Reactions of 2-Pentynyl Trimethylsilylethynyl Selenides with Primary Amines *via* Allenyl Selenoketene

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Reactions of 2-pentynyl trimethylsilylethynyl selenide **3** with primary amines **5** *via* allenyl selenoketene **4** afforded the corresponding selenine **6**, selenophene **7** and β,γ-unsaturated selenoamide **8**, respectively.

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The selenoketene has been extensively investigated because of the interesting properties and the reactivity has been reported using theoretical calculations [1]. From those results, the selenoketene is found to be more reactive than ketene [2]. Recently, we confirmed interesting evidence for allenyl selenoketene formation [3] *via* a [3+3] sigmatropic rearrangement by trapping with primary amines and its cyclization [4]. Herein, we investigated interesting reactivities of allenyl selenoketene.

The reaction leading to 2-pentynyl trimethylsilylethynyl selenides **3** is described. 2-Pentynyl chloride **2** was added to tetrahydrofuran solution of the lithium alkyneselenoate, generated *in situ* from trimethylsilylacetylene **1**, *n*-BuLi and elementary selenium, and the mixture was stirred at room temperature for 1.5 hours. Subsequent silica gel flash column chromatography afforded 2-pentynyl trimethylsilylethynyl selenide **3** in a 91 % yield.

In the case of allenylketene, it could be isolated by the ketene-stabilizing effect of silyl substitution [2f,5]. Similarly, though we tried to isolate the present allenyl selenoketene bearing silyl group, it failed [4,6]. In order to confirm the evidence for allenyl selenoketene formation *via* a [3+3] sigmatropic rearrangement, reactions with amines were carried out. The mixture of **3** and *n*-butyl amine **5a** in benzene was refluxed for 5 hours. After standard workup 2-butylimino-4-ethyl-2*H*-5,6-dihydroselenine **6a** was isolated in a 53% yield as a major product. 2-Butylimino-4-ethyl-5-methylidene-2,5-dihydroselenophene **7a** and *N*-butyl-3-ethyl-2-trimethylsilyl-3,4-pentadieneselenoamide **8a** were also isolated in 5 % and 21 %, respectively (Scheme 1). The ir and nmr spectra of **8a** were typical of a terminal allene [7]. Compound **8** bore trimethylsilyl group, while the trimethylsilyl group of precursors of compounds **6** and **7** was eliminated. The reaction of 2-pentynyl phenylethynyl selenide with amine **5** gave 2-imino-4-ethyl-3-phenyl-2*H*-5,6-dihydroselenine [4], while the present reaction gave thermodynamically stable compounds **6** and **7** by the elimination of the trimethylsilyl group [8]. The reactions using four kinds of primary amines **5** were investigated and gave **6** in 49-59% yields (Table 1).

Scheme 1

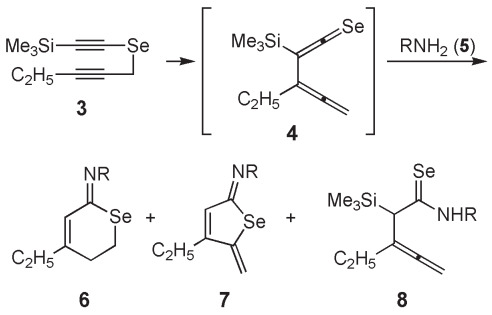


Table 1

Reaction of 2-Pentynyl Trimethylsilylethynyl Selenide **3** and Primary Amines **5**

