

Cesium Salt-Catalyzed Addition of Diphenyl Dichalcogenides to Alkynes: Selective Synthesis of Bis- and Mono(phenylchalcogeno)alkenes

Yutaka Nishiyama,* Haruko Ohnishi, and Yuya Koguma

Faculty of Chemistry, Materials and Bioengineering, Kansai University, Suita, Osaka 564-8680

Received June 6, 2008; E-mail: nishiya@ipcku.kansai-u.ac.jp

A cesium salt has a unique catalytic ability for the reaction of alkynes with diphenyl dichalcogenides. When the diphenyl dichalcogenides, such as the disulfide, diselenide, or ditelluride, were allowed to react with alkynes in the presence of a catalytic amount of a cesium fluoride or carbonate, the bisphenylchalcogenation of the alkynes efficiently proceeded to give the corresponding *vic*-bis(phenylchalcogeno)alkenes in moderate to good yields with high selectivity. When H₂O was added to the reaction medium, monophenylchalcogenation of the alkynes occurred giving the mono(phenylchalcogeno)alkenes in moderate yields.

One direct synthetic method of *vic*-bis(phenylchalcogeno)-alkenes involves the addition of diphenyl dichalcogenides, such as the disulfide, diselenide, or ditelluride, to the carbon–carbon triple bond of alkynes. It has already been reported that the diphenyl dichalcogenides add to terminal alkynes in the presence of a transition-metal catalyst¹ or under irradiation of near-UV light² to produce *vic*-bis(phenylchalcogeno)alkenes in moderate to good yields. As another method, Oshima et al. recently showed that GaCl₃ assisted the bisphenylthiolation of alkynes with diphenyl disulfide.³ It was shown that reaction of diphenyl dichalcogenides proceeds with propargylic alcohols in the presence of butyllithium⁴ or with phenylacetylene in the presence of alumina-supported sodium borohydride.⁵ We now discovered the cesium-catalyzed bisphenylchalcogenation of alkynes with diphenyl dichalcogenides to give the corresponding *vic*-bis(phenylchalcogeno)alkenes in moderate to good yields with high selectivity. Furthermore, in the presence of water, the monophenylchalcogenation of alkynes predominantly occurs to give mono(phenylchalcogeno)alkenes in moderate yields (Scheme 1).^{6,7}

Results and Discussion

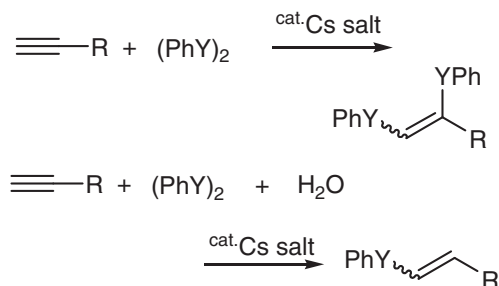
When diphenyl diselenide was allowed to react with ethyl propiolate (**1a**) in the presence of a catalytic amount of cesium fluoride (8 mol %) in THF solvent at 67 °C for 5 h, the bisphenylselenenation of the carbon–carbon triple bond

smoothly proceeded to give the ethyl 2,3-bis(phenylseleno)-acrylate (**2a**) in 74% yield (E/Z = 22/78) along with the formation of the ethyl 3-(phenylseleno)acrylate (16%) and ethyl 3-(phenylseleno)propiolate (3%) as by-products (Entry 3 in Table 1).⁶ In the absence of the cesium salt, **2a** was not formed, and the starting materials were recovered (Entry 1). By increasing the amount of the diselenide, the yield of **2a** was improved (Entry 4). Similarly, in the presence of a catalytic amount of cesium carbonate, the bisphenylselenenation of **1a** occurred to give **2a** in 82% yield (Entry 8). In contrast, in the case of other cesium salts, such as cesium chloride, bromide,

