

A Novel and Efficient Alkoxylation of Alkenes

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Summary: A novel and efficient alkoxylation from alkenes, diselenides, and alcohols mediated by iodine is developed, with which a series of β -alkoxy selenides are synthesized. In this procedure, firstly, I_2 reacts with diselenide to form *in situ* the active electrophilic selenium species $RSeI$, then following an electrophilic addition of it to alkenes provides β -alkoxy selenides with high regioselectivity and in good yields. This new method for achieving β -alkoxy selenides has some advantages over other methods such as using available and cheap iodine as the oxidizing species at room temperature, which makes this reaction has milder reaction conditions and simpler procedure.

Keywords: Alkoxylation, β -alkoxy selenides, Alkene, Diselenide, I_2 .

Introduction

Recently, the vicinal difunctionalization of alkenes has been increasing in importance for the synthesis of complex organic compounds [1-5]. The alkoxylation of alkenes is a representative for the difunctionalization of alkenes so that both an organoselenium group and an alkoxy group can be introduced into organic molecules. β -Alkoxy selenides is a significant class of organoselenium compounds [6-8], and there are several methods for their preparation. The traditional method is the electrophilic addition of $PhSeX$ ($X = Br, Cl$) to alkenes [9-11], although the selenylating reagent $PhSeX$ is commercially available, the toxic and moisture-sensitive nature of them, as well as the nucleophilic halide anions, can give rise to undesirable side processes. Alternatively, the oxidation of less expensive and less toxic diphenyl diselenide for obtaining the electrophilic organoselenium cation is the simpler procedure. There are several suitable oxidants such as ammonium peroxydisulfate $(NH_4)_2S_2O_8$ [9, 10, 12], *m*-nitrobenzenesulfonyl peroxide $(O_2NC_6H_4SO_3)_2$ [13, 14], 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) [15], Oxone [16], hypervalent iodine reagent $PhI(OAc)_2$ [17-21], and other oxidative systems [22-26]. However, the drawback of some oxidants are toxic or expensive, and some reactions need a long reaction time or a high reaction temperature, which limit some of the above methods in further applications.

In order to develop simpler and general methods for the preparation of β -alkoxy selenides, we recently developed a convenient alkoxylation of alkenes which was promoted by *p*-toluenesulfonic acid [27]. More

recently, we used molecular iodine to treat diselenides to form the active electrophilic selenium species $RSeI$, and a new synthesis of aminoselenides was reported [28]. Based on this, we have investigated the alkoxylation of alkenes in the presence of I_2 . Now, we wish to report an iodine-mediated alkoxylation of alkenes.

Experimental

IR spectra were recorded on a Thermo-Nicolet 6700 instrument, NMR spectra were measured on a Bruker AVANCE III (500MHz) spectrometer, and Mass spectra were determined on Thermo-ITQ 1100 mass spectrometer. Alkenes, diselenides, I_2 , MeOH, EtOH, and benzyl alcohol were commercially available.

Typical procedure for the alkoxylation of alkenes mediated by I_2

To ethyl acetate (2.0 mL), alkene **1** (1.2 mmol), diselenide **2** (0.5 mmol), alcohol **3** (1.0 mL) and I_2 (0.5 mmol) were added successively. The mixture was vigorously stirred at r.t. for 10 h. Upon completion, the reaction was quenched by addition of sat. aq $Na_2S_2O_3$ (2 mL), basified with sat. aq Na_2CO_3 (8 mL) and H_2O (5 mL). The mixture was extracted with CH_2Cl_2 (3×5 mL), and the combined organic phase was dried over anhydrous Na_2SO_4 , filtered, and concentrated under reduced pressure. The residue was then purified by TLC technique (petroleum ether/ethyl acetate (4/1)) to furnish β -alkoxy selenides **4**.

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2-Methoxy-2-phenylethyl phenyl selenide (4a) [29]

Colorless oil. $^1\text{H-NMR}$ (500 MHz, CDCl_3): 7.54-7.48 (m, 2H), 7.41-7.29 (m, 5H), 7.30-7.25 (m, 3H), 4.38 (dd, $J = 8.4, 5.0$ Hz, 1H), 3.35 (dd, $J = 12.4, 8.5$ Hz, 1H), 3.27 (s, 3H), 3.13 (dd, $J = 12.3, 5.0$ Hz, 1H). $^{13}\text{C-NMR}$ (125 MHz, CDCl_3): 141.1, 132.6, 130.8, 129.0, 128.6, 128.1, 126.8, 126.7, 83.5, 57.2, 35.5. IR (cm^{-1}): 3059, 2933, 2822, 1579, 1478, 1106, 736, 702. MS (EI, m/z , %): 293 ($\text{M}+1^+$, 66.8).

