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PhI Catalyzed Acetoxyselenylation and Formyloxyselenylation of Alkenes

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Abstract: With PhI as catalyst and *m*CPBA as oxidant, a novel and efficient catalytic procedure has been developed for the acetoxyselenylation and formyloxyselenylation of alkenes. In this protocol, PhI is first oxidized into hypervalent iodine intermediate, which promotes the cleavage of Se–Se bond in diselenides. The *in situ* generated electrophilic selenium species then reacts with alkenes, affording 2-acetoxy-1-selenides and 2-formyloxy-1-selenides in high regioselectivity and good yields.

Keywards: Acetoxyselenylation, Formyloxyselenylation, Hypervalent iodine intermediate, Alkene, Catalysis

Introduction The chemistry of hypervalent iodine organic compounds has experienced impressive developments since the early 1990s. Because of the low toxicity, ready availability and easy handling, especially the reactivity similar to that of heavy-metal reagents, they have been broadly used in organic chemistry and frequently used in synthesis [1-7]. The hypervalent iodine reagents are usually used as stoichiometric oxidants. However, after oxidations at least equimolar amounts of iodoarenes are produced as by-products. Due to iodoarenes are expensive and most of them are disposed of after the oxidations, which restrict hypervalent iodine reagents further applications. In 2005, Ochiai et al. and Kita's group independently reported the first hypervalent iodine-catalyzed oxidative coupling reactions [8-9]. Since then, the substoichiometric utilization of hypervalent iodine reagents has been increasing in importance, with growing interest in the development of environmentally benign synthetic transformations [10-15]. In these catalyzed reactions, a catalytic amount of an iodine-containing molecule together with a stoichiometric oxidant is used. The oxidant generates the hypervalent iodine reagent *in situ* and, after the oxidative transformation, the reduced iodine-containing molecule is re-oxidized.

In recent years, organoselenium compounds have been increasing in importance due to their synthetic applications, biological activities and other properties [16-23]. The introduction of organolselenium groups into organic molecules has been widely studied, in which the oxyselenenylation reaction is a very useful procedure for the *anti*-l,2-addition of an organylselenium group and an oxygen substituent (HO, RO, RCO_2) to an olefin [24-26]. In the electrophilic addition, the most common selenenylating reagent is normally available by the oxidation of cheaper and less toxic diphenyl diselenide with oxidants. Tingoli's group used hypervalent iodine reagent $PhI(OAc)_2$ to treat diphenyl diselenide, they found that the oxidative cleave the Se-Se bond was easily, and the electrophilic addition of the *in situ* generated reactive electrophilic selenium species to alkenes proceeded smoothly [27-29]. Although several papers about the further application of this methodology in organic synthesis have recently been reported [30-34], the catalytic oxyselenenylation using hypervalent iodine reagents as catalysts has been developed rarely. Therefore, to extend the scope of catalytic application of hypervalent iodine reagents in organic synthesis, we have investigated the oxyselenenylation of alkenes with iodobenzene (PhI) as catalyst.

Herein, we would like to report the novel and effective catalytic acetoxyselenylation and formyloxyselenylation of alkenes.

