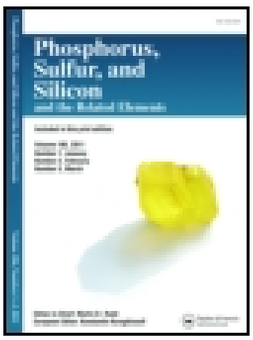


Taylor & Francis
Taylor & Francis Group

Phosphorus, Sulfur, and Silicon and the Related Elements

ISSN: 1042-6507 (Print) 1563-5325 (Online) Journal homepage: http://www.tandfonline.com/loi/gpss20

KI Catalyzed Azidoselenenylation of Alkenes with Sodium Azide and Diselenides via an Oxidative Cleavage of Se-Se Bond

Yikun Zhang, Sixue Wu, Hongwei Shi & Jie Yan

To cite this article: Yikun Zhang, Sixue Wu, Hongwei Shi & Jie Yan (2016): KI Catalyzed Azidoselenenylation of Alkenes with Sodium Azide and Diselenides via an Oxidative Cleavage of Se-Se Bond, Phosphorus, Sulfur, and Silicon and the Related Elements, DOI: 10.1080/10426507.2016.1192625

To link to this article: http://dx.doi.org/10.1080/10426507.2016.1192625

Accepted author version posted online: 26 May 2016.
Published online: 26 May 2016.

KI Catalyzed Azidoselenenylation of Alkenes with Sodium Azide and Diselenides via an Oxidative Cleavage of Se-Se Bond

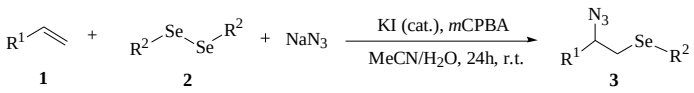
Yikun Zhang, Sixue Wu, Hongwei Shi, and Jie Yan*

College of Chemical Engineering, Zhejiang University of Technology, Hangzhou 310015, P. R .China

**corresponding authors E-mail: jieyan87@zjut.edu.cn*

Abstract

Using potassium iodide as a catalyst and *m*-chloroperbenzoic acid as an oxidant, an efficient catalytic procedure has been developed for the azidoselenenylation of alkenes with sodium azide and diselenides, and a series of corresponding β-azidoselenides, most of which are new compounds, have been prepared in moderate to good yields under mild reaction conditions. This *in situ* generation of the electrophilic selenenylating reagents with addition to alkenes is a stereospecific *anti* addition, which occurs with a Markovnikov orientation.



Keywords

Azidoselenenylation, diselenide, alkene, sodium azide, potassium iodide, catalysis

Introduction

Organoselenium chemistry has developed as an important synthetic tool in the hands of synthetic chemists since the discovery of the selenoxide elimination in the early 1970s.[1-5] Because of their synthetic applications[6] and biological activities such as antitumor, antibacterial activities and other properties,[7-14] selenium compounds have been increasing in importance in recent years. β-Azidoselenides is a significant class of organoselenium compounds which have a greater synthetic importance since they combine the well known reactivity of the azido group with that of the selenium containing group.[15-18] The first example of the azidoselenenylation of alkenes was reported by Hassner and Amarasekara.[19] The reaction was effected with PhSeCl and sodium azide in DMSO, resulting in the stereospecific (*anti*) but not regiospecific products. Using a particular but expensive silver salt, silver triflate (AgOTf), the generated highly electrophilic phenylselenenyl triflate can promote the azidoselenenylation of alkenes efficiently, and the corresponding β-azidoselenides have been obtained with stereospecific and regiospecific selectivity.[20] In the similar manner, the asymmetric azidoselenenylation of alkenes can be carried out, affording a series of β-azidoselenides with high facial selectivity.[21] The radical azidoselenenylation of alkenes was discovered by Tingoli and co-workers when treatment of diphenyl diselenide with hypervalent iodine reagent $PhI(OAc)_2$ in the presence of sodium azide, gave the anti-Markovnikov products.[22] More recently, an iodine catalyzed seleno-functionalization of olefins under microwave irradiation has been reported.[23] However, the product β-azidoselenide was obtained only in 21% yield. Although β-azidoselenides can be prepared by above methods, the use of toxic, moisture-sensitive and expensive selenenylating reagents limit this application, so the members of β-azidoselenides are still limited. Therefore,

the development of simple and convenient methods, especially catalytic protocols for preparation of β-azidoselenides is still desired.