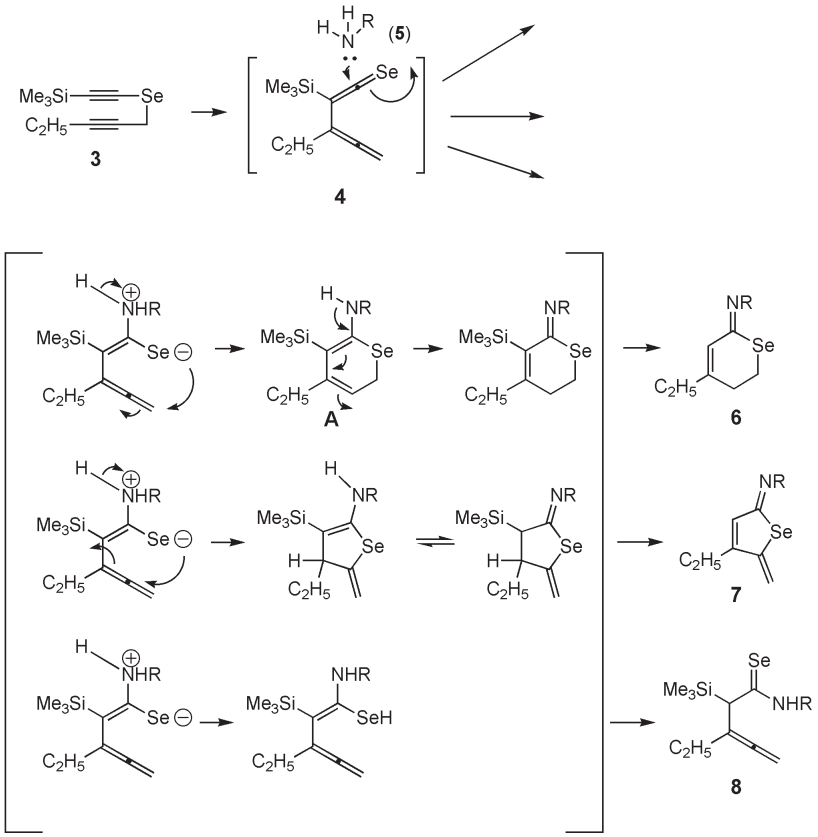
Entry	Primary amine **5** (R=)	Yield (%) [a] **6**	**7**	**8**
1	**5a**, $CH_3(CH_2)_3$	53	5	21
2	**5b**, $CH_3(CH_2)_2$	52	10	18
3	**5c**, $C_6H_5(CH_2)_2$	49	0	0
4	**5d**, $C_6H_5CH_2$	59	0	0

[a] Isolated yield.

The reactions with phenethyl amine **5c** and benzyl amine **5d** afforded only **6c** and **6d**, respectively, but did not give derivatives **7** and **8**. The isolation of **8a**, bearing a terminal allene, could confirm the formation of an allenyl selenoketene intermediate **4** in the present reaction and be explained by the mechanism presented in Scheme 2. Subsequent nucleophilic attack of allenyl selenoketene **4**, which was generated from **3** through a [3,3] sigmatropic rearrangement, by primary amine **5** afforded the observed products **6**, **7** and **8**, respectively (Scheme 2).

Previously, a generation of allenyl selenoketene intermediate **4** by heating of selenide **3** was confirmed [4]. The present reactions could confirm the generation of the allenyl selenoketene intermediate **4** in the reaction process again. The allenyl selenoketene intermediate **4** leads to 6-membered ring 2*H*-5,6-dihydroselenine **6**, 5-membered ring 2*H*-5-hydroselenophene **7**, and 3,4-pentadieneselenoamide **8**, respectively, by the reactions with the amines.

Scheme 2



The allenyl selenoketene contains interesting and highly active sites, and gave individual products by the substituent groups or reaction conditions.

EXPERIMENTAL

2-Pentynyl Trimethylsilylethynyl Selenide (**3**).

