A Facile Preparation of *O*-Alkyl Selenocarboxylates and Selenoamides via Se-Alkynyl Selenocarboxylates[1)]

Hideharu Ishihara, Michinari Yoshimi, Nobuhiko Hara, Hiroyuki Ando, and Shinzi Kato*
Department of Chemistry, Faculty of Engineering, Gifu University, 1-1 Yanagido, Gifu 501-11
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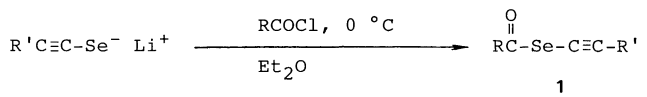
Se-Alkynyl selenocarboxylates (**1**) were found to readily react with alcohols and amines to give *O*-alkyl selenocarboxylates (**4**) and selenoamides (**6**) in moderate to good yields, respectively. The formation mechanisms of **4** and **6** via selenoketene and ammonium alkyneselenolate, respectively, are proposed.

Past two decades, great advances have been made in the chemistry of selenium reagents.[2-12)] Little have been known in the chemistry of selenium isologues of carboxylic acid derivatives,[13)] though the high utility of selenocarboxylic acid esters for organic synthesis has been described.[14-17)] In the previous studies concerning the sulfur isologues of carboxylic acid derivatives, we have found that *S*-alkenyl thio- and dithiocarboxylates serve as efficient precursors for generation of alkenethiolate anions.[18,19)] To our best knowledge, however, no preparation of *Se*-alkenyl and *Se*-alkynyl selenocarboxylates has been still remained. Herein we report *Se*-alkynyl selenocarboxylates (**1**) serve as excellent precursors for the synthesis of *O*-alkyl selenocarboxylates (**4**) (hereafter called selenoesters) and selenoamides (**6**).

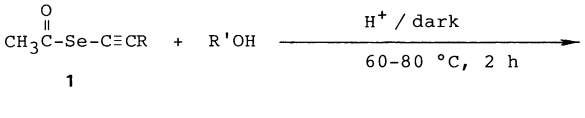
Results and Discussion

The starting *Se*-alkynyl selenocarboxylates (1) can be readily obtained in good yields from the reaction of lithium alkyneselenolates with acyl chlorides (Eq. 1; Table 1). The *Se*-alkynyl selenocarboxylates (**1**) obtained are stable thermally and towards moisture and oxygen. They can be stored in refrigerator (−5 °C) for 3 months. Even under refluxing conditions of benzene, *Se*-phenylethynyl selenoacetate (**1b**) was stable at least for 24 h.



(1)

In general, *Se*-alkynyl selenocarboxylates (**1**) do not react with alcohols at room temperature. Under acidic and dark conditions, however, **1** readily reacted with aliphatic alcohols to yield selenoesters **4** in moderate to good yields together with the corresponding carboxylic acid ester (Eq. 2; Table 2). For example, when a solution of *Se*-phenylethynyl selenoacetate (**1b**) (3.0 mmol) in ethanol containing a catalytic amount of *p*-toluenesulfonic acid was refluxed for 2 h, the solution quickly changed from colorless to orange. After the usual work-up of the reaction mixture, chromatographic separation of the residue on silica gel afforded 86% of *O*-ethyl α-phenylselenoacetate (**4d**) as yellow liquid. Under similar conditions, the reactions with other alcohols such as methanol and 1-propanol, etc. yielded the corresponding selenonesters (**4a—4c**, **4e—4f**) in 60—88% yields. Although hydrogen chloride, sulfuric acid, and trifluoroacetic acid were also examined as a catalyzer, *p*-toluenesulfonic acid and trifluoroacetic acid appear to be



(2)

Table 1. *Se*-Alkynyl Selenocarboxylates **1**

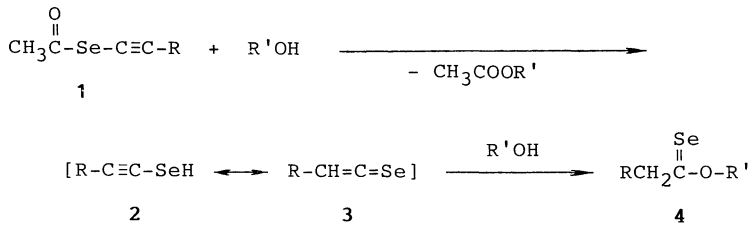
No.	RCOSeC≡CR′ R	R′	Yield[a)] %	Mp °C	IR (cm^{-1}) ν(C≡C)	^{13}C NMR[e)] δ(C=O)
1a	CH_3	*n*-C_4H_9	40	100/1.3[b)]	2170[c)]	196.6
1b		C_6H_5	67	130/2.0[b)]	2200[c)]	195.3
1c		4-ClC_6H_4	84	83—84	2170[d)]	194.4
1d	C_6H_5	*n*-C_4H_9	61	133/0.3[b)]	2175[c)]	191.0
1e		C_6H_5	87	88—91	2175[d)]	189.4
1f		4-$CH_3C_6H_4$	91	81—82	2170[d)]	188.7
1g	4-$CH_3C_6H_4$	C_6H_5	92	77—78	2170[d)]	188.7

a) Isolated yield. b) Bp (°C/Torr). c) Neat. d) KBr-disk. e) $CDCl_3$.

Table 2. Yields of *O*-Alkyl Selenocarboxylates (**4**)

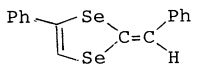
No.	$RCH_2C(Se)$-OR′		Reaction conditions		Yield[b]
	R	R′	Catalyzer[a]	Temp/°C	%
4a	*n*-C_4H_9	CH_3	TsOH	66	67
4b		C_2H_5	TsOH	80	60
4c	C_6H_5	CH_3	TsOH	66	88
4d		C_2H_5	TsOH	80	86
			H_2SO_4	80	72
			HCl	80	76
			CF_3COOH	80	77
4e		*i*-C_3H_7	TsOH	80	83
4f		$CH(CH_3)CH(CH_3)_2$	TsOH	80	77
4g		*cyclo*-C_6H_{11}	TsOH	80	80
4h	4-ClC_6H_4	CH_3	TsOH	66	64
4i		C_2H_5	TsOH	80	70

a) Used 10 mol%. b) Isolated yield.

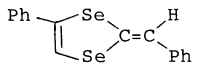


Scheme 1.

more preferable than the others in a viewpoint of purification. In contrast with aliphatic alcohols, the reaction of **1b** with phenol did not afford the expected *O*-phenyl α-phenylselenoacetate under various conditions. Instead, *cis*-(**5a**) and *trans*-2,6-diphenyl-1,4-diselenafulvenes (**5b**)[20] were obtained as pale yellow crystals in moderate yields.[21] In addition, the same reaction in the presence of catalytic amount of acid such as trifluoroacetic acid and *p*-toluenesulfonic acid led to the formation of *trans*-diselenafulvene (**5b**).[22] The structures of **4** and **5** were established by Mass, IR, ^1H and ^{13}C NMR, and electron spectra and microanalyses.