Table 1. Reaction of Ethyl Propiolate with Diphenyl Diselenide^{a)}

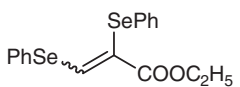
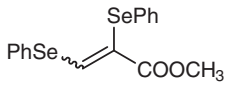
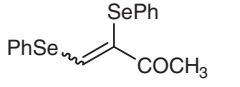
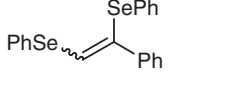
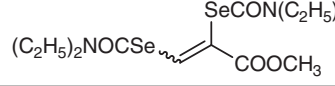
$\text{HC}\equiv\text{C}-\text{COOC}_2\text{H}_5 + \text{PhSeSePh} \xrightarrow{\text{catalyst}} \text{PhSe}-\text{CH}=\text{CH}(\text{SePh})-\text{COOC}_2\text{H}_5$ 1a 2a		
Entry	Catalyst	Yield/(%) ^{b)}
1	None	trace
2 ^{c)}	CsF	3
3 ^{d)}	CsF	74 (22/78) ^{e)}
4 ^{f)}	CsF	89
5	CsCl	9
6	CsBr	5
7	CsI	9
8	Cs ₂ CO ₃	82
9	KF	49
10	NaF	40
11	LiF	22

a) Reaction conditions: PhSeSePh (0.30 mmol), **1a** (0.25 mmol), catalyst (0.02 mmol), and THF (2.5 mL) at 67 °C for 5 h. b) GC yield based on **1a**. c) Reaction was carried out at 25 °C. d) Ethyl 3-(phenylseleno)acrylate (16%) and ethyl 3-(phenylseleno)propiolate (3%) were formed. e) The number in parenthesis shows the ratios of the E and Z isomers. f) PhSeSePh (3.00 mmol) was used.



Scheme 1.

Table 2. Cesium Salt-Catalyzed Reaction of Alkynes with Diselenides^{a)}

Entry	Diselenide	Alkyne	Product	Yield/% ^{b)} (E/Z)
1	(PhSe) ₂	$\equiv\text{C}-\text{COOC}_2\text{H}_5$ 1a	 2a	74 (22/78)
2	(PhSe) ₂	$\equiv\text{C}-\text{COOCH}_3$ 1b	 2b	72 (22/78)
3	(PhSe) ₂	$\equiv\text{C}-\text{COCH}_3$ 1c	 2c	51 (35/65)
4 ^{c)}	(PhSe) ₂	$\equiv\text{C}-\text{Ph}$ 1d	 2d	68 ^{d)} (71/29)
5	$\left((\text{C}_2\text{H}_5)_2\text{N}-\overset{\text{O}}{\underset{\text{O}}{\parallel}}\text{C}-\text{Se} \right)_2$	$\equiv\text{C}-\text{COOCH}_3$ 1b	 2e	50 (25/75)

a) Reaction conditions: diselenide (0.30 mmol), alkyne (0.25 mmol), CsF (0.02 mmol), and THF (2.5 mL) at 67 °C for 5 h. b) GC yield based on alkyne. c) Reaction conditions: PhSeSePh (0.30 mmol), phenylacetylene (0.60 mmol), Cs₂CO₃ (0.02 mmol), and dimethylacetamide (DMA) (2.5 mL) at 125 °C for 5 h. d) GC yield based on diselenide.

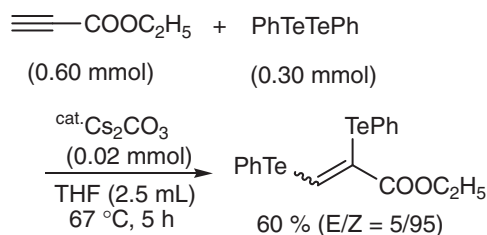
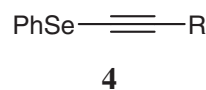
Table 3. Cesium Carbonate-Catalyzed Reaction of Alkynes with Diphenyl Disulfide^{a)}