It is known that hypervalent iodine reagents can promote the oxidative cleavage of Se-Se bond of diphenyl diselenide to generate the reactive electrophilic selenium species.[24-28] In our recent research, we have found that some inorganic iodides such as KI combined with oxidants can be used to replace hypervalent iodine reagents, resulting in the similar results.[29-30] On this basis, we have investigated the novel procedure for the azidoselenenylation of alkenes. Herein, we wish to report an efficient azidoselenenylation of alkenes with sodium azide and diphenyl diselenide using KI as catalyst and *m*-chloroperbenzoic acid as oxidant. To the best of our knowledge, this method has not been reported before.

Results and Discussion

Initially, we examined the reaction of styrene **1a** with diphenyl diselenide **2a** and sodium azide (NaN_3) in the presence of oxidant *m*-chloroperbenzoic acid (*m*CPBA) and catalyst KI at room temperature. It was observed that stirring the mixture of 1.0 equiv of **2a**, 1.5 equiv of NaN_3, 1.2 equiv of **1a** and *m*CPBA with 0.1 equiv of KI in MeCN for 24 h, the expected addition product (2-azido-2-phenylethyl)(phenyl)selane **3a** was obtained in 24 % yield (Table 1, entry 1). As a control experiment, **3a** was isolated only in 3% yield in the absence of KI (entry 2). Then, the catalytic azidoselenenylation of 1.2 equiv of **1a** with 1.0 equiv of **2a** using KI as catalyst and *m*CPBA as oxidant at room temperature for 24 h was optimized. The reaction was first evaluated in several solvents. As a result, a poor yield was obtained in CH_2Cl_2, and in DMF or THF no product was detected (Table 1, entries 3-5). With the observation of the low solubility of NaN_3 in

MeCN, to improve the reaction, several mixed solvents of MeCN were treated in the reaction. It was obvious that when the volume ratio of MeCN to H_2O was 10:1, the yield of the azidoselenenylation increased greatly to 57% (entry 6). Other mixed solvents can also promote the azidoselenenylation, resulting in the desired product in yields ranging from 42-50% (entries 7-9). After then more H_2O was added and when the ratio of MeCN to H_2O reached 5:6, this mixed solvent had the best effect (entries 6, 10-17). In the mixed solvent MeCN/H_2O (5:6), other iodine-containing compounds such as NH_4I, PhI and C_3H_7I had the catalytic effect, but the given yields were not more than 80% (entries 15, 18-20). When the amount of KI was increased from 0.1 equiv to 0.2 equiv, the yields of **3a** dropped down, so 0.1 equiv was the best choice (entries 15 and 21). Finally, the amounts of *m*CPBA and NaN_3 were also evaluated, and as a result, 1.2 equiv and 1.5 equiv were found to be the suitable amounts for *m*CPBA and NaN_3, respectively (entries 22-25).

Based on the extensive screening process, we arrived at the optimal reaction conditions. The catalytic azidoselenenylation of 1.2 equiv of alkenes **1** with 1.0 equiv of diselenides **2**, 1.5 equiv of NaN_3, 1.2 equiv of *m*CPBA and 0.1 equiv of KI in MeCN/H_2O (5/6) at room temperature for 24 h was investigated (Scheme 1), and as a consequence a series of corresponding β-azidoselenides **3** were obtained. The results were summarized in Table 2.