To a solution of trimethylsilylacetylene **1** (0.29 g, 3.0 mmole) in dry tetrahydrofuran (20 ml), *n*-butyllithium, in *n*-hexane (2.0 ml, 3.0 mmole) was added and stirred at 0 °C for 15 minutes under an argon atmosphere. Then selenium powder (0.24 g, 3.0 mmole) was added to the mixture and stirred for 30 minutes. Moreover, 2-pentynyl chloride **2** (0.31 ml, 3.0 mmole) was added to the reaction mixture and stirred at room temperature for 1 hour. The mixture was extracted with diethyl ether and washed with saturated NaCl solution. The organic layer was dried over sodium sulfate and evaporated to dryness. The residue was purified by flash chromatography on silica gel with *n*-hexane: diethyl ether (50:1) to give 0.66 g **3** (91%) as yellow green oil, ir (neat): 2089 cm^{-1}; ^1H nmr (400 MHz, deuteriochloroform): δ 0.00 (s, 9H, CH_3), 0.95 (t, 3H, J = 7.6 Hz, CH_3), 2.04 (qt, 2H, J = 7.6, 2.4 Hz, CH_2), 3.35 (t, 2H, J = 2.6 Hz, CH_2); ^{13}C nmr (100 MHz, deuteriochloroform): δ -0.1, 12.6, 13.8, 15.3, 74.0, 85.8, 87.4, 109.8; ^{77}Se nmr (76 MHz, deuteriochloroform): δ 248.6; ms (EI): m/z = 244 (M^+).

General Procedure for Synthesis of 2-Alkylimino-4-ethyl-2*H*-5,6-dihydroselenine (**6**) and 2-Alkylimino-4-ethyl-5-methylidene-2,5-dihydroselenophene (**7**) and *N*-Alkyl-3-ethyl-2-trimethylsilyl-3,4-pentadiene Selenoamide (**8**).

To a solution of 2-pentynyl trimethylsilylethynyl selenide **3** (0.24 g, 1.0 mmole) in dry benzene (20 ml), *n*-butyl amine **5a** (0.20 ml, 2.0 mmole) was added. The mixture was refluxed with stirring for 5 hours under an argon atmosphere. The mixture was extracted with diethyl ether and washed with saturated NaCl solution. The organic layer was dried over sodium sulfate and evaporated to dryness. The residue was purified by column chromatography on silica gel with *n*-hexane:diethyl ether (10:1) to give **6a** (0.13 g, 53%), **7a** (0.01 g, 5%) and **8a** (0.07 g, 21%), respectively.

2-Butylimino-4-ethyl-2*H*-5,6-dihydroselenine (**6a**).

This compound was obtained as orange oil, ir (neat): 1644 cm^{-1}; ^1H nmr (400 MHz, deuteriochloroform): δ 0.95 (t, 3H, J = 7.2 Hz, CH_3), 1.08 (t, 3H, J = 7.2 Hz, CH_3), 1.37-1.47 (m, 2H, CH_2), 1.72 (quint, 2H, J = 7.3 Hz, CH_2), 2.16 (q, 2H, J = 7.5 Hz, CH_2), 2.60 (t, 2H, J = 6.0 Hz, CH_2), 2.97 (t, 2H, J = 6.2 Hz, CH_2), 3.34 (t, 2H, J = 7.2 Hz, CH_2), 6.05 (s, 1H, CH); ^{13}C nmr (100 MHz, deuteriochloroform): δ 11.6, 13.8, 18.7, 20.7, 29.8, 32.508, 32.512, 55.8, 123.4, 151.8, 155.2; ^{77}Se nmr (76 MHz, deuteriochloroform): δ 292.3; ms (CI): m/z = 246 (M^++1).

Anal. Calcd. for $C_{11}H_{19}NSe$: C, 54.09; H, 7.84; N, 5.73. Found: C, 54.13; H, 7.88; N, 5.76.

4-Ethyl-2-propylimino-2*H*-5,6-dihydroselenine (**6b**).

This compound was obtained as orange oil, ir (neat): 1644 cm^{-1}; ^1H nmr (400 MHz, deuteriochloroform): δ 0.99 (t, 3H, J = 7.6 Hz, CH_3), 1.08 (t, 3H, J = 7.6 Hz, CH_3), 1.72-1.81 (m, 2H, CH_2), 2.16 (q, 2H, J = 7.6 Hz, CH_2), 2.60 (t, 2H, J = 6.0 Hz, CH_2), 2.97 (t, 2H, J = 6.2 Hz, CH_2), 3.30 (t, 2H, J = 7.0 Hz, CH_2), 6.05 (s, 1H, CH); ^{13}C nmr (100 MHz, deuteriochloroform): δ 11.6, 12.1, 18.8, 23.7, 29.8, 32.5, 57.8, 123.4, 151.9, 155.4; ^{77}Se nmr (76 MHz, deuteriochloroform): δ 292.6; ms (CI): m/z = 232 (M^++1).