$\equiv\text{C}-\text{R} + \text{PhSSPh} \xrightarrow{\text{cat. Cs}_2\text{CO}_3} \text{PhS}-\text{C}(\text{SPh})=\text{C}(\text{R})-\text{R}$		
1		3
Entry	R	Yield/% ^{b)} (E/Z)
1	COOC ₂ H ₅ (1a)	3a 73 (23/77)
2	COOCH ₃ (1b)	3b 73 (25/75)
3 ^{c)}	Ph (1d)	3c 89 ^{d)} (3/97)

a) Reaction conditions: PhSSPh (1.0 mmol), alkyne (1.0 mmol), Cs₂CO₃ (0.2 mmol), and DMA (2.5 mL) at 67 °C for 5 h. b) GC yield based on alkyne. c) Phenylacetylene (2.0 mmol) was used. At 125 °C. d) GC yield based on phenylacetylene.

and iodide, the bisphenylselenolation hardly proceeded (Entries 5–7). In the presence of another alkaline metal fluoride, the yields of **2a** slightly decreased (Entries 9–11).

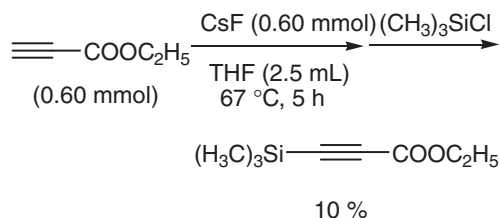
To determine the scope and limitations of the cesium salt-catalyzed bisphenylselenolation of alkynes with diphenyl diselenide, the diphenyl diselenide was allowed to react with various alkynes in the presence of a catalytic amount of cesium fluoride (8 mol %) and these results are shown in Table 2. For the reaction of the methyl and ethyl propiolates, and 3-oxobutynone, which have an electron-withdrawing group adjacent to the carbon–carbon triple bond, the bisphenylselenolation of the carbon–carbon triple bond smoothly took place to give the corresponding *vic*-bis(phenylseleno)alkenes in moderate yields (Entries 1–3). In the case of phenylacetylene, the product yield was low (19%) under the same reaction conditions as that of ethyl propiolate, however the product yield was improved using two equimolar amounts of phenylacetylene (0.60 mmol) (Entry 4). When bis(*N,N*-diethylcarbamoyl) diselenide instead of diphenyl diselenide was used as the diselenide, methyl 2,3-

**Scheme 2.****Figure 1.**

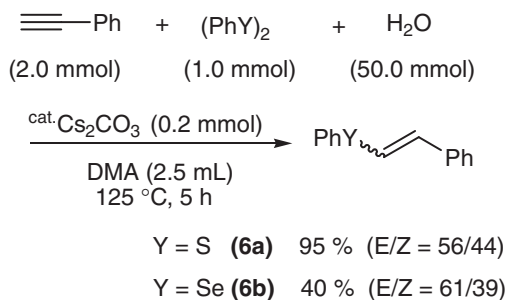
bis(*N,N*-diethylcarbamoylseleno)acrylate was formed in 50% yield (Entry 5).

Next, the cesium salt-catalyzed bisphenylthiolation of alkynes with diphenyl disulfide was examined and these results are shown in Table 3. Similarly, the addition of diphenyl disulfide to the carbon–carbon triple bond of ethyl and methyl propiolates occurred to give both the ethyl and methyl 2,3-bis(phenylthio)acrylates in 73% yield (Entries 1 and 2). In the case of the phenylacetylene, the bisphenylthiolation did not proceed under the same reaction conditions as that of ethyl propiolate; however, the bisphenylthiolation did occur by raising the reaction temperature (Entry 3). Similarly, the bisphenyltellurolation of ethyl propiolate with diphenyl ditelluride took place to afford the *vic*-bis(phenyltelluro)alkenes in 60% yield (Scheme 2).