The azidoselenenylation proceeded efficiently, affording the corresponding β-azidoselenides **3a-3f** in moderate to good yields when **2a** was treated with aromatic alkenes (Table 2, entries 1-6). Dibenzyl diselenide **2b**, similar to **2a**, an aliphatic diselenide also reacted with alkenes, resulting in the corresponding products **3h-3j** in moderate to good yields (entries 8-10). This

azidoselenenylation is a regiospecific reaction as all the obtained β-azidoselenides are the Markovnikov orientation products. In order to investigate the stereospecificity of the azidoselenenylation, cyclohexene **1g** was selected to react with **2a**, and the obtained product **3f** showed a *trans* single stereoisomer with 48% yield (entry 7).

A proposed catalytic mechanism for the azidoselenenylation of alkenes is shown in Scheme 2. KI is first oxidized by *m*CPBA into hypoiodous acid **A**, which reacts smoothly with diselenide **2** to form the active intermediate **B**, followed by a rapid cleavage of Se-Se bond.[29-31] The *in situ* generated active electrophilic selenium species then reacts with alkene to form cyclic intermediate **C**. Finally, intermediate **C** is attacked by anion of azide to provide the desired product β-azidoselenide **3,** which is a single isomer via an S_N1 mechanism for the aromatic alkenes. When aliphatic alkene **1g** is treated in the reaction, the trans single stereoisomer via an S_N2 mechanism is obtained. In the cycle, another active intermediate ArSeI[32-33] can further transfer a second equivalent of electrophilic selenium to alkene.

Conclusions

We have developed an efficient catalytic processor for synthesis of β-azidoselenide compounds by the azidoselenenylation of alkenes with diselenides, sodium azide and *m*CPBA in the presence of catalytic amount of KI at room temperature. This method has some advantages such as mild reaction conditions, simple procedure, and affording a series of β-azidoselenide, most are new compounds with high regioselectivity and good yields. Furthermore, the use of KI in the catalytic reaction will extend the application scope of inorganic iodides in organic synthesis.

Experimental

General IR spectra were recorded on a Thermo-Nicolet 6700 instrument, ^{1}H NMR and ^{13}C NMR spectra were measured on a Bruker-AVANCE Ⅲ (500 MHz) spectrometer, Mass spectra were determined on Waters-GCT Premier, Thermo-DECAX-60000 LCQ Deca XP and Thermo-ITQ 1100 mass spectrometers. Alkenes, diselenides, *m*CPBA, KI, NaN_3 and solvents were commercially available. The Supplemental Materials contains sample ^{1}H and ^{13}C NMR spectra of the products 3a – 3j (Figures S 1 – S 12)

General procedure for the KI catalyzed azidoselenenylation of alkenes. In a mixed solvent of MeCN and H_2O (5:6, V/V) (2.0 mL), alkenes **1** (0.24 mmol), diselenide **2** (0.10 mmol), NaN_3 (0.3mmol), KI (0.02 mmol) and *m*CPBA (0.24 mmol) were added successively. The suspension mixture was vigorously stirred at room temperature for 24 h. Upon completion, the reaction was quenched by addition of sat. aq. $Na_2S_2O_3$ (2 mL), sat. aq. Na_2CO_3 (8 mL) and H_2O (5 mL), respectively. 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 (10:1 petroleum ether-ethyl acetate) to furnish products **3**.

(2-azido-2-phenylethyl)(phenyl)selane **3a**

Pale yellow oil.[23]

IR (neat): 2101 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.56 – 7.49 (m, 2H), 7.43 – 7.32 (m, 3H), 7.32 – 7.26 (m, 5H), 4.65 (dd, *J* = 8.3, 6.2 Hz, 1H), 3.27 (dd, *J* = 12.7, 6.3 Hz, 1H), 3.22

(dd, J = 12.7, 6.2 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 138.8, 133.3, 129.4, 129.3, 128.9, 128.7, 127.5, 126.9, 66.0, 34.0. MS (ESI): *m/z* (%) 320 (M+18).