Anal. Calcd for $C_{10}H_{17}NSe$: C, 52.17; H, 7.44; N, 6.08. Found: C, 52.33; H, 7.64; N, 5.96.

4-Ethyl-2-phenethylimino-2*H*-5,6-dihydroselenine (**6c**).

This compound was obtained as orange oil, ir (neat): 1643 cm^{-1}; ^1H nmr (400 MHz, deuteriochloroform): δ 1.08 (t, 3H, J = 7.4 Hz, CH_3), 2.16 (q, 2H, J = 7.5 Hz, CH_2), 2.59 (t, 2H, J = 6.0 Hz, CH_2), 2.96 (t, 2H, J = 6.2 Hz, CH_2), 3.05 (t, 2H, J = 7.8 Hz, CH_2), 3.60 (t, 2H, J = 8.0 Hz, CH_2), 6.06 (s, 1H, CH), 7.15-7.34 (m, 5H, Ar); ^{13}C nmr (100 MHz, deuteriochloroform): δ 11.6, 18.9, 29.8, 32.6, 36.9, 57.7, 123.4, 126.0, 128.3, 128.7, 140.1, 152.3, 156.3; ^{77}Se nmr (76 MHz, deuteriochloroform): δ 295.9; ms (CI): m/z = 294 (M^++1).

Anal. Calcd for $C_{15}H_{19}NSe$: C, 61.64; H, 6.55; N, 4.79. Found: C, 61.76; H, 6.77; N, 4.83.

2-Benzylimino-4-ethyl-2*H*-5,6-dihydroselenine (**6d**).

This compound was obtained as orange oil, ir (neat): 1643 cm^{-1}; ^1H nmr (400 MHz, deuteriochloroform): δ 1.08 (t, 3H, J = 7.2 Hz, CH_3), 2.16 (q, 2H, J = 7.3 Hz, CH_2), 2.61 (t, 2H, J = 6.0 Hz, CH_2), 2.99 (t, 2H, J = 6.2 Hz, CH_2), 4.56 (s, 2H, CH_2), 6.14 (s, 1H, CH), 7.26-7.32 (m, 5H, Ar); ^{13}C nmr (100 MHz, deuteriochloroform): δ 11.6, 19.0, 29.7, 32.5, 59.7, 123.6, 126.7, 128.0, 128.3, 139.4, 152.4, 156.7; ^{77}Se nmr (76 MHz, deuteriochloroform): δ 297.2; ms (CI): m/z = 280 (M^++1).

Anal. Calcd for $C_{14}H_{17}NSe$: C, 60.43; H, 6.16; N, 5.03. Found: C, 60.22; H, 6.23; N, 5.26.

2-Butylimino-4-ethyl-5-methylidene-2,5-dihydroselenophene (**7a**).

This compound was obtained as orange oil, ir (neat): 1622 cm^{-1}; ^1H nmr (400 MHz, deuteriochloroform): δ 0.95 (t, 3H, J = 7.6 Hz, CH_3), 1.24 (t, 3H, J = 7.2 Hz, CH_3), 1.38-1.47 (m, 2H, CH_2), 1.72 (quint, 2H, J = 7.3 Hz, CH_2), 2.51 (q, 2H, J = 7.5 Hz, CH_2), 3.27 (t, 2H, J = 7.2 Hz, CH_2), 5.45 (s, 1H, CH_2), 5.89 (s, 1H, CH_2), 6.46 (s, 1H, CH); ^{13}C nmr (100 MHz, deuteriochloroform): δ 12.9, 13.9, 20.7, 21.5, 32.4, 61.8, 112.3, 133.0, 143.6, 156.7, 164.7; ^{77}Se nmr (76 MHz, deuteriochloroform): δ 428.9; ms (CI): m/z = 244 (M^++1).