Results and Discussion

Recently, we have developed the acetoxyselenylation of alkenes use of inorganic haloid salts as catalysts [35-36]. On the basis, we first explored the reaction of styrene **1a**, diphenyl diselenide **2a** and oxidant *m*-chloroperbenzoic acid (*m*CPBA) in the presence of catalytic amount of PhI with AcOH at room temperature. We found that only stirring the mixture of 1.0 equiv of **2a**, 1.2 equiv of **1a** and *m*CPBA with 0.1 equiv of PhI in a mixed solvent of AcOH and EtOAc (1:1) for 3 h, the expected addition product, 1-phenyl-2-(phenylselanyl)ethyl acetate **3a** was obtained in 61% yield (Table 1, entry 1). As a control experiment, **3a** was observed in only 5% yield in the absence of PhI (entry 2). Therefore, it was obvious that PhI played a key action in the reaction. Encouraged by this result, the acetoxyselenenylation of 1.2 equiv of **1a** and 1.0 equiv of **2a** with *m*CPBA using PhI as catalyst at room temperature for 3 h was then optimized (Table 1). As shown from Table 1, the yield decreased when the ratio of AcOH decreased in the mixed solvent AcOH/EtOAc, meaning more AcOH should be favorable for the reaction (entry 3). When AcOH was used as solvent, the yield increased greatly to 87%, so the neat AcOH was the suitable solvent for the reaction (entry 4). In AcOH (2.0 mL), the amount of *m*CPBA was optimized, and 0.8 equiv of it showed the best effective to the reaction (entries 4-7). Finally, the amount of catalyst was also determined: 0.1 equiv of it was the best choice (entries 8-11).

Having established the optimal conditions, the acetoxyselenenylation of 1.2 equiv of alkenes **2** with 1.0 equiv of diselenides **1**, 0.8 equiv of *m*CPBA and 0.1 equiv of PhI proceeded fluently in AcOH, and a series of corresponding 2-acetoxy-1-selenenylation compounds **3a-3l** were obtained. The results are summarized in Table 2.

As shown in Table 2, the reaction was compatible with the studied styrene and a few derivatives, which provided the corresponding products in good to excellent yields (entries 1-5). Similar to **2a**, dibenzyl diselenide **2b**, an aliphatic diselenide, also reacted easily with these aromatic alkenes, giving

good yield products (entries 7-11). It was obvious that when the groups on the benzene ring were electron-donating groups, the alkenes had higher yields than those with electron-withdrawing groups on benzene ring (entries 2-5, 8-11). Nevertheless, 4-acetoxystyrene, an oxygen-containing substrate, failed to provide the desired product, only giving a complicated inseparable mixture. Cyclohexene **1f**, when it was treated under the same conditions, the addition proceeded in a *trans* fashion and the stereoisomer mixtures were obtained in moderate to good yields (entries 6, 12). Other aliphatic terminal alkenes were also checked, however, the reaction led to some complicated mixtures which were not to be isolated, also the yields were not determined. Therefore, this protocol is suitable for aromatic alkenes and aliphatic cyclic alkenes, resulting in the corresponding products in high regioselectivity. In order to extent the content of this methodology, with the similar manner we tried to investigate the formyloxyselenylation of alkenes which has not been reported before. Unfortunately, the desired products were obtained in much low yields when acetic acid was replaced by formic acid. While in a mixed solvent of formic acid and ethyl acetate (1:3), the formyloxyselenylation was found to proceed well. Based on this success, three alkenes **1a**, **1c** and **1d** were selected as represents of alkenes to be treated in the formyloxyselenylation, and the corresponding products **3m**-**3o** were afforded in yields ranging from 37-69% (entries 13-15). As for other acids, benzyl acid was used as represent to replace formic acid, but it was unreactive for the reaction.

A proposed mechanism for the PhI catalyzed acetoxyselenenylation and formyloxyselenylation of alkenes is shown in Scheme 1. PhI is first oxidized by *m*CPBA to hypervalent iodine reagent **A**, which reacts smoothly with diselenide **2** to form the active intermediate **B,** following a rapid cleavage of Se-Se bond. The *in situ* generated electrophilic selenium species reacts with alkene to produce the unstable cyclic intermediate **D**. Another active intermediate **C** can also further transfer a second equivalent of electrophilic selenium to alkenes to form the cyclic intermediate **D**. After a solvolysis of **D** in AcOH, the desired product **3** as a single isomer is obtained via an S_N1 mechanism for the aromatic alkenes. While an aliphatic alkene **1f** is used as substrate, the reaction provides the *trans* stereoisomers via an S_N2 mechanism. This result supports that the first formation of the cyclic selenium intermediate **D**, then acetate anion attacks the cyclic intermediate affording the

corresponding *anti*-I, 2-addition products **3f** and **3l**. To support the mechanism, Ishihara catalyst was added in the reaction; however, no asymmetric induction had been achieved.