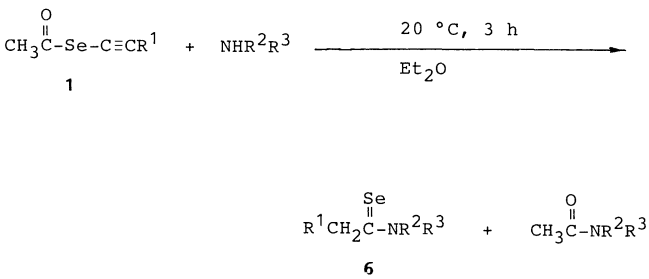
5a



5b

A plausible reaction pathway for the formation of selenonesters (**4**) is shown in Scheme 1. Thus, the carbonyl carbon of *Se*-alkynyl esters (**1**) is firstly attacked by alcohol to form alkyneselenol (**2**) or selenoketene (**3**) as an intermediate. Then the formed selenoketene further reacts with alcohol to give selenonester (**4**). At the present stage, attempts to obtain the spectral evidences for the formation of these intermediates failed. The similar formation mechanism has been proposed for the preparation of selenonesters by treatment of 1,2,3-selenadiazoles with alcohols.[23]

Previously, Brandsma and his co-workers reported a preparation of *N,N*-diethylselenoamides from the reaction of lithium alkyneselenolates with diethylamine.[24] Similar treatment of *Se*-alkynyl selenocarboxylates (**1**) with amines is expected to yield selenoamides. In fact, the *Se*-alkynyl esters (**1**) were found to readily react with primary and secondary amines at 20 °C to give the corresponding selenoamides in good yields (Eq. 3). For example,

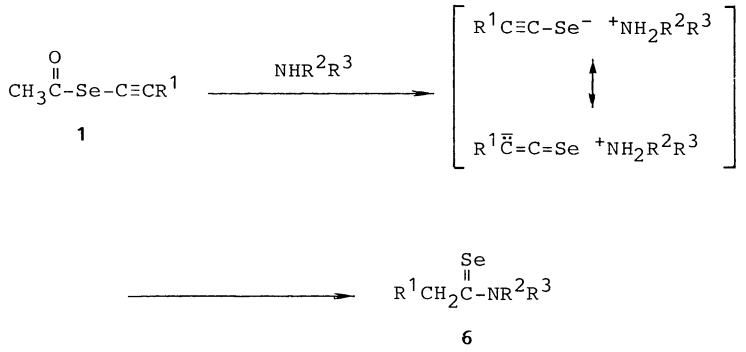


diethylamine (440 mg, 6.0 mmol) was added to a solution of *Se*-phenylethynyl selenoacetate (**1b**) (670 mg, 3.0 mmol) and the mixture was stirred at 20 °C for 3 h. After usual work-up, purification on silica-gel column chromatograph yielded 88% of *N,N*-diethyl-α-phenylselenoacetamide (**6h**) as yellow crystals. The reaction with other *Se*-alkynyl esters (**1**) under the same conditions afforded the corresponding selenoamides (**6a—g, i,j**) in 48—97% yields. The structures

Table 3. Yields of Selenoamides **6**

No.	R^1CH_2-C(Se)-NR^2R^3		Yield[a]	Mp
	R^1	NR^2R^3	%	°C
6a	n-C_4H_9	$NHCH_2C_6H_5$	82	48—49
6b		$N(C_2H_5)_2$	91	Oil
6c	C_6H_5	$NHCH_2C_6H_5$	95	95—97
6d		NHC_3H_7-i	68	89—91
6e		NHC_8H_{17}-n	48	65—67
6f		$NHC_{18}H_{37}$-n	59	68—70
6g		NHC_6H_5	97	99—102
6h		$N(C_2H_5)_2$	88	70—72
6i			77	91—93
6j			78	110—112

a) Isolated yield.



Scheme 2.

of **6** were established by high-resolution mass spectroscopy, IR, and ^1H and ^{13}C NMR spectral data. Presumably, the selenoamides (**6**) would be formed via the corresponding ammonium alkyneselenolate, though no spectral evidence is not on hand. Selenoamides (**6**) have also been obtained by several methods: treatment of selenadiazoles with amine,[25] treatment of nitrile with hydrogen selenide,[26] reaction of amides with phosphorus pentaselenide,[27] treatment of imidic esters or its hydrochloride salts with hydrogen selenide,[14,28,29] and reaction of lithium alkyneselenolates with diethylamine.[22] These methods, however, involve the use of less available and unpleasant smell reagents. The present method provides the readily available starting compounds, the simple procedures, and high yields.

Experimental

Measurments. The IR spectra were measured on a JASCO grating IR spectrometer IR-G. The ^1H and ^{13}C NMR spectra were recorded on a JEOL JNM-GX-270 (270 and 67.9 MHz) spectrometer with tetramethylsilane as an internal standard. The mass specta were taken from a Shimazu high-resolution mass spectrometer (GCMS-QP1000 and GCMS-9020DF).

Materials. Selenium (powder), phenylacetylene, 1-hexyne, acyl chlorides, *p*-toluenesulfonic acid, trifluoroacetic acid, alcohols, amines, and butyllithium were commercial grade, and used without further purification. Solvents were dried with sodium metal or phosphorus pentaoxide and degassed.

Typical procedures are described for the preparation of *Se*-alkynyl selenocarboxylates (**1**), *O*-alkyl selenocarboxylates (**4**), and selenoamides (**6**). All manipulations were carried out under argon atmosphere.

***Se*-(1-Hexynyl) Selenoacetate (1a):** Similarly to *Se*-phenylethynyl selenoacetate (**1b**), the reaction of lithium 1-hexyneselenolate (3 mmol) with acetyl chloride (236 mg, 3 mmol) yielded 244 mg (40%) of **1a** as colorless liquid; 100 °C/1.3 Torr (1 Torr≈133.322 Pa). IR (neat) 2980, 2960, 2860, 2170 (C≡C), 1745, 1722 (C=O), 1610, 1460, 1423, 1350, 1325, 1230, 1097, 995, 935, 562 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.90 (t, 3H), 1.4—1.6 (m, 4H), 2.48 (t, 2H), 2.49 (s, 3H); ^{13}C NMR ($CDCl_3$) δ=13.5, 20.4, 21.9, 30.6, 33.1, 56.4 (≡C–C), 109.9 (Se–C≡), 196.6 (C=O); MS (EI, 20 eV) m/z 204 (M^+), 124, 119, 81; Found: m/z 204.0060. Calcd for $C_8H_{12}OSe$: M, 204.0053.