2-Methoxy-2-(p-tolyl)ethyl phenyl selenide (4b) [27]

Colorless viscous oil. $^1\text{H-NMR}$ (500 MHz, CDCl_3): 7.54-7.50 (m, 2H), 7.29-7.20 (m, 7H), 4.35 (dd, $J = 8.4, 5.1$ Hz, 1H), 3.36 (dd, $J = 12.2, 8.4$ Hz, 1H), 3.26 (s, 3H), 3.13 (dd, $J = 12.2, 5.1$ Hz, 1H), 2.38 (s, 3H). $^{13}\text{C-NMR}$ (125 MHz, CDCl_3): 138.0, 137.8, 132.4, 130.9, 129.4, 129.1, 126.7, 126.6, 83.1, 57.1, 35.5, 21.3. IR (cm^{-1}): 2931, 2820, 1730, 1579, 1478, 1103, 737. MS (EI, m/z , %): 307 ($\text{M}+1^+$, 7.7).

2-(4-t-Butyl)phenyl)-2-methoxyethyl phenyl selenide (4c) [27]

Pale yellow viscous oil. $^1\text{H-NMR}$ (500 MHz, CDCl_3): 7.51-7.48 (m, 2H), 7.39-7.35 (m, 2H), 7.30-7.22 (m, 5H), 4.38 (dd, $J = 8.5, 4.9$ Hz, 1H), 3.36 (dd, $J = 12.3, 8.5$ Hz, 1H), 3.28 (s, 3H), 3.13 (dd, $J = 12.3, 4.9$ Hz, 1H), 1.35 (s, 9H). $^{13}\text{C-NMR}$ (125 MHz, CDCl_3): 151.0, 137.9, 132.6, 131.0, 129.1, 126.7, 126.5, 125.4, 83.0, 57.1, 35.4, 34.5, 31.5. IR (cm^{-1}): 3056, 2963, 2821, 1477, 1106, 832, 736, 691. MS (EI, m/z , %): 349 ($\text{M}+1^+$, 7.5).

(2-(4-Bromophenyl)-2-methoxyethyl phenyl selenide (4d) [27]

Colorless viscous oil. $^1\text{H-NMR}$ (500 MHz, CDCl_3): 7.51-7.44 (m, 4H), 7.27-7.16 (m, 5H), 4.33 (dd, $J = 8.1, 5.6$ Hz, 1H), 3.31 (dd, $J = 12.4, 7.9$ Hz, 1H), 3.26 (s, 3H), 3.10 (dd, $J = 12.1, 5.5$ Hz, 1H). $^{13}\text{C-NMR}$ (125 MHz, CDCl_3): 140.1, 132.8, 131.8, 130.5, 129.1, 128.5, 127.2, 122.0, 82.6, 57.0, 35.1. IR (cm^{-1}): 2931, 1728, 1580, 1479, 1260, 823, 737.2 690. MS (EI, m/z , %): 371 ($\text{M}+1^+$, 13.7).

(2-(4-Chlorophenyl)-2-methoxyethyl phenyl selenide (4e) [27]

Colorless viscous oil. $^1\text{H-NMR}$ (500 MHz, CDCl_3): 7.51-7.46 (m, 2H), 7.35-7.25 (m, 7H), 4.35 (dd, $J = 8.0, 5.6$ Hz, 1H), 3.31 (dd, $J = 12.4, 7.8$ Hz, 1H), 3.25 (s, 3H), 3.10 (dd, $J = 12.5, 5.6$ Hz, 1H). $^{13}\text{C-NMR}$ (125 MHz, CDCl_3): 139.5, 133.8, 132.8, 130.5, 129.0, 128.7, 128.3, 127.1, 82.7, 57.0, 35.2. IR

(cm^{-1}): 2933, 2922, 1730, 1479, 1088, 828, 737, 691. MS (EI, m/z , %): 327 ($\text{M}+1^+$, 44.8).