In summary, we have developed a novel and efficient catalytic processor for synthesis of 2-acetoxy-1-selenides and 2-formyloxy-1-selenides using PhI as catalyst. This method has some advantages such as mild reaction conditions and simple procedure, which providing a series of corresponding compounds with high regioselectivity and good yields. Furthermore, the scope of catalytic use of hypervalent iodine reagent in organic synthesis could be extended.

Experimental Part

IR spectra were recorded on a Thermo Nicolet 6700 instrument. ^{1}H-NMR and ^{13}C-NMR spectra were measured in $CDCl_3$ on a Bruker Avance III (500MHz) spectrometer. Mass spectra were determined on a Thermo ITQ 1100 mass spectrometer. Alkenes, diselenides, *m*CPBA, PhI and solvents were commercially available.

Typical Procedure for the Catalytic Acetoxyselenenylation of Alkenes Using PhI as Catalytic: In AcOH (2.0 mL), alkene **1** (0.48 mmol), diselenide **2** (0.2 mmol), PhI (0.04 mmol) and *m*CPBA (0.32 mmol) were added successively. The suspension mixture was vigorously stirred at r. t. for 3 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 on a silica gel plate (4:1 petroleum ether-ethyl acetate) to furnish 2-acetoxy-1-selenenylation compounds **3.**

1-Phenyl-2-(phenylselanyl)ethyl acetate (3a) [27]

Colorless viscous oil, Yield: 97%.

IR (film): 3061, 3033, 1742, 1371, 1236, 1020, 738, 698.

^{1}H-NMR: 7.52 (dd, *J* = 6.5, 2.9 Hz, 2H), 7.39-7.30 (m, 5H), 7.30-7.24 (m, 3H), 5.96 (dd, *J* = 8.0, 5.7 Hz, 1H), 3.40 (dd, *J* = 12.9, 8.0 Hz, 1H), 3.25 (dd, *J* = 12.9, 5.7 Hz, 1H), 2.04 (s, 3H).

^{13}C-NMR: 170.0, 139.4, 133.1, 129.8, 129.1, 128.5, 128.4, 127.2, 126.6, 75.2, 33.4, 21.0.

ESI-MS: 338 (4.8, [M + 18]), 261 (100).

2-(Phenylselanyl)-1-(4-tolyl)ethyl acetate (3b) [35]

Colorless viscous oil, Yield: 77%.

IR (film): 3055, 3027, 1742, 1370, 1236, 1020, 816, 738, 692.

^{1}H-NMR: 7.64-7.42 (m, 2H), 7.28 (dd, *J* = 4.9, 1.7 Hz, 3H), 7.24 (d, *J* = 8.1 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 5.93 (dd, *J* = 7.9, 5.9 Hz, 1H), 3.40 (dd, *J* = 12.8, 8.0 Hz, 1H), 3.24 (dd, *J* = 12.8, 5.9 Hz, 1H), 2.36 (s, 3H), 2.02 (s, 3H). ^{13}C-NMR: 170.1, 138.3, 136.5, 133.1, 129.9, 129.3, 129.1, 127.2, 126.7, 75.2, 33.3, 21.2, 21.1.

ESI-MS: 334 (6.5, M^{+}), 194 (100).

1-(4-*tert*-Butylphenyl)-2-(phenylselanyl)ethyl acetate (3c) [35]

Colorless viscous oil, Yield: 75%.

IR (film): 3057, 2963, 1745, 1370.0, 1235, 1021, 828, 737, 691.