***Se*-Phenylethynyl Selenoacetate (1b):** Butyllithium (3 mmol) was added to a solution of phenylacetylene (306 mg, 3 mmol) in ether (20 mL) at 0 °C in 50 mL flask covered on aluminum foil and mixture was stirred at this temperature for 15 min. Then, selenium (240 mg, 3 mmol) was added, followed by stirring at 20 °C for 1 h. To the resulting lithium phenylethyneselenolate (3 mmol) was added acetyl

chloride (236 mg, 3 mmol) and the mixture was stirred at 0 °C for 1 h. The solvent was evaporated by rotary evaporator. Distillation of the residue in vacuo yielded 450 mg (67%) of **1b** as a slightly yellow liquid; bp 130 °C/2.0 Torr. IR (Neat) 3060, 3030, 2970, 2940, 2860, 2200 (C≡C), 1735sh, 1723 (C=O), 1600, 1578, 1492, 1443, 1418, 1335, 1282, 1268, 1225, 1090, 1027, 992, 940, 758, 693, 563, 528 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.61 (s, 3H), 7.2—7.5 (m, 5H); ^{13}C NMR ($CDCl_3$) δ=33.1, 67.7 (≡C–Ar), 108.0 (Se–C≡), 122.7, 128.9, 131.7, 133.0, 195.3 (C=O); MS (EI, 20 eV) *m/z* 224 (M^+), 182, 144, 129, 89, 63; Found: *m/z* 223.9709. Calcd for $C_{10}H_8OSe$: M, 223.9739.

***Se*-(4-Chlorophenylethynyl) Selenoacetate (1c):** Similarly to **1b**, the reaction of lithium (4-chlorophenyl)ethynesenolate (3 mmol) with acetyl chloride (236 mg, 3 mmol) yielded 654 mg (84%) of **1c** as colorless crystals; mp 83—84 °C. IR (KBr) 3040, 2940, 2170 (C≡C), 1745sh, 1715 (C=O), 1583, 1485, 1394, 1343, 1260, 1230, 1093, 1076, 1008, 945, 820, 672, 569, 519 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.63 (s, 3H), 7.3—7.4 (m, 4H); ^{13}C NMR ($CDCl_3$) δ=33.2, 69.1, 106.9, 121.4, 132.9, 135.1, 194.4 (C=O); MS (EI, 20 eV) *m/z* 258 (M^+), 216, 215, 180, 43; Found: *m/z* 257.9337. Calcd for $C_{10}H_7OClSe$: M, 257.9350.

***Se*-(1-Hexynyl) Selenobenzoate (1d):** Similarly to **1b**, the reaction of lithium 1-hexyneselenolate (3 mmol) with benzoyl chloride (422 mg, 3 mmol) yielded 485 mg (61%) of **1d** as colorless liquid; bp 133 °C/0.3 Torr. IR (Neat) 3050, 2940, 2920, 2860, 2175 (C≡C), 1740, 1705 (C=O), 1600, 1580, 1443, 1380, 1313, 1270, 1198, 1172, 1100, 1070, 1000, 865, 760, 705, 683, 660, 617, 500 cm^{-1}; ^1H NMR ($CDCl_4$) δ=0.94 (t, 3H) 1.4—1.7 (m, 4H), 2.55 (t, 2H), 7.40—8.20 (m, 5H); ^{13}C NMR ($CDCl_3$): δ=13.6, 20.4, 21.9, 30.7, 54.9, 110.0 (Se–C≡), 127.1, 129.2, 130.6, 134.4, 191.0 (C=O); MS (EI, 20 eV) *m/z* 266 (M^+), 186, 119, 105, 77, 50; Found: *m/z* 266.0214. Calcd for $C_{13}H_{14}OSe$: M, 266.0209.

***Se*-Phenylethynyl Selenobenzoate (1e):** Similarly to **1b**, the reaction of lithium phenylethyneselenolate (3 mmol) with benzoyl chloride (422 mg, 3 mmol) followed by silica-gel column chromatograph [hexane/ether (5:1), the second eluent] yielded 744 mg (87%) of **1e** as colorless crystals; mp 89—91 °C. IR (KBr) 3050, 2175 (C≡C), 1740, 1706 (C=O), 1595, 1576, 1480, 1440, 1315, 1198, 1175, 1065, 1020, 995, 868, 765, 757, 692, 660, 515, 425 cm^{-1}; ^1H NMR ($CDCl_3$) δ=7.20—7.85 (m); ^{13}C NMR ($CDCl_3$) δ=66.4 (C≡CSe), 108.0 (C≡CSe), 122.9—136.8 (Ar), 189.4 (C=O); MS (EI, 20 eV) *m/z* 286 (M^+), 206, 181, 105, 77, 51; Found: *m/z* 285.9905. Calcd for $C_{15}H_{10}OSe$: M, 285.9896.

***Se*-(*p*-Tolylethynyl) Selenobenzoate (1f):** Similarly to **1b**, the reaction of lithium *p*-tolylethyneselenolate (3 mmol) with benzoyl chloride (422 mg, 3 mmol), followed silica-gel column chromatograph [hexane/ether (5:1), the first eluent] yielded 816 mg (91%) of **1f** as colorless drystals; mp 81—82 °C. IR (Neat) 3015, 2910, 2820, 2170 (C≡C), 1738sh, 1712 (C=O), 1600, 1577, 1488, 1447, 1302, 1202, 1163, 1073, 1020, 920, 870, 814, 780, 735, 690, 595, 470 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.39 (s, 3H), 7.2—7.7 (m, 9H); ^{13}C NMR ($CDCl_3$) δ=21.8, 66.6, 100.8 (Se–C≡), 123.0—134.3, 145.9, 188.7 (C=O); MS (EI, 20 eV) *m/z* 300 (M^+), 220, 195, 105, 77, 51; Found: *m/z* 300.0075. Calcd for $C_{16}H_{12}OSe$: M, 300.0053.

***Se*-Phenylethynyl 4-Methylbenzenecarboselenoate (1g):** Similarly to **1b**, the reaction of lithium phenylethyneselenoate (3 mmol) with *p*-toluoyl chloride (464 mg, 3 mmol) followed by silica-gel column chromatograph [hexane/ether (5:1), the secound eluent] yielded 826 mg (92%) of **1q** as colorless crystals; mp 77—78 °C. IR (Neat) 2170 (C≡C), 1742, 1712 (C=O), 1602, 1570, 1480, 1418, 1402, 1304, 1212, 1200, 1177, 1065, 1022, 916, 868, 818, 778, 757, 710, 690, 610, 522, 482, 450 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.39 (s, 3H), 7.2—7.7 (m, 9H); ^{13}C NMR ($CDCl_4$) δ=21.8, 66.6, 100.8, 123.0 127.0, 128.3, 128.7, 129.9, 131.8, 134.3, 145.9, 188.7 (C=O); MS (EI, 20 eV): *m/z* 300 (M^+), 220, 181, 119, 91, 65; Found: *m/z* 300.0055. Calcd for $C_{16}H_{12}OSe$: M, 300.0053.

