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Dialkynyl Selenides: Synthesis, ^{13}C NMR Spectra, and Molecular Orbital Calculations

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ABSTRACT

*Reactions of $SeCl_4$ with lithium bis(trimethylsilyl)amide and terminal acetylenes in the presence of BuLi or AIBN afforded the corresponding dialkynyl selenides in moderate to high yields. The reaction may proceed via a selenium amide **7** and an alkynyl selenium amide **8**. The comparison of ^{13}C NMR spectra of dialkynyl selenides and tellurides has disclosed that the differences of the chemical shift of acetylenic carbons between Se and Te derivatives are consistent regardless of their substitution patterns. Ab initio molecular orbital calculations are reported for dialkynyl ether and chalcogenides. The calculated structures, charge distributions, and orbital energies are discussed.*

Dialkynyl ethers and chalcogenides are compounds of great interest because of their potential synthetic utility as well as their structural properties, resulting from the situation that two electronically rich alkynyl groups are attached to an electronegative atom [1]. However, only limited examples have been reported concerning synthetic efforts to attain such compounds. Several kinds of dialkynyl sulfides have been prepared by mono- or dialkynylation of sulfur dichloride or alkynyl thiocyanates [2]. Only two Se derivatives were synthesized by alkynylation of lithium alkyneselenolates [3]. We have found recently that the combination of $TeCl_4$ and lithium bis(trimethylsilyl)amide (**1**) accomplishes the in situ generation of a Te(2+) species which successively reacts with two molecules of terminal acetylenes to give dialkynyl tellurides in good to high yields [4,5]. Herein, we report that the application of this method to $SeCl_4$ and terminal acetylenes afforded the corresponding dialkynyl selenides. Furthermore, ^{13}C NMR spectra of dialkynyl selenides and tellurides and their molecular orbital calculations have disclosed their structural and electronic properties.

Similarly to the reaction of $TeCl_4$ with **1** and terminal acetylenes [4], $SeCl_4$ was treated with **1** at 0°C for 30 minutes, phenylacetylene was added, and the mixture was stirred at temperatures ranging from 25 to 67°C. However, a black tar was mainly obtained, and the desired selenide **2a** was obtained only in poor yields in tetrahydrofuran (THF), as shown in Table 1. The reaction in C_6H_6 afforded silylacetylene **3a** as a major product (run 4). To enhance the yield of **2a**, the effect of an additive was examined. As a result, the addition of 1 equiv of BuLi to THF or the addition of 0.1 equiv of 2,2′-azobis(isobutyronitrile) (AIBN) to C_6H_6 gave **2a** in better yields (runs 3 and 5).

The reaction with a variety of terminal acetylenes was carried out. As summarized in Table 2, the optimum reaction conditions are highly de-

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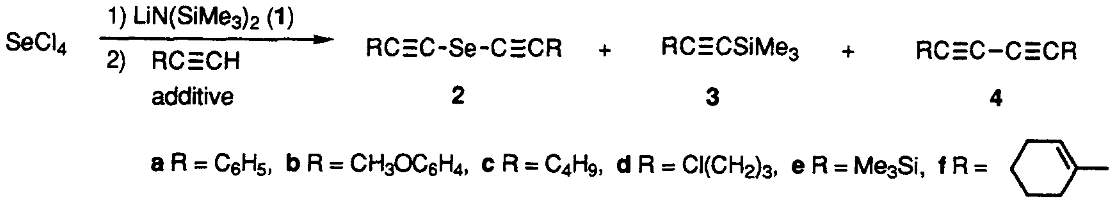


(1)

TABLE 1 Reaction of $SeCl_4$ with **1** and Phenylacetylene

Run	*Solvent*	*Additive*	*Temperature (°C)*[a]	*Time (h)*[a]	*Yield (%)*		
					2	*3*	*4*
1	THF	—	67	8	3	0	4
2	THF	BuLi	−20	8	32	0	38
3	THF	AIBN	67	1.5	15	6	22
4	C_6H_6	—	80	5	21	51	14
5	C_6H_6	AIBN	80	5	43	24	9

[a] Temperature and time after the addition of **2a** were shown.

pendent on the substrates. The reaction of aromatic acetylenes gave **2** only in moderate yields, together with **3** or **4** (runs 1 and 2). Attempts to obtain the dialkynyl selenide from 4-chlorophenylacetylene have failed. Alkynyl selenide **5** and alkynyl diselenide **6** were obtained from the reaction using BuLi as an additive.

Alternatively, the reaction in C_6H_6 gave quantitatively **3** (R = $4\text{-}ClC_6H_4$). In contrast, the reaction of aliphatic acetylenes and the silylacetylene afforded **2** in good to high yields (runs 3–6).