(2-azido-2-(4-tolyl)ethyl)(phenyl)selane **3b**

Pale yellow oil.

IR (neat): 2095 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.55 – 7.51 (m, 2H), 7.31 – 7.26 (m, 3H), 7.20 (s, 4H), 4.65 – 4.60 (m, 1H), 3.27 (dd, J = 12.5, 8.3 Hz, 1H), 3.21 (dd, J = 12.7, 6.3 Hz, 1H), 2.38 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 138.6, 135.7, 133.2, 129.6, 129.5, 129.2, 127.4, 126.8, 65.8, 33.9, 21.2. MS (ESI): *m/z* (%) 334 (M+18). HRMS: *m/z* calcd for $C_{15}H_{19}N_4Se$ [M+18]: 335.0775; found: 335.0743.

(2-azido-2-(4-*tert*-butylphenyl)ethyl)(phenyl)selane **3c**

Pale yellow oil.

IR (neat): 2103 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.54 – 7.51 (m, 2H), 7.42 – 7.40 (m, 2H), 7.30 – 7.27 (m, 3H), 7.26 – 7.23 (m, 2H), 4.65 (dd, J = 8.4, 6.1 Hz, 1H), 3.28 (dd, J = 12.7, 8.4 Hz, 1H), 3.23 (dd, J = 12.7, 6.0 Hz, 1H), 1.35 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 151.6, 135.7, 133.2, 129.6, 129.2, 127.4, 126.5, 125.8, 65.8, 34.6, 34.0, 31.3. MS (ESI): *m/z* (%) 376 (M+18). HRMS: *m/z* calcd for $C_{18}H_{25}N_4Se$ [M+18]: 377.1244; found: 377.1241.

(2-(4-Acetoxyphenyl)-2-azidoethyl)(phenyl)selane **3d**

Pale yellow oil.

IR (neat): 2101 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.53 – 7.50 (m, 2H), 7.33 – 7.27 (m, 5H), 7.13 – 7.10 (m, 2H), 4.65 (dd, *J* = 8.3, 6.0 Hz, 1H), 3.24 (dd, *J* = 12.8, 8.3 Hz, 1H), 3.19 (dd, *J* = 12.8, 6.0 Hz, 1H), 2.32 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 169.2, 150.8, 136.4, 133.3, 129.3, 127.9, 127.5, 122.0, 65.5, 34.1, 21.1. MS (ESI): *m/z* (%) 378 (M+18). HRMS: *m/z* calcd for $C_{16}H_{19}N_4SeO_2$ [M+18]: 379.0673; found: 379.0661.

(2-azido-2-(4-fluorophenyl)ethyl)(phenyl)selane **3e**

Pale yellow oil.

IR (neat): 2103 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.52 – 7.49 (m, 2H), 7.33 – 7.24 (m, 5H), 7.10 – 7.04 (m, 2H), 4.64 (dd, *J* = 7.6, 6.9 Hz, 1H), 3.26 (dd, *J* = 12.7, 7.9 Hz, 1H), 3.18 (dd, *J* = 12.7, 6.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 163.7, 161.7, 134.53, 134.50, 133.3, 129.3, 129.2, 128.8, 128.74, 128.7, 128.6, 127.6, 116.2, 116.0, 115.9, 115.7, 65.3, 34.0. MS (ESI): *m/z* (%) 319 (M-1). HRMS: *m/z* calcd for $C_{14}H_{12}N_3FSe$: 321.0180; found: 321.0173.

(2-azido-2-(4-chlorophenyl)ethyl)(phenyl)selane **3f**

Pale yellow oil.