***O*-Methyl Hexaneselenoate (4a):** Similarly to *O*-ethyl α-phenylselenoacetate (**4d**), the reaction of *Se*-(1-hexynyl) selenoacetate (**1a**) (610 mg, 3 mmol) with methanol (20 mL) in the presence of *p*-toluenesulfonic acid (55 mg, 0.3 mmol) yielded 388 mg (67%) of **4a** as yellow liquid. IR (Neat) 2950, 2930, 2860, 2850, 1438, 1377, 1278, 1240, 1217, 1190, 1140, 1075, 997, 940, 782, 724 cm^{-1}; UV/Vis (cyclohexane) 255 (log ε 4.39), 378sh, 454 nm (1.92); ^1H NMR ($CDCl_4$) δ=0.90 (t, 3H), 1.32—1.35 (m, 4H), 1.78 (tt, 2H), 2.66 (t, 2H), 4.21 (s, 3H); ^{13}C NMR ($CDCl_3$) δ=13.7, 22.2, 28.2, 30.7, 52.4 (CH_2CSe), 62.9, 237.5 (C=Se); MS (EI, 20 eV) *m/z* 194 (M^+), 113 (M^+—SeH), 99 ($C_5H_{11}CO^+$), 81, 71 ($C_5H_{11}^+$); Found: *m/z* 194.0227. Calcd for $C_7H_{14}OSe$: M, 194.0209.

***O*-Ethyl Hexaneselenoate (4b):** Similarly to **4d**, the reaction of *Se*-1-hexynyl selenoacetate (**1a**) (610 mg, 3 mmol) with ethanol (20 mL) in the presence of *p*-toluenesulfonic acid (55 mg, 0.3 mmol) yielded 373 mg (60%) of **4b** as yellow liquid. IR (Neat) 2955, 2930, 2870, 2860, 1460, 1366, 1290, 1280, 1243, 1210, 1187, 1075, 1016, 974, 882, 786, 760, 727 cm^{-1}; UV/Vis (cyclohexane) 260 (log ε 4.73), 369sh, 450 (1.93) nm; ^1H NMR ($CDCl_3$) δ=0.90 (t, 3H), 1.31—1.36 (m, 4H), 1.47 (t, 3H), 1.77 (tt, 2H), 2.66 (t, 2H), 4.62 (q, 2H); ^{13}C NMR ($CDCl_3$) δ=13.6, 13.9, 22.3, 28.3, 30.8, 53.1 (CH_2CSe), 72.7, 236.8 (C=Se); MS (EI, 20 eV) *m/z* 208 (M^+), 127 (M^+—SeH), 99 ($BuCH_2CO^+$), 81, 71 ($C_5H_{11}^+$); Found: *m/z* 208.0339. Calcd for $C_8H_{16}OSe$: M, 208.0366.

***O*-Methyl α-Phenylselenoacetate (4c):** Similarly to **4d**, the reaction of *Se*-phenylethynyl selenoacetate (**1b**) 670 mg, 3 mmol) with methanol (20 mL) in the presence of *p*-toluenesulfonic acid (55 mg, 0.3 mmol) yielded 562 mg (88%) of **4c** as yellow liquid. IR (neat) 3060, 3030, 2990, 2945, 2840, 1600, 1497, 1450, 1440, 1290, 1260, 1195, 1184, 1177, 1093, 1027, 1002, 913, 882, 784, 760, 698 cm^{-1}; UV/Vis (cyclohexane) 265 (log ε 4.33), 465 nm (1.97); ^1H NMR ($CDCl_3$) δ=4.00 (s, 2H), 4.12 (s, 3H), 7.29 (m, 5H); ^{13}C NMR ($CDCl_3$) δ=59.1 (CH_2CSe), 63.5, 127.0, 128.4, 129.0, 134.8, 232.8 (C=Se); MS (EI, 20 eV) *m/z* 214 (M^+), 182 ($PhCHCSe^+$), 134 (M^+—Se), 118 ($PhCHCO^+$), 91 ($C_7H_7^+$), 65; Found: *m/z* 213.9871. Calcd for $C_9H_{10}OSe$: M, 213.9896.

***O*-Ethyl α-Phenylselenoacetate (4d):** *Se*-Phenylethynyl selenoacetate (**1b**) (672 mg, 3.0 mmol) was added to ethanol (20 mL) containing *p*-toluenesulfonic acid (55 mg, 0.3 mmol) and the reaction mixture was refluxed for 2 h under dark. After washing with water (20 mL×3) and drying with anhydrous sodium sulfate, the solvent was evaporated in vacuo. Chromatography of the resulting residue on silica-gel column [tetrachloromethane/chloroform (95:5), yellow eluent] gave 589 mg (86%) of **4d** as yellow liquid. IR (Neat) 3060, 3030, 2980, 2955, 2930, 2860, 1600, 1495, 1454, 0364, 1298, 1256, 1178, 1125, 1083, 1017, 855, 754, 697 cm^{-1}; UV/Vis (cyclohexane) 278 (log ε 4.09), 457 nm (1.97); ^1H NMR ($CDCl_3$) δ=1.37 (t, 3H), 4.00 (s, 2H), 4.55 (q, 2H), 7.2—7.4 (m, 5H); ^{13}C NMR ($CDCl_3$) δ=13.5, 59.5 (CH_2CSe), 73.1, 127.0,

128.4, 129.0, 134.9, 231.7 (C=Se); MS (EI, 20 eV) *m/z* 228 (M^+), 182 ($PhCHCSe^+$), 148 (M^+-Se), 118 ($PhCHCO^+$), 91 ($C_7H_7^+$), 65; Found: *m/z* 228.0079. Calcd for $C_{10}H_{12}OSe$: M, 228.0053.

***O*-Propyl α-Phenylselenoacetate (4e):** Similarly to **4d**, the reaction of *Se*-phenylethynyl selenoacetate (**1b**) (670 mg, 3 mmol) with 1-propanol (20 mL) in the presence of *p*-toluenesulfonic acid (55 mg, 0.3 mmol) yielded 600 mg (83%) of **4e** as yellow liquid. IR (Neat) 3050, 2990, 2950, 2820, 1600, 1497, 1452, 1385, 1350, 1294, 1262, 1175, 1114, 1090, 1025, 998, 968, 880, 760, 700 cm: UV/Vis (cyclohexane) 279 (log ε 4.28), 460 nm (1.81); ^1H NMR ($CDCl_3$) δ=0.93 (t, 3H), 1.82 (m, 2H), 4.02 (s, 2H), 4.48 (t, 2H), 7.2—7.3 (m, 5H); ^{13}C NMR ($CDCl_3$) δ=10.3, 21.5, 59.7 ($\underline{C}H_2CSe$), 78.8, 127.1, 128.5, 129.2, 135.1, 232.1 (C=Se); MS (EI, 20 eV) *m/z* 242 (M^+), 182 ($PhCHCSe^+$), 118 ($PhCHCO^+$), 102, 91 ($C_7H_7^+$), 65; Found: *m/z* 242.0234. Calcd for $C_{11}H_{14}OSe$: M, 242.0209.