$4\text{-}ClC_6H_4C{\equiv}CSeBu$
5

$4\text{-}ClC_6H_4C{\equiv}CSeSeBu$
6

$(Me_3Si)_2N\text{-}Se\text{-}N(SiMe_3)_2$
7

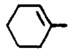
$RC{\equiv}CSeN(SiMe_3)_2$
8

In the present reaction, the selenium diamide **7** is initially formed via reduction and amination of $SeCl_4$ with **1** [6].

Alkynyllithium generated from a terminal acetylene and BuLi may successively attack the selenium atom of **7** and also that of the intermediate **8** to give the product. As for the reaction with $TeCl_4$, the corresponding amide could undergo proton abstraction of the terminal acetylenes, whereas **7** was less basic probably because of the stronger selenium–nitrogen bond compared with a tellurium–nitrogen bond [7,8]. This stability can also be seen in the reaction in the presence of AIBN. The cleavage of the silicon–nitrogen bond becomes competitive with that of the selenium–nitrogen bond.

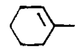
The chemical shifts of alkynyl carbons of dialkynyl selenides **2** were compared with those of Te derivatives on the basis of ^{13}C NMR spectra [9]. As shown in Table 3, the alkynyl carbons adjacent to Se were observed in the range of δ 54 to δ 90, whereas the carbons away from Se were in the

TABLE 2 Reaction of $SeCl_4$ with **1** and Terminal Acetylenes

Run	*Acetylene (R)*	*Solvent and Additive*	*Temp. (°C)*[a] *and Time (h)*	*Yield (%)*		
				2	*3*	*4*
1	$CH_3C_6H_4$	THF BuLi	−78 °C 3 h	28	0	42
2	$CH_3OC_6H_4$	C_6H_6 AIBN	80 °C 5 h	38	47	11
3	C_4H_9	THF BuLi	25 °C 24 h	42	0	0
4	$Cl(CH_2)_3$	THF BuLi	−20 °C 5 h	55	0	0
5	Me_3Si	THF AIBN	25 °C 5 h	72	0	0
6		C_6H_6 —	25 °C 5 h	69	16	10

[a] Temperature and time after the addition of terminal acetylene were shown.

TABLE 3 ^{13}C NMR Spectra of Dialkynyl Chalcogenides

RC≡CEC≡CR R	RC≡CEC≡CR E = Se (δ)	 E = Te (δ)	 Δ(Se-Te) (ppm)	RC≡CEC≡CR E = Se (δ)	 E = Te (δ)	 Δ(Se-Te) (ppm)
C_6H_5	64.8	43.4	21.4	100.3	112.6	−12.3
4-$CH_3OC_6H_4$	63.2	41.3	21.9	100.1	112.5	−12.4
C_4H_9	54.0	30.8	23.2	101.6	114.3	−12.7
$Cl(CH_2)_3$	55.4	32.6	22.8	99.7	112.2	−12.5
Me_3Si	89.8	59.3	30.5	113.8	123.6	−9.8
	61.8	39.7	22.1	101.7	114.4	−12.7

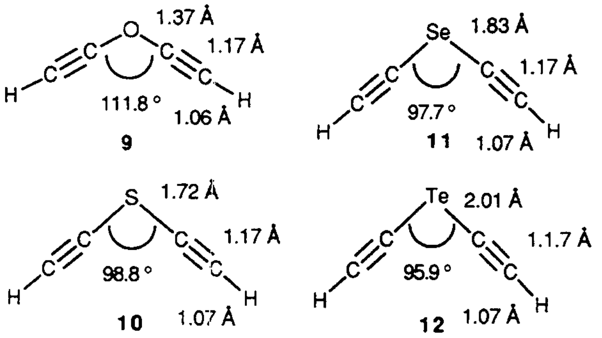


FIGURE 1 Optimized geometries of the most stable conformations of **9–12**.

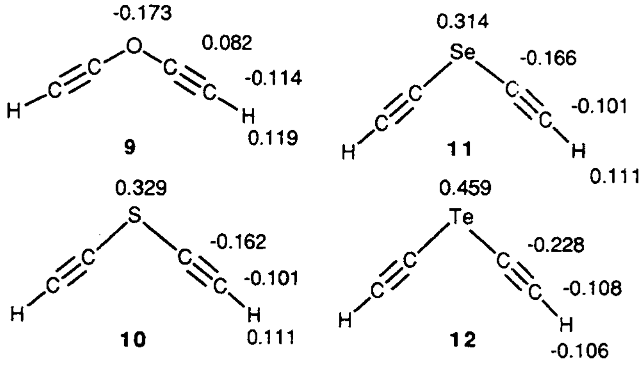


FIGURE 2 Total atomic charges in **9–12**.

range of δ 99 to δ 114. When the Se atom was replaced with Te, the resonances of both carbons were shifted to higher and lower fields, respectively. Regardless of the substituents attached to the acetylenic carbon, the differences of the chemical shifts between Se and Te derivatives are within the range of 1.8 ppm except for the Me_3Si derivatives.