2-Methoxycyclohexyl phenyl selenide (4f) [30]

Colorless viscous oil. $^1\text{H-NMR}$ (500 MHz, CDCl_3): 7.63-7.59 (m, 2H), 7.30-7.24 (m, 3H), 3.39 (s, 3H), 3.31-3.27 (m, 1H), 3.23-3.16 (m, 1H), 2.21-2.14 (m, 1H), 2.03-1.96 (m, 1H), 1.78-1.50 (m, 3H), 1.34-1.22 (m, 3H). $^{13}\text{C-NMR}$ (125 MHz, CDCl_3): 135.3, 132.9, 128.8, 127.4, 82.2, 56.4, 47.4, 32.1, 30.3, 25.7, 23.4. IR (cm^{-1}): 2932, 1730, 1437, 1188, 740, 693. MS (EI, m/z , %): 270 (M^+ , 18.4).

2-Ethoxy-2-phenylethyl phenyl selenide (4g) [29]

Colorless viscous oil. $^1\text{H-NMR}$ (500 MHz, CDCl_3): 7.54-7.50 (m, 2H), 7.40-7.22 (m, 8H), 4.49 (dd, $J = 8.7, 5.0$ Hz, 1H), 3.46-3.30 (m, 3H), 3.12 (dd, $J = 12.4, 5.0$ Hz, 1H), 1.21 (t, $J = 7.0$ Hz, 3H). $^{13}\text{C-NMR}$ (125 MHz, CDCl_3): 141.7, 132.7, 131.0, 128.9, 128.5, 127.8, 126.8, 126.6, 81.6, 64.7, 35.6, 15.4. IR (cm^{-1}): 2975, 2863, 1580, 1477, 1092, 736, 702. MS (EI, m/z , %): 307 ($\text{M}+1^+$, 23.4).

2-(4-t-Butyl)phenyl)-2-ethoxyethyl phenyl selenide (4h) [27]

Colorless viscous oil. $^1\text{H-NMR}$ (500 MHz, CDCl_3): 7.53-7.48 (m, 2H), 7.38-7.34 (m, 2H), 7.30-7.22 (m, 5H), 4.48 (dd, $J = 8.7, 5.1$ Hz, 1H), 3.49-3.30 (m, 3H), 3.11 (dd, $J = 12.2, 5.0$ Hz, 1H), 1.33 (s, 9H), 1.21 (t, $J = 7.0$ Hz, 3H). $^{13}\text{C-NMR}$ (125 MHz, CDCl_3): 150.8, 138.6, 132.5, 131.1, 128.9, 126.6, 126.3, 125.3, 81.7, 64.6, 35.6, 34.5, 31.4, 15.2. IR (cm^{-1}): 2966, 2868, 1579, 1478, 1093, 735. MS (EI, m/z , %): 363 ($\text{M}+1^+$, 10.2).

2-(4-Chlorophenyl)-2-ethoxyethyl phenyl selenide (4i) [27]

Colorless viscous oil. $^1\text{H-NMR}$ (500 MHz, CDCl_3): 7.51-7.48 (m, 2H), 7.33-7.22 (m, 7H), 4.46 (dd, $J = 8.2, 5.5$ Hz, 1H), 3.42-3.27 (m, 3H), 3.08 (dd, $J = 12.1, 5.6$ Hz, 1H), 1.20 (t, $J = 7.0$ Hz, 3H). $^{13}\text{C-NMR}$ (125 MHz, CDCl_3): 140.4, 133.6, 132.8, 130.6, 129.2, 128.7, 127.9, 126.8, 80.8, 64.7, 35.3, 15.3. IR (cm^{-1}): 2976, 2869, 1579, 1478, 1090, 826, 737. MS (EI, m/z , %): 341 ($\text{M}+1^+$, 2.1).

2-Benzoyloxy-2-phenylethyl phenyl selenide (4j) [27]

Colorless viscous oil. $^1\text{H-NMR}$ (500 MHz, CDCl_3): 7.50-7.30 (m, 12H), 7.27-7.21 (m, 3H), 4.62 (dd, $J = 8.5, 5.0$ Hz, 1H), 4.54 (d, $J = 12.0$ Hz, 1H), 3.43 (dd, $J = 12.2, 8.5$ Hz, 1H), 3.19-3.14 (m, 1H).