^{1}H-NMR: 7.52-7.50 (m, 2H), 7.37-7.36 (m, 2H), 7.29-7.26 (m, 5H), 5.96 (dd, *J* = 8.0, 5.7 Hz, 1H), 3.40 (dd, *J* = 12.8, 8.1 Hz, 1H), 3.25 (dd, *J* = 12.8, 5.6 Hz, 1H), 2.03 (s, 3H), 1.33 (s, 9H).

^{13}C-NMR: 169.5, 150.2, 139.9, 133.1, 129.3, 127.4, 126.9, 121.6, 71.7, 38.3, 21.1.

ESI-MS: 376 (14.1, M^{+}), 219 (100).

1-(4-Chlorophenyl)-2-(phenylselanyl)ethyl acetate (3d) [35]

Pale yellow viscous oil, Yield: 62%.

IR (film): 3057, 1741, 1371, 1235, 1051, 1016, 824, 738, 692.

^{1}H-NMR: 7.54-7.44 (m, 2H), 7.33-7.29 (m, 2H), 7.29-7.20 (m, 5H), 5.93-5.85 (m, 1H), 3.42-3.30 (m, 1H), 3.26-3.14 (m, 1H), 2.02 (s, 3H).

^{13}C-NMR: 169.9, 137.8, 134.2, 133.2, 129.5, 129.2, 128.7, 128.1, 127.4, 74.6, 33.1, 21.0.

ESI-MS: 354 (11.2, M^{+}), 214 (100).

1-(4-Bromophenyl)-2-(phenylselanyl)ethyl acetate (3e) [35]

Pale yellow viscous oil, Yield: 69%.

IR (film): 3056, 1741, 1481, 1072, 1007, 823, 736, 690.

^{1}H-NMR: 7.50-7.45 (m, 4H), 7.28-7.26 (m, 3H), 7.21-7.19 (m, 2H), 5.93-5.82 (m, 1H), 3.43-3.29 (m, 1H), 3.28-3.13 (m, 1H), 2.02 (s, 3H).

^{13}C-NMR: 169.9, 138.3, 133.2, 131.6, 129.5, 129.2, 128.4, 127.4, 122.4, 74.7, 33.1, 21.0.

ESI-ES: 398 (58.5, M^{+}), 338 (100).

2-(Phenylselanyl)cyclohexyl acetate (3f) [27]

Colorless viscous oil, Yield: 52%.

IR (film): 3056, 2936, 2858, 1738, 1373, 1238, 1036, 741, 693.

^{1}H-NMR: 7.63-7.53 (m, 2H), 7.30-7.27 (m, 3H), 4.89-4.81 (m, 1H), 3.29-3.15 (m, 1H), 2.20-2.05 (m, 2H), 1.96 (s, 3H), 1.75-1.65 (m, 2H), 1.54-1.29 (m, 4H).

^{13}C-NMR: 170.3, 135.0, 128.9, 128.7, 127.6, 75.4, 46.1, 32.3, 31.8, 25.8, 23.6, 21.1.

ESI-MS: 298 (4.5, M^{+}), 81 (100).

2-(Benzylselanyl)-1-phenylethyl acetate (3g) [35]

Pale yellow viscous oil, Yield: 81%.

IR (film): 3061, 3029, 1739, 1371, 1237, 1018, 758, 698.

^{1}H-NMR: 7.50-7.09 (m, 10H), 5.83 (dd, *J* = 7.6, 6.3 Hz, 1H), 3.67 (d, *J* = 2.4 Hz, 2H), 2.92 (dd, *J* = 13.0, 7.7 Hz, 1H), 2.78 (dd, *J* = 13.0, 6.2 Hz, 1H), 2.09 (s, 3H).

^{13}C-NMR: 169.9, 139.7, 138.9, 129.0, 128.5, 128.3, 126.9, 126.7, 75.5, 29.0, 27.8, 21.1.

ESI-MS: 352 (11.0, [M + 18]), 336 (100).

2-(Benzylselanyl)-1-(4-tolyl)ethyl acetate (3h) [35]

Pale yellow viscous oil, Yield: 71%.