In order to gain further insight into the properties of dialkynyl chalcogenides, the molecular orbital calculations with the minimum STO-3G basis set [10] were carried out on dialkynyl ether **9** and dialkynyl chalcogenides **10–12**. The optimized geometries of the most stable conformers are presented in Figure 1.

Comparison of the optimized geometries of **9–12** indicates that the bond lengths between the chalcogen atom and the acetylenic carbon are longer in the order of O, S, Se, and Te because of their atomic radii. On the other hand, the bond angles of C-E-C (E = O, S, Se, Te) become smaller in the order of O, S, Se, and Te.

The results of the Mulliken population analysis of the total atomic charges for each compound are shown in Figure 2.

The relatively large negative charge of −0.23 at the carbon adjacent to Te in **12** is consistent with the fact that, in the ^{13}C NMR spectra of dialkynyl tellurides, the resonances of the carbons next to Te are observed to be at ca. 21 ppm higher field than those in dialkynyl selenides, although the atomic charge and ^{13}C NMR spectra of the alkynyl carbon atoms away from Se and Te do not correlate with each other.

The energies of the frontier orbitals are also of interest (Table 4). The energies of the LUMOs, the main component of which is the π LUMO of the acetylene moiety in each case, are dramatically lower in going from O to S, Se, and Te, whereas the differences of energies of the NHOMO's composed of the π HOMOs of the acetylene moieties are within 0.7 eV of one another.

TABLE 4 Frontier Orbitals (LUMO, HOMO, NHOMO) of **9–12**

	NHOMO (eV)	HOMO (eV)	LUMO (eV)
9	−9.80	−8.49	10.13
10	−9.60	−7.20	9.67
11	−9.66	−7.18	8.35
12	−9.13	−6.52	6.83

EXPERIMENTAL

Instrument and Materials

THF was distilled from sodium benzophenone ketyl prior to use. Benzene was distilled from sodium and stored under nitrogen. The acetylenes were distilled either from CaH_2 or under reduced pressure. Selenium powder was purchased from Nacalai Tesque and used without further purification. ^1H and ^{13}C NMR spectra were recorded on a JEOL JNM-GX-270 spectrometer using $CDCl_3$ as a solvent with Me_4Si as an internal standard. IR spectra were obtained on a Perkin-Elmer Model 1650 spectrometer. Mass spectra and high resolution mass spectra were measured on a Shimadzu model 9020DF instrument. Melting points were determined by using a Yanagimoto melting point apparatus and are uncorrected.

General Procedure for the Preparation of Dialkynyl Selenides

To lithium bis(trimethylsilyl)amide **1** (2 mmol) in THF (8 mL) was added a THF solution (2 mL) containing $SeCl_4$ (0.5 mmol), and the mixture was stirred at 0°C for 2 hours. To the resulting deep red solution were injected successively an acetylene (1 mmol) and a hexane solution of BuLi (1 mmol) at an appropriate temperature, and the mixture was stirred. It was poured onto ice water and extracted with ether. The combined organic layer was dried over Na_2SO_4, concentrated, and purified by thin layer chromatography using CH_2Cl_2/*n*-hexane (1:10) as an eluent to give the dialkynyl selenide.

Bis(4-methoxyphenylethynyl) Selenide

2b: a yellow solid; mp 100–103°C; IR (KBr) 2915, 2120, 1655, 1600, 1510, 1435, 1285, 1245, 1165, 1070, 1025, 820, 745, 660, 530 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.80 (s, 6H, CH_3O), 6.83 (d, J = 8.8 Hz, 4H, Ar), 7.42 (d, J = 8.8 Hz, 4H, Ar); ^{13}C NMR ($CDCl_3$) δ 55.3, 63.2, 100.1, 114.0, 114.7, 133.8, 160.2; CIMS (m/z) 343 (M^+ + 1); HRMS calcd for $C_{18}H_{14}O_2Se$: 342.01584. Found: 342.01736.

Bis(1-hexynyl) Selenide

2c: a yellow liquid; IR (neat) 2960, 2945, 2250, 2175, 1460, 1430, 1375, 1325, 1240, 1105, 960, 910, 735, 655 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.89 (t, 6H, J = 7.1 Hz, CH_3), 1.38–1.54 (m, 8H, CH_2), 2.34 (t, 4H, J = 7.0 Hz, CH_2); ^{13}C NMR ($CDCl_3$) δ 13.6, 20.1, 21.9, 30.5, 54.0, 101.6; EIMS (m/z) 242 (M^+); HRMS calcd for $C_{12}H_{18}Se$: 242.05728. Found: 242.05718.