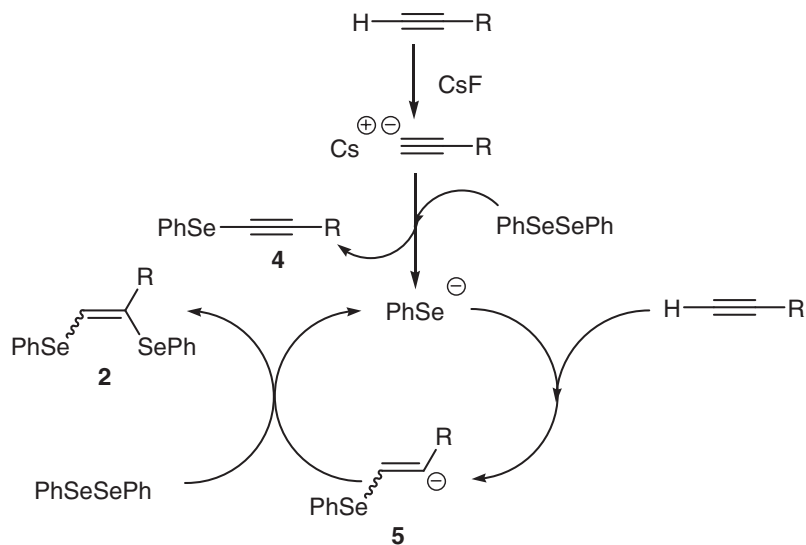
Upon the cesium salt-catalyzed addition of the dichalcogenides to terminal alkynes, the alkynyl phenyl selenide **4** (Figure 1) was observed as the by-product. The result suggested that the acetylide was generated in situ by depro-



Scheme 3.



Scheme 5.



Scheme 4.

nation of the terminal alkynes. In fact, when ethyl propiolate was treated with cesium fluoride and subsequently the reaction mixture was quenched with chlorotrimethylsilane the reaction gave ethyl 3-trimethylsilylpropiolate in 10% yield (Scheme 3).

We cannot explain the reaction pathway in detail, but a plausible reaction pathway is shown in Scheme 4. The first step of the reaction is the generation of the acetylide by deprotonation of the terminal alkynes with the cesium salt. The acetylide is trapped with diselenide to form the alkynyl phenyl selenide **4**, and the phenyl selenolate.⁸ The phenyl selenolate adds to the carbon–carbon triple bond to form the vinyl anion **5** and **5** is quenched with diphenyl diselenide giving the corresponding bis(phenylseleno)alkenes **2** and regenerating the phenyl selenolate. Another generation pathway of the phenyl selenolate by the reaction of the diphenyl diselenide with the cesium salt cannot be ruled out.⁹

Mono(phenylchalcogeno)alkenes are widely used as synthetic intermediates in organic synthetic reactions¹⁰ and as electrophotographic photoreceptors.¹¹ There is increasing interest in development of a method for the synthesis of mono(phenylchalcogeno)alkenes.¹² The addition of a thiol or selenol or alkali metal salts of these compounds to the carbon–carbon triple bond is one direct synthetic method for mono(phenylchalcogeno)alkenes; however, there are some disadvantages to these methods: (i) handling of the thiol and selenol, which are bad smelling and unstable compounds in air (ii) the

use of an excess amount of alkali metals, and (iii) the reaction under nonaqueous conditions. From the proposed reaction pathways including the formation of the vinyl anion **5**, the cesium-catalyzed reaction of alkynes with diphenyl dichalcogenide in the presence of H₂O was investigated to prepare the mono(phenylchalcogeno)alkenes. When diphenyl disulfide or diselenide was allowed to react with phenylacetylene in the presence of a catalytic amount of cesium carbonate (20 mol %) and an excess amount of water in DMA solvent at 125 °C for 5 h, the monophenylthiolation and monophenylselenolation of the phenylacetylene smoothly proceeded to give the corresponding mono(phenylchalcogeno)alkenes **6** in 95 and 40% yields (Scheme 5).

Conclusion

In summary, we discovered the unique catalytic ability of cesium fluoride and carbonate for the reaction of alkynes with diphenyl dichalcogenides. The bisphenylchalcogenolation of the carbon–carbon triple bond with diphenyl dichalcogenides, such as the disulfide, diselenide, or ditelluride in the presence of a cesium fluoride or carbonate catalyst efficiently proceeded to give the *vic*-bis(phenylchalcogeno)alkenes in moderate to good yields. In addition, the mono(phenylchalcogeno)alkenes were formed by the cesium salt-catalyzed reaction of the alkynes with the diphenyl dichalcogenides and water.