***O*-(1,2-Dimethylpropyl) α-Phenylselenoacetate (4f):** Similarly to **4d**, the reaction of *Se*-phenylethynyl selenoacetate (**1b**) (670 mg, 3 mmol) with 1,2-dimethyl-1-propanol (2 mL) in THF (10 mL) containing of *p*-toluenesulfonic acid (20 mg, 0.1 mmol) yielded 621 mg (77%) of **4f** as yellow liquid. IR (Neat) 3050, 3000, 2950, 2820, 1600, 1498, 1451, 1365, 1345, 1298, 1255, 1169, 1085, 1024, 988, 944, 902, 840, 758, 698 cm^{-1}; UV/Vis (cyclohexane) 282 (log ε 4.10), 454 nm (1.86); ^1H NMR ($CDCl_3$) δ=0.83 (d, 6H), 1.24 (d, 3H), 1.96 (m, 1H), 4.10 (m, 2H), 5.52 (m, 1H), 7.2—7.3 (m, 5H); ^{13}C NMR ($CDCl_3$) δ=15.3, 17.8, 17.9, 32.4, 60.4 ($\underline{C}H_2CSe$), 88.2, 127.0, 128.4, 129.2, 131.5, 231.4 (C=Se); MS (EI, 20 eV) *m/z* 270 (M^+), 200, 182 ($PhCHCSe^+$), 118 ($PhCHCO^+$), 91 ($C_7H_7^+$), 65; Found; *m/z* 270.0538. Calcd for $C_{13}H_{18}OSe$: M, 270.0522.

***O*-Cyclohexyl α-Phenylselenoacetate (4g):** Similarly to **4d**, the reaction of *Se*-phenylethynyl selenoacetate (**1b**) (670 mg, 3 mmol) with cyclohexanol (20 mL) in the presence of *p*-toluenesulfonic acid (55 mg, 0.3 mmol) yielded 674 mg (80%) of **4g** as yellow liquid. IR (Neat) 3050, 2940, 2860, 1600, 1496, 1450, 1350, 1290, 1251, 1168, 1090, 1029, 1000, 958, 1000, 985, 885, 761, 698 cm^{-1}; UV/Vis (cyclohexane) 260 (log ε 4.56), 310sh, 456 nm (1.81); ^1H NMR ($CDCl_3$) δ=1.3—1.6 (m, 8H), 1.90 (m, 2H), 4.00 (s, 2H), 5.55 (m, 1H), 7.2—7.3 (m, 5H); ^{13}C NMR ($CDCl_3$) δ=23.2, 25.2, 30.3, 60.2 ($\underline{C}H_2CSe$), 84.8, 126.9, 128.4, 129.0, 135.1, 230.8 (C=Se); MS (EI, 20 eV) *m/z* 282 (M^+), 201 (M^+-Se), 118 ($PhCHCO^+$), 91 ($C_7H_7^+$), 65; Found: *m/z* 282.0545. Calcd for $C_{14}H_{18}OSe$: M, 282.0522.

***O*-Methyl α-(4-Chlorophenyl)selenoacetate (4h):** Similarly to **4d**, the reaction of *Se*-(4-chlorophenyl)ethynyl selenoacetate (**1c**) (773 mg, 3 mmol) with methanol (20 mL) in the presence of *p*-toluenesulfonic acid (55 mg, 0.3 mmol) yielded 456 mg (64%) of **4h** as yellow liquid. IR (neat) 3025, 2990, 2940, 2870, 2840, 1595, 1495, 1440, 1404, 1297, 1256, 1182, 1105, 1082, 1014, 1002, 884, 837, 800, 783, 755, 735, 668 cm^{-1}; UV/Vis (cyclohexane) 260 (log ε 4.65), 456 nm (1.99); ^1H NMR ($CDCl_3$) δ=3.95 (s, 2H), 4.15 (s, 3H), 7.24 (m, 4H); ^{13}C NMR ($CDCl_3$): δ=58.2 ($\underline{C}H_2CSe$), 63.5, 128.5, 130.4, 133.0, 133.2, 231.9 (C=Se); MS (EI, 20 eV) *m/z* 248 (M^+), 216 ($ClC_6H_4CHCSe^+$), 168 (M^+-Se), 152 ($ClC_6H_4CHCO^+$), 125 ($ClC_7H_6^+$), 65; Found: *m/z* 247.9524. Calcd for C_9H_9ClOSe: M, 247.9507.

***O*-Ethyl α-(4-Chlorophenyl)selenoacetate (4i):** Similarly to **4d**, the reaction of *Se*-(4-chlorophenyl)ethynyl selenoacetate (**1c**) (773 mg, 3 mmol) with ethanol (20 mL) in the presence of *p*-toluenesulfonic acid (55 mg, 0.3 mmol) yielded 530 mg (70%) of **4i** as yellow liquid. IR (neat) 2980, 2950, 2920, 2855, 1590, 1490, 1402, 1362, 1296, 1250, 1178, 1124, 1086, 1013, 833, 798, 726, 655 cm^{-1}; UV/Vis (cyclohexane) 263 (log ε 4.44), 457 nm (1.98); ^1H NMR ($CDCl_3$) δ=1.43 (t, 3H), 3.95 (s, 2H), 4.58 (t, 2H), 7.27 (s, 4H); ^{13}C NMR ($CDCl_3$) δ=13.5, 58.7 ($\underline{C}H_2CSe$), 73.3, 128.6, 130.5, 133.0, 133.4, 231.1 (C=Se); MS (EI, 20 eV) *m/z* 262 (M^+), 216 ($ClC_6H_4CHCSe^+$), 182 (M^+-Se), 152 ($ClC_6H_4CHCO^+$), 137, 125 ($ClC_7H_6^+$); Found: *m/z* 261.9655. Calcd for $C_{10}H_{11}ClOSe$: M, 261.9663.

Reaction of *Se*-Phenylethynyl Selenoacetate with Phenol: A solution of phenylethynyl selenoacetate (**1b**) (670 mg, 3 mmol) and phenol (1.12 g, 12 mmol) in ether (20 mL) was stirred at 20 °C for 5 h and then refluxed for 2 h. After evaporation of the solvent in vacuo, column chromatography of the resulting residue on silica gel (eluent CCl_4) afforded 160 mg (34%) of *cis*-2,6-diphenyl-1,4-diselenafulvene (**5a**) as pale yellow crystals; mp 144—146 °C, and 310 mg (46%) of **1b**.

5a: IR (KBr) 3100 (w), 1575 (m), 1582 (m), 1548 (w), 1430 (m), 1335 (w), 1270 (w), 1178 (w), 1140 (w), 1090 (w), 1068 (w), 1022 (w), 903 (w), 890 (w), 880 (m), 815 (m), 750 (s), 687 (s), 610 (w), 600 (w), 550 (w), 520 (w), 500 (m) cm^{-1}; ^1H NMR (DMSO-d_6) δ=7.84 (s, 1H), 7.2—7.5 (m, 11H); ^{13}C NMR (DMSO-d_6) δ=114.2 (d), 122.6 (d), 125.3 (s), 126.3 (d), 126.4 (d), 127.0 (d), 128.2 (d), 128.6 (d), 128.9 (d), 136.0 (s), 138.1 (s), 138.4 (s); MS (EI, 20 eV) *m/z* (rel intensity) 364 (M^+, 53), 284 (M^+-Se, 6), 262 ($PhCHCSe_2^+$, 3), 204 (M^+-2Se, 10), 203 (14), 202, 182 ($PhCH=C=Se^+$, 58), 102 ($PhC\equiv CH^+$, 100).