^{13}C -NMR (125 MHz, CDCl_3): 141.1, 138.2, 132.6, 130.8, 129.1, 128.6, 128.4, 128.1, 127.8, 127.6, 126.9, 126.7, 81.0, 70.9, 35.5. IR (cm^{-1}): 3063, 3031, 2865, 1578, 1453, 1092, 736, 701. MS (EI, m/z , %): 369 ($\text{M}+1^+$, 31.2).

2-Benzoyloxy-2-(4-t-butyl)phenylethyl phenyl selenide (4k) [27]

Colorless viscous oil. ^1H -NMR (500 MHz, CDCl_3): 7.47-7.44 (m, 2H), 7.41-7.39 (m, 2H), 7.37-7.28 (m, 7H), 7.23-7.20 (m, 3H), 4.61 (dd, $J = 8.5, 5.1$ Hz, 1H), 4.54 (d, $J = 11.8$ Hz, 1H), 4.35 (d, $J = 11.8$ Hz, 1H), 3.43 (dd, $J = 12.2, 8.7$ Hz, 1H), 3.15 (dd, $J = 12.3, 5.0$ Hz, 1H), 1.36 (s, 9H). ^{13}C -NMR (125 MHz, CDCl_3): 151.2, 138.2, 138.1, 132.7, 131.1, 129.1, 128.3, 127.8, 127.6, 126.7, 126.5, 125.7, 80.6, 70.9, 35.6, 34.8, 31.5. IR (cm^{-1}): 3061, 2866, 1580, 1477, 1093, 835, 734. MS (EI, m/z , %): 425 ($\text{M}+1^+$, 10.4).

2-Benzoyloxy-2-(4-chlorophenyl)ethyl phenyl selenide (4l) [27]

Colorless viscous oil. ^1H -NMR (500 MHz, CDCl_3): 7.49-7.42 (m, 2H), 7.40-7.21 (m, 12H), 4.57 (dd, $J = 8.0, 5.6$ Hz, 1H), 4.50 (d, $J = 12.0$ Hz, 1H), 4.32 (d, $J = 12.0$ Hz, 1H), 3.38 (dd, $J = 12.4, 8.0$ Hz, 1H), 3.11 (dd, $J = 12.4, 5.6$ Hz, 1H). ^{13}C -NMR (125 MHz, CDCl_3): 139.5, 137.9, 133.7, 132.6, 130.6, 129.2, 128.8, 128.5, 128.1, 127.8, 127.7, 126.9, 80.1, 70.9, 35.4. IR (cm^{-1}): 3064, 2866, 1723, 1491, 1088, 828, 736. MS (EI, m/z , %): 403 ($\text{M}+1^+$, 2.6).

Benzyl 2-methoxy-2-phenylethyl selenide (4m) [29]

Colorless viscous oil. ^1H -NMR (500 MHz, CDCl_3): 7.44-7.37 (m, 2H), 7.35-7.27 (m, 7H), 7.23-7.18 (m, 1H), 4.22 (dd, $J = 8.1, 5.5$ Hz, 1H), 3.75-3.68 (m, 2H), 3.24 (s, 3H), 2.91 (dd, $J = 12.7, 8.1$ Hz, 1H), 2.69 (dd, $J = 12.7, 5.5$ Hz, 1H). ^{13}C -NMR (125 MHz, CDCl_3): 141.2, 139.7, 129.1, 128.6, 128.4, 128.1, 126.8, 126.7, 84.3, 57.1, 30.9, 27.9. IR (cm^{-1}): 2930, 2822, 1729, 1493, 1107, 758, 700. MS (EI, m/z , %): 307 ($\text{M}+1^+$, 22.9).

Benzyl 2-(4-chlorophenyl)-2-methoxyethyl selenide (4n) [27]

Colorless viscous oil. ^1H -NMR (500 MHz,

CDCl_3): 7.38-7.33 (m, 2H), 7.31-7.20 (m, 7H), 4.18 (dd, $J = 7.8, 5.6$ Hz, 1H), 3.74 (dd, $J = 15.6, 11.9$ Hz, 2H), 3.22 (s, 3H), 2.87 (dd, $J = 12.8, 7.8$ Hz, 1H), 2.66 (dd, $J = 12.8, 5.6$ Hz, 1H). ^{13}C -NMR (125 MHz, CDCl_3): 139.8, 139.4, 133.6, 129.0, 128.8, 128.4, 128.1, 126.7, 83.6, 56.9, 30.9, 28.1. IR (cm^{-1}): 2931, 2822, 1598, 1492, 1088, 826, 699. MS (EI, m/z , %): 341 ($\text{M}+1^+$, 3.3).