Experimental

General Procedures. The ^1H and ^{13}C NMR spectra were recorded on 400 and 100 MHz spectrometers using CDCl_3 as the solvent with tetramethylsilane as the internal standard. The IR spectra were recorded on an FT-IR spectrometer. Gas chromatography (GC) was carried out using a flame-ionizing detector-equipped instrument and a capillary column (0.25 mm $\times$ 1200 mm). The HPLC separation was performed using a recycling preparative HPLC equipped with GPC columns (20 mm $\times$ 1200 mm).

Reagents. Diphenyl disulfide, the alkynes, the cesium salts, and alkaline metal salts were purchased as high grade products, and used without further purification. Diphenyl diselenide¹³ and bis(*N,N*-diethylcarbamoyl) diselenide¹⁴ were synthesized as described in the literature. The solvents were purified before use by the usual methods.

General Procedure for Cesium Salt-Catalyzed Reaction of Alkyne with Diphenyl Diselenide. A THF (2.5 mL) solution of diselenide (0.30 mmol), alkyne (0.25 or 0.60 mmol), and cesium fluoride (3 mg, 0.02 mmol) was stirred at 67 °C for 5 h under a nitrogen atmosphere. After the reaction was complete, aq HCl (5%) (20 mL) was added to the reaction mixture, and the resultant solution was extracted with diisopropyl ether (20 mL $\times$ 3). The organic layer was dried over MgSO_4 . The resulting mixture was filtered, and the filtrate was then concentrated. Purification of the residue by HPLC afforded the corresponding *vic*-bis(chalcogeno)alkenes. The product was characterized by comparing its spectral data with those of authentic samples **2a**,^{2b} **2b**,^{1a} and **2d**.^{1c} The structures of the product were assigned by their ^1H and ^{13}C NMR, IR, and mass spectra.

2c (a mixture of *E/Z* isomers) ^1H NMR (CDCl_3 , 400 MHz): δ 8.83 (s, 0.35H), 8.43 (s, 0.65H), 7.62–7.19 (m, 10H), 2.46 (s, 0.65 $\times$ 3H), 2.36 (s, 0.35 $\times$ 3H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 198.9, 159.3, 134.1, 133.6, 132.9, 132.1, 131.0, 129.9, 129.6, 129.5, 129.4, 129.4, 128.4, 126.9, 119.9, 22.8; IR (KBr): 687, 745, 1031, 1273, 1403, 1651, 3050 cm^{-1} ; MS m/z 382 ($\text{M}^+ + ^{80}\text{Se}$); Anal. Calcd for $\text{C}_{16}\text{H}_{14}\text{OSe}_2$: C, 50.54; H, 3.71%. Found: C, 50.67; H, 3.52%. **2e** (a mixture of *E/Z* isomers) ^1H NMR (CDCl_3 , 400 MHz): δ 9.25 (s, 0.75H), 8.88 (s, 0.25H), 3.82 (s, 0.25 $\times$ 3H), 3.80 (s, 0.75 $\times$ 3H), 3.49–3.27 (m, 8H), 1.84 (t, J = 7.2 Hz, 0.75 $\times$ 12H), 1.25 (t, J = 7.2 Hz, 0.25 $\times$ 12H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 166.9, 162.6, 161.9, 153.4, 113.2, 52.9, 52.8, 43.2, 42.8, 42.7, 42.5, 42.2, 14.3, 14.2, 14.1, 13.1; IR (KBr): 652, 842, 1071, 1273, 1403, 1667, 1688, 2936, 2975 cm^{-1} ; MS m/z 458. ($\text{M}^+ + ^{80}\text{Se}$); Anal. Calcd for $\text{C}_{14}\text{H}_{24}\text{N}_2\text{O}_4\text{Se}_2$: C, 38.02; H, 5.47; N, 6.33%. Found: C, 38.27; H, 5.74; N, 6.08%.