IR (neat): 2102 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.53 – 7.48 (m, 2H), 7.37 – 7.32 (m, 2H), 7.31 – 7.26 (m, 3H), 7.25 – 7.20 (m, 2H), 4.63 (dd, *J* = 7.7, 6.7 Hz, 1H), 3.24 (dd, *J* = 12.7, 7.9 Hz, 1H), 3.17 (dd, *J* = 12.7, 6.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 137.2, 134.5, 133.4, 129.3, 129.14, 129.06, 128.3, 127.6, 65.3, 33.9. MS (ESI): *m/z* (%) 354 (M+18). HRMS: *m/z* calcd for $C_{14}H_{16}N_4ClSe$ [M+18]: 355.0229; found: 355.0201.

(2-azidocyclohexyl)(phenyl)selane **3g**

Pale yellow oil.[15]

IR (neat): 2095 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.66 – 7.61 (m, 2H), 7.37 – 7.26 (m, 3H), 3.30 (td, *J* = 9.9, 4.0 Hz, 1H), 3.06 (td, *J* = 10.3, 4.0 Hz, 1H), 2.19 – 2.08 (m, 2H), 1.84 – 1.59 (m, 2H), 1.52 – 1.35 (m, 2H), 1.32 – 1.22 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 135.9, 129.0, 128.0, 127.7, 64.5, 47.0, 32.9, 31.7, 25.8, 23.9. MS (ESI): *m/z* (%) 298 (M+18). HRMS: *m/z* calcd for $C_{12}H_{19}N_4Se$ [M+18]: 299.0775; found: 299.0771.

(2-azido-2-phenylethyl)(benzyl)selane **3h**

Pale yellow oil.

IR (neat): 2100 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.45 – 7.32 (m, 5H), 7.31 – 7.22 (m, 5H), 4.48 (dd, *J* = 8.1, 6.4 Hz, 1H), 3.76 (s, 2H), 2.91 – 2.84 (m, 1H), 2.78 (dd, *J* = 13.0, 6.2 Hz,

1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 138.8, 133.3, 129.4, 129.3, 128.9, 128.7, 127.5, 126.9, 66.0, 34.0, 21.3. MS (ESI): *m/z* (%) 334 (M+18). HRMS: *m/z* calcd for $C_{15}H_{19}N_4Se$ [M+18]: 335.0775; found: 335.0742.

(2-azido-2-(4-tolyl)ethyl)(benzyl)selane **3i**

Pale yellow oil.

IR (neat): 2101 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.37 – 7.24 (m, 5H), 7.23 – 7.20 (m, 2H), 7.18 – 7.15 (m, 2H), 4.47 (dd, *J* = 7.8, 6.6 Hz, 1H), 3.78 (s, 2H), 2.88 (dd, *J* = 12.9, 8.2 Hz, 1H), 2.78 (dd, *J* = 12.9, 6.3 Hz, 1H), 2.40 (d, *J* = 6.8 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 138.9, 138.4, 135.9, 129.4, 128.9, 128.5, 126.9, 126.7, 66.6, 29.4, 28.0, 21.1. MS (ESI): *m/z* (%) 348 (M+18). HRMS: *m/z* calcd for $C_{16}H_{21}N_4Se$ [M+18]: 349.0931; found: 349.0913.

(2-azido-2-(4-chlorophenyl)ethyl)(benzyl)selane **3j**

Pale yellow oil.

IR (neat): 2103 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.37 – 7.32 (m, 3H), 7.32 – 7.25 (m, 4H), 7.20 – 7.15 (m, 2H), 4.42 (dd, *J* = 7.7, 6.6 Hz, 1H), 3.78 (s, 2H), 2.83 (dd, *J* = 12.9, 7.9 Hz, 1H), 2.73 (dd, *J* = 12.9, 6.4 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 138.8, 137.5, 134.4, 129.3, 129.0, 128.7, 128.3, 128.2, 127.0, 66.1, 29.4, 28.2. MS (ESI): *m/z* (%) 368 (M+18). HRMS: *m/z* calcd for $C_{15}H_{18}N_4ClSe$ [M+18]: 369.0385; found: 369.0379.