IR (film): 3059, 3027, 1741, 1370, 1237, 1018, 817, 759, 698.

^{1}H-NMR: 7.33-7.17 (m, 9H), 5.83 (dd, *J* = 7.5, 6.5 Hz, 1H), 3.72 (d, *J* = 3.2 Hz, 2H), 2.95 (dd, *J* = 12.9, 7.7 Hz, 1H), 2.80 (dd, *J* = 12.9, 6.3 Hz, 1H), 2.36 (s, 3H), 2.10 (s, 3H).

^{13}C-NMR: 169.9, 139.0, 138.1, 136.7, 129.2 129.0, 128.5, 126.8 (d, *J* = 19.7 Hz), 75.4, 29.0, 27.8, 21.2.

ESI-MS: 348 (3.5, M^{+}), 369 (100)

2-(Benzylselanyl)-1-(4-*tert*-butylphenyl)ethyl acetate (3i)

Pale yellow viscous oil, Yield: 87%.

IR (film): 3028, 2962, 1744, 1370, 1237, 1017, 829, 758, 698.

^{1}H-NMR: 7.43-7.40 (m, 2H), 7.36-7.21 (m, 7H), 5.89 (dd, *J* = 7.9, 6.2 Hz, 1H), 3.73 (s, 2H), 2.98 (dd, *J* = 13.0, 8.0 Hz, 1H), 2.83 (dd, *J* = 13.0, 6.1 Hz, 1H), 2.13 (s, 3H), 1.36 (s, 9H).

^{13}C-NMR: 169.9, 151.2, 138.8, 136.5, 128.9, 128.4, 126.7, 126.3, 125.3, 75.1, 34.5, 31.3, 28.8, 27.6, 21.1.

ESI-MS: 413 (3.5, [M + 23]), 369 (100).

HR-MS: calc. for $C_{21}H_{26}NaO_2Se$ [M + 23]: 413.0996; found: 413.0983.

2-(Benzylselanyl)-1-(4-chlorophenyl)ethyl acetate (3j) [35]

Colorless viscous oil, Yield: 63%.

IR (film): 3061, 3028, 1739, 1371, 1236, 1015, 825, 759, 698.

^{1}H-NMR: 7.35-7.12 (m, 9H), 5.82-5.66 (m, 1H), 3.77-3.62 (m, 2H), 2.89 (dd, *J* = 13.0, 7.6 Hz, 1H), 2.74 (dd, *J* = 13.0, 6.4 Hz, 1H), 2.08 (s, 3H).

^{13}C-NMR: 169.8, 138.7, 138.2, 134.2, 129.0, 128.7, 128.6, 128.1, 126.9, 74.7, 28.7, 27.9, 21.1.

ESI-MS: 369 (13.0, [M + 1]), 289 (100).

2-(Benzylselanyl)-1-(4-bromophenyl)ethyl acetate (3k)

Colorless viscous oil, Yield: 61%.

IR (film): 3060, 3027, 2928, 1738, 1594, 1490, 1370, 1233, 1010, 819, 758, 697.

^{1}H-NMR: 7.49 (d, *J* = 8.4 Hz, 1H), 7.35-7.23 (m, 5H), 7.19 (d, *J* = 8.4 Hz, 2H), 5.77 (t, *J* = 6.9 Hz, 1H), 3.78-3.65 (m, 2H), 2.91 (dd, *J* = 13.0, 7.6 Hz, 1H), 2.76 (dd, *J* = 13.0, 6.3 Hz, 1H), 2.11 (s, 3H).

^{13}C-NMR: 169.8, 138.7, 138.6, 131.6, 129.0, 128.6, 128.4, 126.9, 122.3, 74.7, 28.6, 27.8, 21.1.

ESI-MS: 430 (3.8, [M + 18]), 274 (100).

