contributed to the high stereo-selectivity for cyclic alkene substrates and led to only *syn*-adducts (Figure 1) because of the double SN2 attacks from the backsides (Scheme 1), as reported by Denmark's group in 2015 [4c].



Scheme 1 Possible mechanisms for the visible light-promoted, iodine-catalyzed selenoalkoxylation of olefins with diselenides and alcohols.

4 Conclusions

In conclusion, an efficient alkene selenoalkoxylation method for the synthesis of *α*-alkoxyl selenides was developed. In the reaction, controlling of the sub-stoichiometric H_2O_2 amount was crucial to avoid the non-selective over-oxidation of diselenides. Catalyzed by I_2 and under visible light irradiation, air could be utilized as a supplemental oxidant to achieve the full conversion of alkenes and diselenides. Further investigations on the applications of *α*-alkoxyl selenides in selenium catalyst development are on the way in our laboratory.

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Conflict of interest The authors declare that they have no conflict of interest.

Supporting information The supporting information is available online at http://chem.scichina.com and http://link.springer.com/journal/11426. The supporting materials are published as submitted, without typesetting or editing. The responsibility for scientific accuracy and content remains entirely with the authors.

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