References

1. Wirth, T. *Tetrahedron* **1999**, *55*, 1-28.
2. Wirth, T. *Angew. Chem., Int. Ed*. **2000**, *39*, 3740-3749.
3. Freudendahl, D. M.; Shahzad, S. A.; Wirth, T. *Eur. J. Org. Chem*. **2009**, 1649-1664.
4. Mukherjee, A. J.; Zade, S. S.; Singh, H. B.; Sunoj, R. B. *Chem. Rev*. **2010**, *110*, 4357-4416.
5. Walter, R.; Roy, J. *J. Org. Chem*. **1971**, *36*, 2561-2563.
6. Zeni, G.; Stracke, M. P.; Nogueira, C. W.; Braga, A. L.; Menezes, P. H.; Stefani, H. A. *Org. Lett*. **2004**, *6*, 1135-1138.
7. Letavayova, L.; Vlckova, V.; Brozmanova, J. *Toxicology* **2006**, *227*, 1-14.
8. Erkekoglu, P.; Rachidi, W.; Yuzugullu, O. G.; Giray, B.; Favier, A.; Ozturk, M.; Hincal, F. *Toxicol. Appl. Pharmacol*. **2010**, *248*, 52-62.
9. Hartwig, A.; Blessing, H.; Schwerdtle, T.; Walter, I. *Toxicology* **2003**, *193*, 161-169.
10. Erkekoglu, P.; Giray, B.; Rachidi, W.; Hininger-Favier, I.; Roussel, A.-M.; Favier, A.; Hincal, F. *Environ. Toxicol*. **2014**, *29*, 98-107.
11. Rayman, M. P. *Proceed. Nutrition Soc.* **2005**, *64*, 527-542.
12. Erkekoglu, P.; Chao, M.-W.; Ye, W.; Ge, J.; Trudel, L. J.; Skipper, P. L.; Kocer-Gumusel, B.; Engelward, B. P.; Wogan, G. N.; Tannenbaum, S. R. *Food Chem. Toxicol*. **2014**, *72*, 98-110.
13. Yu, L.; Chen, F.-L.; Ding, Y.-H. *ChemCatChem*, **2016**, *8*, 1033-1037.
14. Tiecco, M.;Testaferri, L.;Temperini, A.; Bagnoli, L.; Marini, F.; Santi, C. *Synth. Commun*. **1998**, *28*, 2167-2179.
15. Riela, S.; Aprile, C.; Gruttadauria, M.; Lo Melo, P.; Noto, R. *Molecules* **2005**, *10*, 383-393.

16. Ward, V. R.; Cooper, N. A.; Ward, A. P. *J. Chem. Soc., Perkin Trans. 1* **2001**, 944-945.

17. Broggini, G.; Molteni, G.; Zucchi, G. *Synthesis* **1995**, 647-648.

18. Hasser, A.; Amarasekara, A. S. *Tetrahedron Lett*. **1987**, *28*, 5185-5188.

19. Tiecco, M.; Testaferri, L.; Santi, C.; Tomassini, C.; Marini, F.; Bagnoli, L.; Temperini, A. *Angew. Chem., Int. Ed*. **2003**, *42*, 3131-3133.

20. Tiecco, M.; Testaferri, L.; Santi, C.; Tomassini, C.; Santoro, S.; Marini, F.; Bagnoli, L.; Temperini, A. *Tetrahedron* **2007**, *63*, 12373-12378.

21. Tingoli, M.; Tiecco, M.; Chianelli, D.; Balducci, R.; Temperini, A. *J. Org. Chem*. **1991**, *56*, 6809-6813.

22. Vieira, A. A.; Azeredo, J. B.; Godoi, M.; Santi, C.; da Silva Junior, E. N.; Braga, A. L. *J. Org. Chem.* **2015**, *80*, 2120-2127.