General Procedure for Cesium Salt-Catalyzed Reaction of Alkyne with Diphenyl Disulfide. A DMA (2.5 mL) solution of diphenyl disulfide (218 mg, 1.0 mmol), alkyne (1.0 or 2.0 mmol), and cesium carbonate (65 mg, 0.2 mmol) was stirred at 67 °C for 5 h under a nitrogen atmosphere. After the reaction was complete, aq HCl (5%) (20 mL) was added to the reaction mixture, and the resultant solution was extracted with diisopropyl ether (20 mL $\times$ 3). The organic layer was dried over MgSO_4 . The resulting mixture was filtered, and the filtrate was then concentrated. Purification of the residue by HPLC afforded the corresponding *vic*-bis(phenylthio)alkenes. The product was characterized by comparing its spectral data with those of an authentic sample **3c**.^{1c} The structures of the products were assigned by their ^1H and ^{13}C NMR, IR, and Mass spectra.

3a (a mixture of *E/Z* isomers) ^1H NMR (CDCl_3 , 270 MHz):

δ 8.39 (s, 0.23H), 7.68–7.19 (m, 10H), 5.33 (s, 0.77H), 4.15 (q, J = 8.1 Hz, 0.23 $\times$ 2H), 4.13 (qd, J = 8.1 and 1.6 Hz, 0.77 $\times$ 2H), 1.23 (t, J = 8.1 Hz, 0.77 $\times$ 3H), 1.14 (t, J = 8.1 Hz, 0.23 $\times$ 3H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 166.5, 164.2, 149.7, 146.7, 136.1, 133.0, 131.1, 129.6, 129.3, 129.1, 128.2, 115.5, 113.3, 60.3, 60.3, 14.3, 14.2; IR (KBr): 3059, 2980, 1690, 1534, 1171, 814, 748, 689 cm^{-1} ; MS m/z 316 (M^+); Anal. Calcd for $\text{C}_{17}\text{H}_{16}\text{O}_2\text{S}_2$: C, 64.53; H, 5.10; S, 20.27%. Found: C, 64.82; H, 4.98; S, 20.53%. **3b** (a mixture of *E/Z* isomers) ^1H NMR (CDCl_3 , 270 MHz): δ 7.69–7.36 (m, 10H), 7.26 (s, 0.25H), 5.30 (s, 0.75H), 3.66 (s, 0.75 $\times$ 3H), 3.49 (s, 0.25 $\times$ 3H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 165.6, 163.7, 136.9, 135.3, 131.3, 130.2, 130.1, 130.0, 129.8, 129.5, 129.0, 128.8, 128.7, 126.3, 107.7, 51.1; IR (KBr): 3058, 2947, 1697, 1534, 1303, 1171, 813, 749, 689 cm^{-1} ; MS m/z 302 (M^+); Anal. Calcd for $\text{C}_{16}\text{H}_{14}\text{O}_2\text{S}_2$: C, 63.55; H, 4.67; S, 21.21%. Found: C, 63.49; H, 4.51; S, 21.56%.

Typical Procedure for Cesium Salt-Catalyzed Reaction of Ethyl Propiolate with Diphenyl Ditelluride. A THF (2.5 mL) solution of diphenyl ditelluride (123 mg, 0.30 mmol), ethyl propiolate (59 mg, 0.60 mmol), and cesium carbonate (65 mg, 0.02 mmol) was stirred at 67 °C for 5 h under nitrogen atmosphere. After the reaction was complete, aq HCl (5%) (20 mL) was added to the reaction mixture and the resultant solution was extracted with diisopropyl ether (20 mL $\times$ 3). The organic layer was dried over MgSO_4 . The resulting mixture was filtered, and the filtrate was then concentrated. Purification of the residue by HPLC afforded the corresponding *vic*-(bisphenyltelluro)alkenes. The product was characterized by comparing its spectral data with those of authentic sample **3c**.^{1a}