Benzyl 2-methoxycyclohexyl selenide (4o) [31]

Pale yellow viscous oil. ^1H -NMR (500 MHz, CDCl_3): 7.37-7.33 (m, 2H), 7.31-7.26 (m, 2H), 7.22 (t, $J = 7.3$ Hz, 1H), 4.00-3.91 (m, 2H), 3.38 (s, 3H), 3.20-3.15 (m, 1H), 2.95-2.91 (m, 1H), 2.10-2.06 (m, 2H), 1.73-1.71 (m, 1H), 1.63-1.61 (m, 1H), 1.53-1.43 (m, 1H), 1.32-1.26 (m, 3H). ^{13}C -NMR (125 MHz, CDCl_3): 139.9, 129.1, 128.3, 126.5, 83.6, 56.5, 43.4, 31.5, 30.4, 27.6, 25.8, 23.3. IR (cm^{-1}): 2996, 2852, 1493, 1111, 1088, 758, 698. MS (EI, m/z , %): 284 (M^+ , 5.1).

Results and Discussion

In order to optimize the reaction conditions, we first examined the alkoxylation of styrene **1a** with diphenyl diselenide **2a**, methanol **3a**, and I_2 at room temperature. It was shown that on simple stirring of the mixture for 24 hours, the expected addition product, 2-methoxy-2-phenylethyl phenyl selenide **4a** was provided in 72% yield (Table-1, entry 1). To improve the yield, solvents were first evaluated. From Table-1, it is obvious that the yield increased when EtOAc was added, and when MeOH/EtOAc was 1/2 (v/v), an excellent 92% yield was reached (entries 2-8). The amount of I_2 was also optimized, 1.0 equiv was a good choice (entries 7, 9-12). As a control experiment, **4a** was not determined if I_2 was absent (entry 13). Finally, 1.2 equiv of **1a** was determined to be the suitable amount for the reaction (entries 7, 14-16). Under the optimal reaction conditions, the reaction proceeded efficiently and completed in 10 hours (entries 7, 17-19).

Under the optimal reaction conditions, the alkoxylation of 1.2 mmol alkene **1**, 0.5 mmol diselenide **2**, 0.5 mmol I_2 and 1 mL alcohol **3** in EtOAc (2 mL) proceeded smoothly for 10 h at room temperature, providing a series of corresponding β -alkoxy selenides **4**. The results were summarized in Table-2.

Table-1: Optimization of the alkoxylation of styrene mediated by I₂.

1a + 2a + 3a $\xrightarrow[\text{Solvent, r.t.}]{\text{I}_2}$ 4a

Entry	1a:2a:I ₂ (equiv.)	MeOH/Solvent (mL)	Time (h)	Yield (%) ^a
1	1.2:1.0:1.0	MeOH (3mL)-	24	72
2	1.2:1.0:1.0	MeOH/MeCN (1.5mL/1.5mL)	24	75
3	1.2:1.0:1.0	MeOH/CH ₂ Cl ₂ (1.5mL/1.5mL)	24	58
4	1.2:1.0:1.0	MeOH/THF (1.5mL/1.5mL)	24	41
5	1.2:1.0:1.0	MeOH/EtOAc (1.5mL/1.5mL)	24	88
6	1.2:1.0:1.0	MeOH/EtOAc (2.0mL/1.0mL)	24	85
7	1.2:1.0:1.0	MeOH/EtOAc (1.0mL/2.0mL)	24	92
8	1.2:1.0:1.0	MeOH/EtOAc (0.5mL/2.5mL)	24	78
9	1.2:1.0:1.2	MeOH/EtOAc (1.0mL/2.0mL)	24	93
10	1.2:1.0:0.8	MeOH/EtOAc (1.0mL/2.0mL)	24	81
11	1.2:1.0:0.5	MeOH/EtOAc (1.0mL/2.0mL)	24	65
12	1.2:1.0:0.2	MeOH/EtOAc (1.0mL/2.0mL)	24	42
13	1.2:1.0:0	MeOH/EtOAc (1.0mL/2.0mL)	24	0
14	1.0:1.0:1.0	MeOH/EtOAc (1.0mL/2.0mL)	24	77
15	1.5:1.0:1.0	MeOH/EtOAc (1.0mL/2.0mL)	24	88
16	2.0:1.0:1.0	MeOH/EtOAc (1.0mL/2.0mL)	24	87
17	1.2:1.0:1.0	MeOH/EtOAc (1.0mL/2.0mL)	15	92
18	1.2:1.0:1.0	MeOH/EtOAc (1.0mL/2.0mL)	10	91
19	1.2:1.0:1.0	MeOH/EtOAc (1.0mL/2.0mL)	6	72