23. Tingoli, M.; Tiecco, M.; Testaferri, L.; Balducci, R. *Synlett* **1993**, 211-212.

24. Tingoli, M.; Tiecco, M.; Testaferri, L.; Temperini, A. *Chem. Commun.* **1994**, 1883-1884.

25. Shi, M.; Wang, B.-Y.; Li, J. *Eur. J. Org. Chem.* **2005**, 759-765.

26. Yu, L.; Chen, B.; Huang, X. *Tetrahedron Lett*. **2007**, *48*, 925-927.

27. Mironov, Y. V.; Sherman, A. A.; Nifantiev, N. E. *Tetrahedron Lett*. **2004**, *45*, 9107-9110.

28. Shi, H-W.; Yu, C.; Zhu, M.; Yan, J. *J. Organomet. Chem*. **2015**, *776*, 117-122.

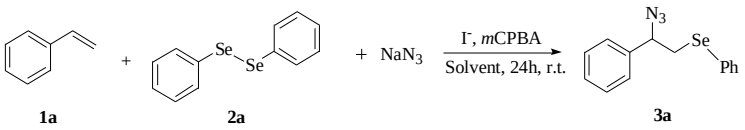
29. Yu, C.; Shi, H-W.; Zhu, M.; Yan, J. *Synlett* **2015**, *26*, 2139-2144.

30. Muangkaew, C.; Katrun, P.; Kanchanarugee, P.; Pohmakotr, M.; Reutrakul, V.; Soorukram, D.; Jaipetch, T.; Kuhakarn, C. *Tetrahedron* **2013**, *69*, 8847-8856.

31. Huang, Z.-Z.; Huang, X.; Huang, Y.-Z. *J. Chem. Soc. Perkin Trans. I* **1995**, 95-96.

32. Toshimitsu, A.; Uemura, S.; Okano, M. *J. Chem. Soc. Chem. Commun*. **1982**, 87-89.

Table 1. Optimization of azidoselenenylation of styrene using KI as catalyst



1a **2a** **3a**

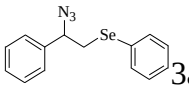
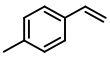
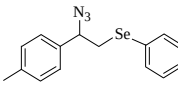
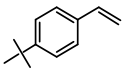
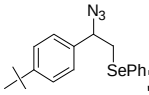
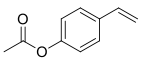
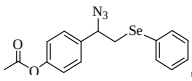
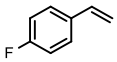
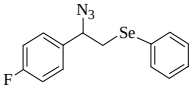
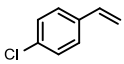
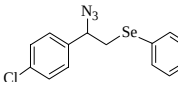
Entry	*m*CPBA (equiv.)	I⁻ (equiv.)	NaN_3 (equiv.)	Solvent	Yield (%)[a]
1	1.2	KI (0.1)	1.5	MeCN	24
2	1.2	-	1.5	MeCN	3
3	1.2	KI (0.1)	1.5	CH_2Cl_2	12
4	1.2	KI (0.1)	1.5	DMF	-
5	1.2	KI (0.1)	1.5	THF	-
6	1.2	KI (0.1)	1.5	MeCN/H_2O (10/1)	57
7	1.2	KI (0.1)	1.5	MeCN/AcOH (10/1)	42
8	1.2	KI (0.1)	1.5	MeCN/MeOH	50