Found: C, 53.14; H, 3.32%. Calcd for $C_{16}H_{12}Se_2$: C, 53.06; H, 3.34%

Reaction of *Se*-Phenylethynyl Selenoacetate with Phenol in the Presence of Trifluoroacetic Acid: A solution of phenylethynyl selenoacetate (**1b**) (670 mg, 3 mmol), phenol (940 mg, 30 mmol) and trifluoroacetic acid (30 mg, 0.3 mmol) in tetrahydrofuran (20 mL) was refluxed for 50 h. To the reaction mixture was added ether (30 mL). The organic was washed with water (3×20 mL) and dried with anhydrous sodium sulfate. The solvent was distilled by rotary evaporater. Column chromatography of the residue on silica gel (eluent: CCl_4) gave 170 mg (31%) of *trans*-2,6-diphenyl-1,4-diselenafulvene (**5b**) as pale yellow crystals; mp 224—226 °C, and 180 mg (27%) of **1b**.

5b: IR (KBr) 3100 (w), 1578 (m), 1548 (w), 1483 (m), 1442 (m), 1335 (w), 1178 (w), 1142 (w), 1090 (w), 1065 (w), 1018 (w), 884 (m), 824 (m), 810 (m), 742 (s), 684 (s), 606 (w), 540 (w), 500 (m) cm^{-1}; ^1H NMR (DMSO-d_6) δ=7.84 (s, 1H), 7.2—7.5 (m, 11H); ^{13}C NMR (DMSO-d_6) δ=114.9 (d), 122.0 (d), 126.3 (d), 126.4 (d), 126.8 (s), 127.0 (d), 128.3 (d), 128.6 (d), 128.9 (d), 135.6 (s), 138.2 (s), 138.6 (s); MS (EI, 20 eV) *m/z* (rel intensity) 364 (M^+, 32), 284 (M^+-Se, 4), 262 ($PhCHCSe_2^+$, 2), 204 (M^+-2Se, 6), 203 (10), 202, 182 ($PhCH=C=Se^+$, 41), 102 ($PhC\equiv CH^+$, 100).

Found: C, 53.16; H, 3.30%. Calcd for $C_{16}H_{12}Se_2$: C, 53.06; H, 3.34%.

Treatment of *cis*-2,6-Diphenyl-1,4-diselenafulvene (5a) with Trifluoroacetic acid: A solution of *cis*-2,6-diphenyl-1,4-diselenafulvene (**5a**) (364 g, 1 mmol) and trifluoroacetic acid (10 mg, 0.1 mmol)in CH_2Cl_2 (10 mL) was stirred at 20 °C for 2 h. After washing with water (3×5 mL), and drying with sodium sulfate, the solvent was removed in vacuo to give 306 mg (84%) of crude *trans*-2,6-diphenyl-1,4-

diselenafulvene (**5b**). Recrystallization from benzene gave 204 mg (56%) of **5b**; mp 220—226 °C.

***N*-Benzylpentaneselenoamide (6a):** Similarly to *N*-benzyl-α-phenylselenoacetamide (**6c**), the reaction of *Se*-(1-hexynyl) selenoacetate (**1a**) (610 mg, 3.0 mmol) with benzylamine (642 mg, 6 mmol) yielded 660 mg (82%) of **6a** as pale yellow crystals; mp 48—49 °C. IR (KBr) 3200, 3050, 2920, 2840, 1720, 1600, 1530, 1490, 1450, 1410, 1380, 1340, 1322, 1198, 1153, 1090, 1018, 970, 925, 720, 685, 550 cm^{-1}; UV/Vis (cyclohexane) 240sh, 312 (log ε 4.27), 440 nm (2.17); ^1H NMR ($CDCl_3$) δ=0.88 (t, 3H), 1.30 (m, 4H), 1.78 (m, 2H), 2.73 (t, 2H), 4.82 (s, 2H), 7.32 (m, 5H), 8.52 (br, 1H); ^{13}C NMR ($CDCl_3$) δ=13.7, 22.1, 29.3, 30.7, 50.5, 53.4, 128.0, 128.1, 128.7, 135.2, 211.0 (C=Se); MS (EI, 20 eV) *m/z* 269 (M^+), 188 (M^+—HSe), 132, 91, 65; Found: *m/z* 269.0668. Calcd for $C_{13}H_{19}NSe$: M, 269.0682.

***N,N*-Diethylpentaneselenoamide (6b):** Similarly to **6c**, the reaction of *Se*-1-hexynyl selenoacetate (**1a**) (610 mg, 3.0 mmol) with diethylamine (440 mg, 6 mmol) yielded 640 mg (91%) of **6b** as a yellow oil. IR (KBr) 2930, 2850, 2840, 1505, 1450, 1420, 1370, 1350, 1280, 1220, 1150, 1090, 1070, 1060, 1050, 815, 720 cm^{-1}; UV/Vis (cyclohexane) 260sh, 307 (log ε 4.34), 435 nm (2.38); ^1H NMR ($CDCl_3$) δ=0.91 (t, 3H), 1.2—1.4 (m, 10H) 1.7—1.9 (m, 2H), 2.91 (t, 2H), 3.58 (q, 2H), 4.11 (q, 2H); ^{13}C NMR ($CDCl_3$) δ=11.0, 12.9, 13.6, 22.1, 29.6, 31.1, 46.1, 46.9, 51.6, 207.0 (C=Se); MS (EI, 20 eV) *m/z* 235 (M^+), 220, 154, 71, 68, 43; Found: *m/z* 235.0834. Calcd for $C_{10}H_{21}NSe$: M, 235.0838.

***N*-Benzyl-α-phenylselenoacetamide (6c):** To the solution of *Se*-phenylethynyl selenoacetate (**1b**) (670 mg, 3.0 mmol) in dry ether (20 mL) was added benzylamine (642 mg, 6.0 mmol) and the reaction mixture was stirred at 20 °C for 3 h, followed by washing with water (20 mL×3) and drying with anhydrous sodium sulfate. The solvent was evaporated in vacuo. Column chromatography of the residue on silica gel (eluent: benzene) gave 822 mg (95%) of **6c** as yellow crystals; mp 95—97 °C, (lit,[25] 95—96 °C). IR (KBr) 3130, 3020, 2875, 1600, 1575, 1545, 1495, 1454, 1443, 1432, 1417, 1318, 1238, 1177, 1100, 1067, 1026, 950, 896, 825, 748, 695, 620, 612, 580, 550 cm^{-1}; UV/Vis (cyclohexane) 260sh, 303 (log ε 4.14), 424 nm (2.09); ^1H NMR ($CDCl_3$) δ=4.19 (s, 2H), 4.83 (s, 1H), 4.85 (s, 1H), 7.15—7.38 (m, 10H), 7.8 (br, 1H); ^{13}C NMR ($CDCl_3$): δ=53.6, 56.8, 127.8—129.4, 134.5, 206.9 (C=Se); MS (EI, 20 eV) *m/z* 289 (M^+), 183, 208, 171, 117, 91, 65; Found: *m/z* 289.0351. Calcd for $C_{15}H_{15}NSe$: M, 289.0369.