General Procedure for Cesium Salt-Catalyzed Reaction of Phenylacetylene with Diphenyl Chalcogenide and Water. A DMA (2.5 mL) solution of diphenyl dichalcogenide (1.0 mmol), phenylacetylene (2.0 mmol), H_2O (50.0 mmol), and cesium carbonate (65 mg, 0.2 mmol) was stirred at 125 °C for 5 h under a nitrogen atmosphere. After the reaction was complete, aq HCl (5%) (20 mL) was added to the reaction mixture, and the resultant solution was extracted with diisopropyl ether (20 mL $\times$ 3). The organic layer was dried over MgSO_4 . The resulting mixture was filtered, and the filtrate was then concentrated. Purification of the residue by HPLC afforded the corresponding mono(phenylchalcogeno)alkenes. The product was characterized by comparing its spectral data to those of authentic samples **6a**¹⁵ and **6b**.¹⁶

General Procedure for Cesium Salt-Catalyzed Reaction of Alkyne with Diphenyl Diselenide in the Presence of Water. A DMA (2.5 mL) solution of diphenyl diselenide (314 mg, 1.0 mmol), alkyne (2.0 mmol), H_2O (50.0 mmol), and cesium carbonate (65 mg, 0.2 mmol) was stirred at 67 °C for 5 h under a nitrogen atmosphere. After the reaction was complete, aq HCl (5%) (20 mL) was added to the reaction mixture, and the resultant solution was extracted with diisopropyl ether (20 mL $\times$ 3). The organic layer was dried over MgSO_4 . The resulting mixture was filtered, and the filtrate was then concentrated. Purification of the residue by HPLC afforded the corresponding mono(phenylseleno)alkenes. The product was characterized by comparing its spectral data to those of authentic sample.¹⁷

Reaction of Ethyl Propiolate with Cesium Fluoride. A THF (2.5 mL) solution of ethyl propiolate (0.60 mmol), and cesium fluoride (90 mg, 0.60 mmol) was stirred at 67 °C for 5 h under a nitrogen atmosphere. After the reaction was complete, Me_3SiCl (1.5 mmol) was added to the reaction mixture and stirred at 25 °C for 5 h under a nitrogen atmosphere. H_2O (10 mL) was added to the

reaction mixture, and the resultant solution was extracted with diisopropyl ether (20 mL $\times$ 3). The organic layer was dried over Mg_2SO_4 . The resulting mixture was filtered, and the filtrate was then purified by distillation to afford 3-trimethylsilylpropiolate. The product was characterized by comparing its spectral data with those of the authentic sample.¹⁷