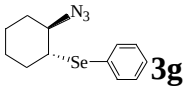
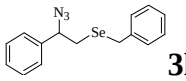
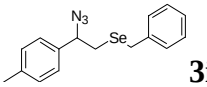
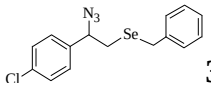
				(10/1)	
9	1.2	KI (0.1)	1.5	MeCN/CF_3CH_2OH (10/1)	49
10	1.2	KI (0.1)	1.5	MeCN/H_2O (5/1)	56
11	1.2	KI (0.1)	1.5	MeCN/H_2O (5/2)	59
12	1.2	KI (0.1)	1.5	MeCN/H_2O (5/3)	62
13	1.2	KI (0.1)	1.5	MeCN/H_2O (5/4)	74
14	1.2	KI (0.1)	1.5	MeCN/H_2O (1/1)	77
15	1.2	KI (0.1)	1.5	MeCN/H_2O (5/6)	80
16	1.2	KI (0.1)	1.5	MeCN/H_2O (5/7)	75
17	1.2	KI (0.1)	1.5	MeCN/H_2O (5/8)	70
18	1.2	NH_4I (0.1)	1.5	MeCN/H_2O (5/6)	70
19	1.2	PhI (0.1)	1.5	MeCN/H_2O (5/6)	31
20	1.2	C_3H_7I(0.1)	1.5	MeCN/H_2O (5/6)	41
21	1.2	KI (0.2)	1.5	MeCN/H_2O (5/6)	75
22	1.5	KI (0.1)	1.5	MeCN/H_2O (5/6)	68

23	1.2	KI (0.1)	2.0	MeCN/H_2O (5/6)	45
24	1.2	KI (0.1)	2.5	MeCN/H_2O (5/6)	69
25	1.2	KI (0.1)	3.0	MeCN/H_2O (5/6)	51

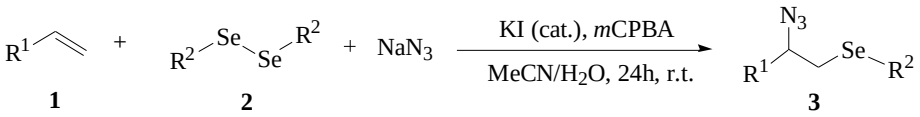
[a] Isolated yield.

Table 2 The result of KI catalyzed azidoselenenylation of alkenes

Entry	Alkene	Diselenide	Product	Yield(%)[a]
1	 **1a**	PhSeSePh **2a**	 **3a**	80
2	 **1b**	**2a**	 **3b**	52
3	 **1c**	**2a**	 **3c**	61
4	 **1d**	**2a**	 **3d**	57
5	 **1e**	**2a**	 **3e**	65
6	 **1f**	**2a**	 **3f**	56

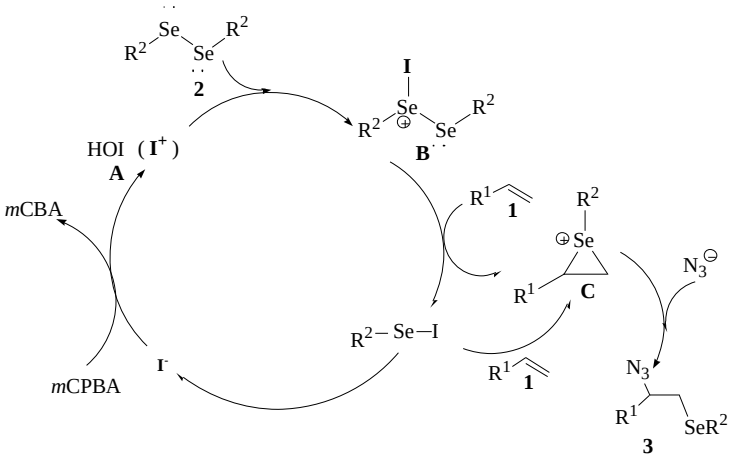
7	 **1g**	**2a**	 **3g**	48
8	**1a**	**$PhCH_2SeSeC$ H_2Ph 2b**	 **3h**	51
9	**1b**	**2b**	 **3i**	71
10	**1f**	**2b**	 **3j**	47

[a] Isolated yields.



1 **2** **3**

Scheme 1 KI catalyzed azidoselenenylation of alkenes



Scheme 2 Proposed mechanism for the catalyzed azidoselenenylation of alkenes