***N*-Isopropyl-α-phenylselenoacetamide (6d):** Similarly to **6c**, the reaction of *Se*-phenylethynyl selenoacetate (**1b**) (670 mg, 3.0 mmol) with isopropylamine (355 mg, 6 mmol) yielded 490 mg (68%) of **6d** as slightly yellow crystals; mp 89—91 °C. IR (KBr) 3150, 3020, 2950, 2870, 1597, 1535, 1488, 1450, 1432, 1417, 1387, 1363, 1335, 1300, 1195, 1163, 1120, 1078, 1058, 1025, 907, 776, 732, 698, 643, 590, 463 cm^{-1}; UV/Vis (cyclohexane) 257sh, 301 (log ε 4.34), 421 nm (2.11); ^1H NMR ($CDCl_3$) δ=1.20 (d, 6H), 4.15 (s, 2H), 4.75 (m, 1H), 7.2—7.4 (m, 5H), 7.80 (br, 1H); ^{13}C NMR ($CDCl_3$) δ=20.7, 50.9, 57.0, 128.0, 129.3, 129.4, 134.3, 204.2 (C=Se); MS (EI, 20 eV) *m/z* 241 (M^+), 183, 160, 91, 65; Found: *m/z* 241.0378. Calcd for $C_{11}H_{15}NSe$: M, 241.0369.

***N*-Octyl-α-phenylselenoacetamide (6e):** Similarly to **6c**, the reaction of *Se*-phenylethynyl selenoacetate (**1b**) (670 mg, 3.0 mmol)with octylamine (744 mg, 6 mmol) yielded 455 mg (48%) of **6e** as slightly yellow crystals; mp 65—67 °C. IR (kbr) 3170, 3020, 2920, 2840, 1600, 1532, 1494, 1452, 1432, 1402, 1283, 1270, 1088, 1037, 765, 730, 675 cm^{-1}; UV/Vis (cyclohexane) 255sh, 301 (log ε 4.14), 417 nm (2.21); ^1H NMR ($CDCl_3$) δ=0.87 (t, 3H), 1.22 (s, 10H), 1.56—1.59 (m, 2H), 3.64 (q, 2H), 4.18 (s, 2H), 7.23—7.40 (m, 5H), 7.55 (br, 1H); ^{13}C NMR ($CDCl_3$) δ=14.0, 22.6, 26.7, 27.4, 29.0, 31.6, 49.5, 56.9, 128.0, 129.4, 129.6, 134.3, 205.8 (C=Se); MS (EI, 20 eV) *m/z* 311 (M^+), 230, 183, 132, 91; Found: *m/z* 311.1161. Calcd for $C_{16}H_{25}NSe$: M, 311.1151.

***N*-Octadecyl-α-phenylselenoacetamide (6f):** Similarly to **6c**, the reaction of *Se*-phenylethynyl selenoacetate (**1b**) (445 mg, 2.0 mmol) with octadecylamine (1.08 g, 4 mmol) yielded 531 mg (59%) of **6f** as slightly yellow crystals; mp 68—70 °C. IR (KBr)3150, 3030, 2920, 2840, 1600, 1580, 1542, 1492, 1464, 1450, 1437, 1418, 1120, 1093, 1065, 765, 720, 700 cm^{-1}; UV/Vis (cyclohexane) 258sh, 301 (log ε 4.25), 410 nm (2.07); ^1H NMR ($CDCl_3$) δ=0.87 (t, 3H), 1.26 (s, 30H), 1.5—1.7 (m, 2H), 3.64 (q, 2H), 4.18 (s, 2H), 7.2—7.5 (m, 5H), 7.55 (br, 1H); ^{13}C NMR ($CDCl_3$) δ=14.1, 22.7—32.0, 40.1, 49.6, 57.1, 126—129, 206.0 (C=O); MS (EI, 20 eV) *m/z* 451 (M^+), 370, 132, 91, 65; Found: *m/z* 451.2725. Calcd for $C_{26}H_{45}NSe$: M, 451.2715.

***N*-Phenyl-α-phenylselenoacetamide (6g):** Similarly to **6c**, the reaction of *Se*-phenylethynyl selenoacetate (**1b**) (670 mg, 3.0 mmol) with aniline (560 mg, 6 mmol) yielded 797 mg (97%) of **6g** as slightly yellow crystals; mp 99—102 °C. IR (KBr) 3150, 3000, 1577, 1492, 1432, 1358, 1365, 1270, 1144, 1088, 1054, 1009, 988, 731, 682, 613, 588, 555, 470 cm^{-1}; UV/Vis (cyclohexane) 228 (log ε 3.97), 332 (4.24), 471 nm (2.20); ^1H NMR ($CDCl_3$) δ=4.25 (s, 2H), 7.25—7.60 (m, 12H), 9.40 (br, 1H). ^{13}C NMR ($CDCl_3$) δ=58.7, 124.0—134.5, 139.4, 206.4 (C=Se); MS (EI, 20 eV) *m/z*=275 (M^+), 194, 183, 91, 65; Found: *m/z* 275.0235. Calcd for $C_{14}H_{13}NSe$: M, 275.0213.

***N,N*-Diethyl-α-phenylselenoacetamide (6h):** Similarly to **6c**, the reaction of *Se*-phenylethynyl selenoacetate (**1b**) (670 mg, 3.0 mmol) with diethylamine (440 mg, 6 mmol) yielded 670 mg (88%) of **6h** as slightly yellow crystals; mp 70—72 °C, (lit,[25] 71—72 °C). IR (KBr) 2940, 2920, 1600, 1517, 1490, 1465, 1450, 1423, 1380, 1375, 1350, 1317, 1300, 1282, 1222, 1183, 1141, 1082, 1070, 1048, 1020, 996, 817, 765, 718, 700, 683, 618, 598, 547, 463 cm^{-1}; UV/Vis (cyclohexane) 260sh, 313 (log ε 4.31), 428 nm (2.33); ^1H NMR ($CDCl_3$): δ=1.10 (t, 3H), 1.33 (t, 3H), 3.46 (q, 2H), 4.11 (q, 2H), 4.47 (s, 2H), 7.2—7.4 (m, 5H); ^{13}C NMR ($CDCl_3$) δ=10.9, 12.6, 47.1, 51.6, 54.2, 126.9, 127.7, 128.8, 135.5, 202.3 (C=Se); MS (EI, 20 eV) *m/z* 255 (M^+), 183, 174, 145, 118, 91, 65; Found: *m/z* 255.0531. Calcd for $C_{12}H_{17}NSe$: M, 255.0525.