Bis(5-chloropent-1-ynyl) Selenide

2d: a light yellow liquid; IR (neat) 2950, 2900, 2850, 2250, 2150, 1440, 1420, 1340, 1290, 1250, 1180, 1040, 935, 910, 840, 800, 760, 700, 660, 640, 560, 490, 440 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.93–2.02 (m, 4H, CH_2), 2.55 (t, 4H, J = 7.0 Hz, CH_2C), 3.63 (t, 4H, J = 6.4 Hz, $ClCH_2$); ^{13}C NMR ($CDCl_3$) δ 17.8, 31.1, 43.5, 55.4, 99.7; EIMS (m/z) 282 (M^+); HRMS calcd for $C_{10}H_{12}Cl_2Se$: 281.94806. Found: 281.94873.

Bis(trimethylsilylethynyl) Selenide

2e: a yellow liquid; IR (neat) 2950, 2800, 2200, 2150, 1410, 1250, 1090, 840, 765, 700, 640, 620, 550 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.19 (s, 18H, CH_3Si); ^{13}C NMR ($CDCl_3$) δ −0.3, 89.8, 113.8; CIMS (m/z) 275 (M^+ + 1); HRMS calcd for $C_{10}H_{18}Si_2Se$: 274.01114. Found: 274.01195.

Bis(1-cyclohexenylethynyl) Selenide

2f: a yellow liquid; IR (neat) 3050, 2950, 2850, 2150, 1620, 1440, 1430, 1345, 1260, 1230, 1160, 1130, 1070, 1040, 960, 910, 850, 835, 790, 770, 660, 520, 440 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.55–1.59 (m, 8H, CH_2), 2.08–2.12 (m, 8H, CH_2), 6.17 (t, 2H, J = 1.8 Hz, CH); ^{13}C NMR ($CDCl_3$) δ 21.4, 22.2, 25.7, 28.8, 61.8, 101.7, 120.6, 137.1; CIMS (m/z) 291 (M^+ + 1); HRMS calcd for $C_{16}H_{18}Se$: 290.05728. Found: 290.05915.

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REFERENCES

[1] I.-H. Ooi, R. H. Smithers, *J. Org. Chem.*, *54*, 1989, 1479.

[2] (a) J. Meijer, P. Vermeer, H. D. Verkruijsse, L. Brandsma, *Recl. Trav. Chim. Pays-Bas*, *92*, 1973, 1326; (b) M. Schoufs, J. Meijer, P. Vermeer, L. Brandsma, *Recl. Trav. Chim. Pays-Bas*, *93*, 1974, 241; (c) A. Zilverschoon, J. Meijer, P. Vermeer, L. Brandsma, *Recl. Trav. Chim. Pays-Bas*, *94*, 1975, 163; (d) W. Verboom, M. Schoufs, J. Meijer, H. D. Verkruijsse, L. Brandsma, *Recl. Trav. Chim. Pays-Bas*, *97*, 1978, 244.

[3] M. J. Dabdoub, J. V. Comasseto, *Synth. Commun.*, *18*, 1988, 1979.

[4] (a) T. Murai, K. Imaeda, S. Kajita, H. Ishihara, S. Kato, *J. Chem. Soc., Chem. Commun.*, 1991, 832; (b) T. Murai, K. Imaeda, S. Kajita, K. Kimura, H. Ishihara, S. Kato, *Phosphorus Sulfur Silicon Relat. Elem.*, *67*, 1992, 239.

[5] Very recently, Gedridge et al. synthesized dialkynyl tellurides from $TeCl_4$ and 4 equiv of alkynyllithium: R. W. Gedridge, Jr., L. Brandsma, R. A. Nissan, H. D. Verkruijsse, S. Harder, R. L. P. de Jong, C. J. O'Connor, *Organometallics*, *11*, 1992, 418.

[6] M. Björgvinsson, H. W. Roesky, F. Pauer, D. Stalke, G. M. Sheldrick, *Inorg. Chem.*, *29*, 1990, 5140.

[7] Several stable selenium diamides have been reported: R. B. King, S. A. Sangokoya, *Inorg. Chem.*, *26*, 1987, 2727.

[8] T. Murai, K. Nonomura, K. Kimura, S. Kato, *Organometallics*, *10*, 1991, 1095.

[9] ^{13}C NMR spectra of alkynyl chalcogenides were reviewed: B. Wrackmeyer, K. Horchler, *Prog. NMR Spectroscopy*, *22*, 1990, 209.

[10] (a) W. J. Hehre, R. F. Stewart, J. A. Pople, *J. Chem. Phys.*, *51*, 1969, 2657; (b) J. B. Collins, P.v. R. Schleyer, J. S. Binkley, J. A. Pople, *J. Chem. Phys.*, *64*, 1976, 5142; (c) W. J. Pietro, W. J. Hehre, *J. Comput. Chem.*, *4*, 1983, 241.