Anal. Calcd for $C_{11}H_{17}NSe$: C, 54.54; H, 7.07; N, 5.78. Found: C, 54.36; H, 7.11; N, 5.92.

4-Ethyl-5-methylidene-2-propylimino-2,5-dihydroselenophene (**7b**).

This compound was obtained as orange oil, ir (neat): 1627 cm^{-1}; ^1H nmr (400 MHz, deuteriochloroform): δ 0.99 (t, 3H, J = 7.2 Hz, CH_3), 1.24 (t, 3H, J = 7.6 Hz, CH_3), 1.73-1.82 (m, 2H, CH_2), 2.51 (q, 2H, J = 7.5 Hz, CH_2), 3.23 (t, 2H, J = 6.8 Hz, CH_2), 5.45 (s, 1H, CH_2), 5.89 (s, 1H, CH_2), 6.46 (s, 1H, CH); ^{13}C nmr (100 MHz, deuteriochloroform): δ 12.1, 12.9, 21.5, 23.6, 29.7, 63.9, 112.3, 133.0, 143.6, 156.8, 164.7; ^{77}Se nmr (76 MHz, deuteriochloroform): δ 29.3; ms (CI): m/z = 230 (M^++1).

Anal. Calcd for $C_{10}H_{16}NSe$: C, 52.40; H, 7.04; N, 6.11. Found: C, 52.46; H, 7.14; N, 5.98.

N-Butyl-3-ethyl-2-trimethylsilyl-3,4-pentadieneselenoamide (**8a**).

This compound was obtained as yellow oil, ir (neat): 3326, 1947, 1525, 844 cm^{-1}; ^1H nmr (400 MHz, deuteriochloroform): δ 0.19 (s, 9H, CH_3), 0.97 (t, 3H, J = 7.4 Hz, CH_3), 0.99 (t, 3H, J = 7.4 Hz, CH_3), 1.37-1.46 (m, 2H, CH_2), 1.63-1.72 (m, 2H, CH_2), 1.90-2.10 (m, 2H, CH_2), 3.52 (s, 1H, CH), 3.61-3.80 (m, 2H, CH_2), 4.99-5.10 (m, 2H, CH_2), 8.26 (br s, 1H, NH); ^{13}C nmr (100 MHz, deuteriochloroform): δ -1.8, 11.8, 13.6, 20.2, 28.5, 30.0, 49.4, 57.4, 79.6, 105.1, 204.6, 206.9; ^{77}Se nmr (76 MHz, deuteriochloroform): δ 543.4; ms (CI): m/z = 318 (M^++1).

Anal. Calcd for $C_{14}H_{27}NSe$: C, 58.32; H, 9.44; N, 4.86. Found: C, 58.45; H, 9.51; N, 4.87.

3-Ethyl-*N*-propyl-2-trimethylsilyl-3,4-pentadieneselenoamide (**8b**).

This compound was obtained as yellow oil, ir (neat): 3329, 1947, 1523, 844 cm^{-1}; ^1H nmr (400 MHz, deuteriochloroform): δ 0.19 (s, 9H, CH_3), 0.99 (t, 3H, J = 7.0 Hz, CH_3), 1.01 (t, 3H, J = 7.0 Hz, CH_3), 1.66-1.77 (m, 2H, CH_2), 1.89-2.10 (m, 2H, CH_2), 3.52 (s, 1H, CH), 3.59-3.77 (m, 2H, CH_2), 4.98-5.06 (m, 2H, CH_2), 8.29 (br s, 1H, NH); ^{13}C nmr (100 MHz, deuteriochloroform): δ -1.7, 11.5, 11.8, 21.3, 28.5, 51.3, 57.3, 79.6, 105.1, 204.7, 206.9; ^{77}Se nmr (76 MHz, deuteriochloroform): δ 543.5; ms (CI): m/z = 304 (M^++1).

Anal. Calcd for $C_{13}H_{25}NSe$: C, 56.92; H, 9.19; N, 5.11. Found: C, 56.88; H, 9.12; N, 5.16.

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