***N*-Pyrrolidinyl-α-phenylselenoacetamide (6i):** Similarly to **6c**, the reaction of *Se*-phenylethynyl selenoacetate (**1b**) (670 mg, 3.0 mmol) with pyrrolidine (425 mg, 6 mmol) yielded 582 mg (77%) of **6i** as slightly yellow crystals; mp 91—93 °C. IR (KBr) 2930, 2860, 1598, 1490, 1443, 1342, 1322, 1267, 1243, 1204, 1181, 1143, 1075, 1062, 1033, 1020, 985, 802, 744, 720, 697, 623, 498, 454 cm^{-1}; UV/Vis (cyclohexane) 255sh, 307 (log ε 4.25), 436 nm (2.22); ^1H NMR ($CDCl_3$) δ=1.92—2.08 (m, 4H), 3.37 (t, 2H), 3.85 (t, 2H), 4.33 (s, 2H), 7.2—7.4 (m, 5H); ^{13}C NMR ($CDCl_3$) δ=24.2, 26.6, 51.8, 58.0, 126.9, 128.3, 128.6, 134.5, 199.2 (C=Se); MS (EI, 20 eV) *m/z* 253 (M^+), 183, 172, 130, 116, 91, 65; Found: *m/z* 235.0378. Calcd for $C_{12}H_{15}NSe$: M, 253.0369.

***N*-Piperidino-α-phenylselenoacetamide (6j):** Similarly to **6c**, the reaction of *Se*-phenylethynyl selenoacetate (**1b**)

(670 mg, 3.0 mmol) with piperidine (510 mg, 6 mmol) yielded 620 mg (78%) of **6j** as slightly yellow crystals; mp 110—112 °C. IR (KBr) 2920, 2840, 1600, 1510, 1495, 1445, 1417, 1358, 1340, 1322, 1284, 1265, 1240, 1198, 1116, 1048, 1028, 1020, 1002, 956, 897, 855, 838, 800, 783, 732, 705, 698, 620, 607, 557, 465 cm^{-1}; UV/Vis (cyclohexane) 255sh, 319 (log ε 3.99), 422 nm (1.95); ^1H NMR ($CDCl_3$) δ=1.2—1.3 (m, 2H), 1.55—1.65 (m, 2H), 1.65—1.75 (m, 2H), 3.51 (t, 2H), 4.38 (t, 2H), 4.51 (s, 2H), 7.2—7.4 (m, 5H); ^{13}C NMR ($CDCl_3$) δ=23.2, 25.1, 25.7, 52.4, 54.5, 56.2, 126.7, 127.6, 128.6, 135.2, 201.3, (C=Se); (EI, 20 eV) *m/z* 267 (M^+), 186, 183, 130, 116, 91, 65; Found: *m/z* 267.0550. Calcd for $C_{13}H_{17}NSe$: 267.0525.

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References

1) A part of this paper was presented at the 39th Symposium on Organic Reactions, Matsuyama, October, 1989.

2) "Organic Selenium Compounds: Their Chemistry and Biology" ed. by D. L. Klayman and W. H. H. Günther, John Wiley & Sons, New York (1973).

3) K. B. Sharpless, K. M. Gordo, R. F. Lauer, D. W. Singer, and M. Y. Young, *Chem. Scripta,* **8A**, 9 (1975).

4) D. L. Cliev, *Tetrahedron,* **34**, 1049 (1978).

5) H. J. Reich, "Oxidation in Organic Chemistry," ed by W. S. Trahanovski, Academic Press, New York, (1978).

6) H. J. Reich, *Acc. Chem. Res.,* **12**, 22 (1979).

7) A. Krief, *Tetrahedron,* **36**, 2531 (1980).

8) J. Martens and K. Praefcke, *J. Organomet. Chem.,* **253**, 131 (1983).

9) D. Liotta, *Acc. Chem. Res.,* **17**, 28 (1984).

10) N. Sonoda and A. Ogawa, "The Chemistry of Organic Selenium and Tellurium Compounds," ed by S. Patai and Z. Rappoport, John Wiley & Sons, New York (1986).

11) C. Paulmier, "Selenium Reagent and Intermediates in Organic Synthesis," Pergamon Press, New York (1986).

12) "Organoselenium Chemistry," ed by D. Liotta, John Wiley & Sons, New York (1986).

13) S. Kato, T. Murai, and M. Ishida, *Org. Prep. Proc. Int.,* **18**, 369 (1986).

14) D. H. R. Barton, P. E. Hansen, and K. Picker, *J. Chem. Soc., Perkin Trans. 1,* **1977**, 1723.

15) K. C. Nicolaou, D. A. Claremon, W. E. Barnette, and S. P. Seitz, *J. Am. Chem. Soc.,* **101**, 3704 (1979).

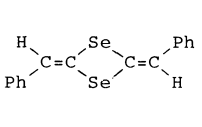
16) P. A. Grieco, J. Y. Jaw, D. A. Claremon, and K. C. Nicolaou, *J. Org. Chem.,* **46**, 1215 (1981).

17) D. L. Boger and R. J. Mathvink, *J. Org. Chem.,* **53**, 3377 (1988).

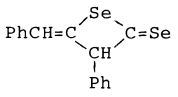
18) M. Ishida, T. Iwata, M. Yokoi, K. Kaga, and S. Kato, *Synthesis,* **1985**, 632.

19) M. Ishida, K. Kaga, H. Sato, M. Yokoi, and S. Kato, *Bull. Chem. Soc. Jpn.,* **59**, 1403 (1986).

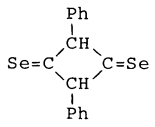
20) The alternative structures (**7**—**12**) were ruled out: The ^{13}C NMR spectrum does not show 12 peaks of the absorptions requiring for **7**. The structures **8**, **9**, and **10** are expected to be highly colored due to the n-π transitions of the C=Se group. The 1,2-diselenetane **11** would not display singlet absortions due to the methylene protons. For the formation of **12**, a hydrogen migration is involved which is not very likely to occur under the reaction conditions.



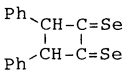
7



8



9



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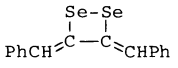
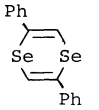


11



12

21) The trans-isomer (**5b**) is considered to be formed via the cis-isomer **5a**.

22) The stirring of **5a** in ether containing a catalytic amount of *p*-toluenesulfonic acid or trifluoroacetic acid at 20 °C for 2 h gave **5b** in a quantitative yield.

23) F. Malek-Yazdi and M. Yalpani, *J. Org. Chem.,* **41**, 729 (1976).

24) R. S. Sukhai, R. de Jong, and L. Brandsma, *Synthesis,* **1977**, 889.

25) F. Malek-Yazdi and M. Yalpani, *Synthesis,* **1977**, 328.

26) C. Collard-Charon, *Bull. Soc. Chim. Belg.,* **72**, 304 (1963).

27) K. A. Jensen and P. H. Nielson, *Acta Chem. Scand.,* **20**, 597 (1966).

28) C. Collard-Charon and M. Renson, *Bull. Soc. Chim. Belg.,* **71**, 563 (1962).

29) R. Mayer, S. Scheithauer and D. Kunz, *Chem. Ber.,* **99**, 1393 (1966).