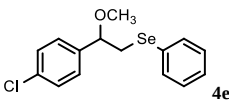
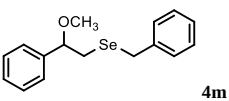
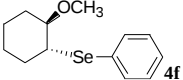
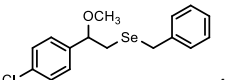
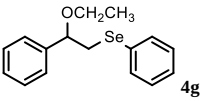
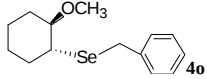
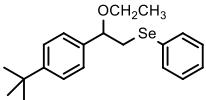
^a Isolated yields.

Table-2: Results for the preparation of β-alkoxy selenides 4

1a-1f + 2a-2b + 3a-3c $\xrightarrow[10 \text{ h, r.t.}]{\text{I}_2, \text{EtOAc}}$ 4a-4o

Entry	β-Alkoxy selenide 4	Yield (%) ^a	Entry	β-Alkoxy selenide 4	Yield (%) ^a
1		91	9		84
2		87	10		84
3		93	11		83
4		87	12		85

^a Isolated yields.

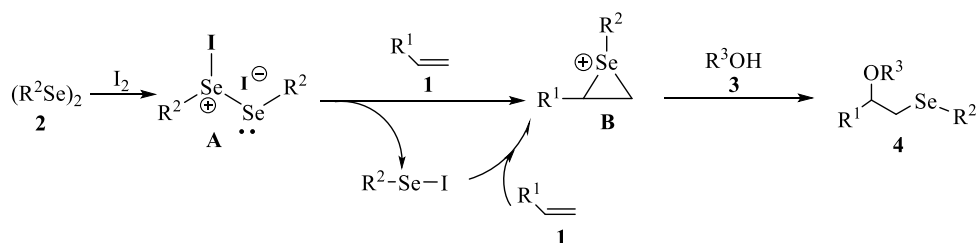
5		85	13		82
6		75	14		80
7		88	15		72
8		89			

^a Isolated yields.

Table-2 shows that the reaction was suitable for the studied alkenes, providing the corresponding β -alkoxy selenides with high regioselectivity and in good yields (Table-2, entries 1-5, 7-12). The substituents on the benzene ring, whether they were electron-withdrawing (Cl and Br) or electron-donating (Me and *t*-Bu) groups, had no significant influence on their reactivity (entries 2-5, 8-9, 11-12). Cyclohexene **1f**, an alicyclic alkene, resulted in the stereoisomer **4f** with a *trans* fashion and in 75% yield (entry 6). Similar to **2a**, dibenzyl diselenide **2b**, as an aliphatic diselenide, also reacted with alkenes easily, affording 72 to 82% yields for the corresponding products (entries 13-15).

2,2,6,6-Tetramethylpiperidine-1-oxyl (TEMPO) is used as a radical scavenger, and when it

was added to the mixture of **1a**, **2a**, **3a**, and I_2 under the optimal reaction conditions, the alkoxylation was not affected by TEMPO and went well. Therefore, an I_2 mediated electrophilic addition mechanism is hypothesized (Scheme 1): I_2 first reacts with diselenide **2** easily to produce the *in situ* generated active electrophilic selenium species RSeI through intermediate **A** [32-34]. Then RSeI attacks alkene **1** to form the unstable cyclic seleniranium intermediate **B**. Finally, **B** is transformed quickly to product **4** as a single isomer via an S_N1 mechanism by a solvolysis of alcohol **3**. In the reaction, another RSeI can further transfer the second equivalent of electrophilic selenium to alkene **1**. When treatment was conducted with alicyclic alkene **1f**, the *trans* stereoisomers were obtained via an S_N2 mechanism.



Scheme-1: A plausible mechanism for the synthesis of β -alkoxy selenides.

Conclusion

A novel and efficient iodine mediated process for the preparation of β -alkoxy selenides has been developed. This method is mild, simple, and provides a series of corresponding compounds with high regioselectivity and in good yields, which enriches the application of molecular iodine in organic synthesis.

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