References

- 1 a) V. P. Ananikov, M. A. Kabeshov, I. P. Beletskaya, V. N. Khrustalev, M. Y. Antipin, *Organometallics* **2005**, *24*, 1275. b) V. P. Ananikov, I. P. Beletskaya, *Russ. Chem. Bull.* **2003**, *52*, 811. c) H. Kuniyasu, A. Ogawa, S. Miyazaki, I. Ryu, N. Kambe, N. Sonoda, *J. Am. Chem. Soc.* **1991**, *113*, 9796.
- 2 a) A. Ogawa, I. Ogawa, N. Sonoda, *J. Org. Chem.* **2000**, *65*, 7682. b) A. Ogawa, H. Yokoyama, K. Yokoyama, T. Masawaki, N. Kambe, N. Sonoda, *J. Org. Chem.* **1991**, *56*, 5721. c) A. Ogawa, N. Takami, M. Sekiguchi, H. Yokoyama, H. Kuniyasu, I. Ryu, N. Sonoda, *Chem. Lett.* **1991**, 2241. d) T. G. Back, M. V. Krishna, *J. Org. Chem.* **1988**, *53*, 2533.
- 3 S. Usugi, H. Yorimitsu, H. Shinokubo, K. Oshima, *Org. Lett.* **2004**, *6*, 601.
- 4 A. V. Moro, C. W. Nogueira, N. B. V. Barbosa, P. H. Menezes, J. B. T. da Rocha, G. Zeni, *J. Org. Chem.* **2005**, *70*, 5257.
- 5 G. Perin, R. G. Jacob, L. G. Dutra, F. de Azambuja, G. F. F. dos Santos, E. J. Lenardão, *Tetrahedron Lett.* **2006**, *47*, 935.
- 6 The other synthetic methods of *vic*-bis(phenylchalcogeno)alkenes: a) R.-L. Lu, X.-H. Xu, W.-Q. Liu, Q.-L. Zhang, X. Chen, *Chin. Chem. Lett.* **2005**, *16*, 325. b) X.-H. Xu, C. Xiong, R.-L. Lu, Q.-L. Zhang, *Huanan Daxue Xuebao, Zira Kexueban* **2004**, *31*, 15. c) A. V. Martynov, V. A. Potapov, S. V. Amosova, A. I. Albanov, *Russ. J. Gen. Chem.* **2003**, *73*, 1398. d) D.-Y. Yang, Y.-D. Wang, J.-B. Yan, X. Huang, *J. Chem. Res.* **2002**, 192. e) A. C. Galindo, J. M. Oliveira, M. A. G. Barboza, S. M. C. Gonçalves, P. H. Menezes, *Phosphorus, Sulfur Silicon Relat. Elem.* **2001**, *172*, 129. f) L. Benati, P. C. Montevicchi, P. Spagnolo, *J. Chem. Soc., Chem. Commun.* **1987**, 1050, and references cited therein.
- 7 Although, Zhangs et al. disclosed that cesium hydroxide acts as a catalyst for the reaction of diphenyl diselenide with alkynes, the alkynes were limited to phenyl-substituted alkynes and acetylene adjacent to alkoxymethyl groups. See: J.-C. Zeng, R.-L. Lu, X.-H. Xu, J.-K. Fang, B. Zhou, Q.-L. Zhang, *Youji. Huaxue* **2004**, *24*, 1482.
- 8 On the reaction of ethyl 3-*d*-propiolate, ethyl 3-(phenylseleno)-2,3-*d*-acrylate was formed in 6% yield. From this result, it was suggested that ethyl 3-(phenylseleno)-2,3-*d*-acrylate was formed by the deprotonation of terminal alkyne with the vinyl anion.
- 9 Diphenyl diselenide (1.0 mmol) was allowed to react with cesium fluoride (2 mmol) in THF (2 mL) at 67 °C for 5 h under a nitrogen atmosphere, and benzyl bromide (5 mmol) was added to the resulting solution to give benzyl phenyl selenide (2%).
- 10 a) B. Mahmoud, F.-G. West, *Tetrahedron Lett.* **2007**, *48*, 5091. b) S.-R. Sheng, X.-L. Liu, Q. Xu, C.-S. Song, *Synthesis* **2003**, 2763. c) L.-S. Zhu, X. Huang, *Synth. Commun.* **1997**, *27*, 39. d) J. V. Comasseto, H. A. Stefani, C. C. Silveira, *Synth. Commun.* **1990**, *20*, 751.
- 11 M. Shiyoji, Jpn. Kokai Tokkyo Koho 85-274674, Patent No. JP62134652, **1987**.
- 12 a) F. Manarin, J. A. Roehrs, M. Prigol, D. Alves, C. W. Nogueira, G. Zeni, *Tetrahedron Lett.* **2007**, *48*, 4805. b) Z. Wang, H. Mo, W. Bao, *Synlett* **2007**, 91. c) V. P. Ananikov, N. V. Orlov, I. P. Beletskaya, *Organometallics* **2007**, *26*, 740. d) J. V. Comasseto, J. T. B. Ferreira, N. Petragnani, *J. Organomet. Chem.* **1981**, *216*, 287.
- 13 H. J. Reich, J. M. Renga, L. L. Reich, *J. Am. Chem. Soc.* **1975**, *97*, 5434.
- 14 K. Kondo, N. Sonoda, K. Yoshida, M. Koishi, S. Tsutsumi, *Chem. Lett.* **1972**, 401.
- 15 C. G. Bates, P. Saejueng, M. Q. Doherty, D. Venkataraman, *Org. Lett.* **2004**, *6*, 5005.
- 16 V. P. Ananikov, D. A. Malyshev, I. P. Beletskaya, G. G. Aleksandrov, I. L. Eremenko, *J. Organomet. Chem.* **2003**, *679*, 162.
- 17 P. J. Dunn, C. W. Rees, *J. Chem. Soc., Perkin Trans. 1* **1987**, 1585.