HR-MS: calc. for $C_{17}H_{21}BrNO_2Se$ [M + 18]: 429.9921; found: 429.9903.

2-(Benzylselanyl)cyclohexyl acetate (3l)

Colorless viscous oil, Yield: 55%.

IR (film): 3061, 3027, 2935, 1736, 1601, 1494, 1451, 1373, 1238, 1035, 759, 697.

^{1}H-NMR: 7.36-7.17 (m, 5H), 4.88 (td, *J* = 8.8, 4.1 Hz, 1H), 3.95-3.80 (m, 2H), 2.88 (td, *J* = 10.0, 4.1 Hz, 1H), 2.17- 2.06 (m, 3H), 2.10 (s, 3H), 1.75-1.54 (m, 3H), 1.47-1.25 (m, 3H).

^{13}C-NMR: 170.2, 139.2, 128.9, 128.4, 126.6, 75.7, 42.3, 32.0, 31.2, 27.1, 25.5, 23.3, 21.3.

ESI-MS: 330 (17.0, [M + 18]), 229 (100).

HR-MS: calc. for $C_{15}H_{24}NO_2Se$ [M + 18]: 330.0972; found: 330.0983.

1-Phenyl-2-(phenylselanyl)ethyl formate (3m)

Colorless viscous oil, Yield: 69%.

IR (film): 3060, 2928, 1723, 1579, 1478, 1438, 1154, 737, 698.

^{1}H-NMR: 8.10 (s, 1H), 7.55-7.48 (m, 2H), 7.40-7.24 (m, 8H), 6.04 (dd, *J* = 7.5, 6.3 Hz, 1H), 3.42 (dd, *J* = 12.9, 8.0 Hz, 1H), 3.28 (dd, *J* = 12.9, 5.8 Hz, 1H).

^{13}C-NMR: 159.9, 138.7, 133.3, 129.4, 129.2, 128.7, 128.6, 127.4, 126.7, 75.0, 33.1.

ESI-MS: 329 (16.8, [M + 23]), 274 (100)

HR-MS: calc. for $C_{15}H_{14}NaO_2Se$ [M + 23]: 329.0057; found: 329.0023.

1-(4-*tert*-Butylphenyl)-2-(phenylselanyl)ethyl formate (3n)

Colorless viscous oil, Yield: 37%.

IR (film): 3057, 2962, 2868, 1726, 1478, 1163, 830, 737, 691.

^{1}H-NMR: 8.09 (s, 1H), 7.52-7.48 (m, 2H), 7.38 (d, *J* = 8.4 Hz, 2H), 7.32-7.23 (m, 5H), 6.03 (dd, *J* = 7.6, 6.2 Hz, 1H), 3.42 (dd, *J* = 12.9, 8.0 Hz, 1H), 3.28 (dd, *J* = 12.9, 5.8 Hz, 1H), 1.33 (s, 9H).

^{13}C-NMR: 160.0, 151.7, 135.6, 133.2, 129.5, 129.1, 127.4, 126.4, 125.5, 74.9, 34.6, 33.1, 31.3.

ESI-MS: 362 (4.2, M^+), 478 (100).

HR-MS: calc. for $C_{19}H_{22}O_2Se$ [M^+]: 362.0777; found: 362.0771.

1-(4-Chlorophenyl)-2-(phenylselanyl)ethyl formate (3o)

Colorless viscous oil, Yield: 51%.

IR (film): 3057, 2930, 1724, 1493, 1154, 1092, 1015, 825, 737, 691.

^{1}H-NMR: 8.07 (s, 1H), 7.51-7.45 (m, 2H), 7.35-7.23 (m, 7H), 5.98 (t, *J* = 6.9 Hz, 1H), 3.38 (dd, *J* = 12.9, 7.6 Hz, 1H), 3.23 (dd, *J* = 12.9, 6.3 Hz, 1H).

^{13}C-NMR: 159.8, 137.1, 134.5, 133.3, 129.2, 129.1, 128.8, 128.1, 127.54, 74.3, 32.9.

ESI-MS: 358 (8.0, [M + 18]), 301 (100).

HR-MS: calc. for $C_{15}H_{17}ClNO_2Se$ [M + 18]: 358.0113; found: 358.0101.

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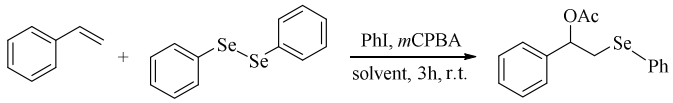
Table 1

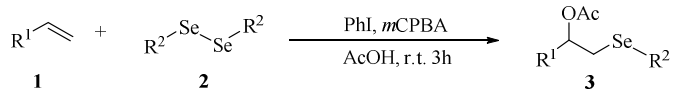
Optimization of the acetoxyselenenylation of styrene using PhI as catalyst



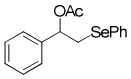
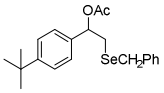
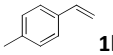
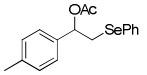
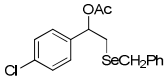
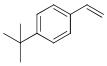
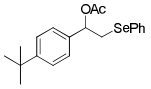
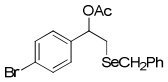
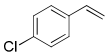
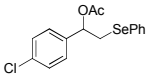
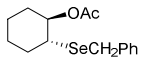
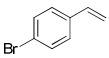
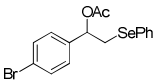
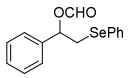
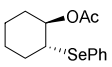
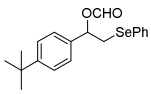
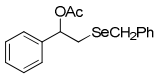
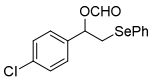
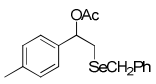
Entry	*m*CPBA (equiv.)	PhI (equiv.)	Solvent	Yield (%)[a]
1	1.2	0.1	AcOH/EtOAc (1:1)	61
2	1.2	-	AcOH/EtOAc (1:1)	5
3	1.2	0.1	AcOH/EtOAc (1:2)	41
4	1.2	0.1	AcOH	87
5	1.4	0.1	AcOH	91
6	1.0	0.1	AcOH	92
7	**0.8**	**0.1**	**AcOH**	**97**
8	0.8	0.2	AcOH	94
9	0.8	0.3	AcOH	93
10	0.8	0.05	AcOH	68
11	0.8	0.02	AcOH	43

[a]Isolated yields.

Table 2 Preparation of 2-acetoxy-1-selenenylation compounds **3**



1 **2** **3**

Entry	Alkene (1)	Diselenide (2)	Product (3)	Yield (%)[a]	Entry	Alkene (1)	Diselenide (2)	Product (3)	Yield (%)[a]
1	 **1a**	PhSeSePh **2a**	 **3a**	97	9	**1c**	**2b**	 **3i**	87
2	 **1b**	**2a**	 **3b**	77	10	**1d**	**2b**	 **3j**	63
3	 **1c**	**2a**	 **3c**	75	11	**1e**	**2b**	 **3k**	61
4	 **1d**	**2a**	 **3d**	62	12	**1f**	**2b**	 **3l**	78
5	 **1e**	**2a**	 **3e**	69	13	**1a**	**2a**	 **3m**	69[b]
6	 **1f**	**2a**	 **3f**	52	14	**1c**	**2a**	 **3n**	37[b]
7	**1a**	$(PhCH_2Se)_2$ **2b**	 **3g**	81	15	**1d**	**2a**	 **3o**	51[b]
8	**1b**	**2b**	 **3h**	71					

[a] Isolated yields.

[b] The formyloxyselenylation was carried out in HCOOH (0.5mL) and EtOAc (1.5mL).

Scheme 1 Proposed mechanism for the catalyzed acetoxyselenenylation of alkenes