Heteroatom Chemistry
Volume 16, Number 2, 2005

Synthesis, Charge Distribution, and Dimerization Behavior of Lithium Alkynylselenolates

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Received 2 August 2004; revised 29 November 2004

ABSTRACT: *The reactivity of alkynyl lithium compounds toward elemental gray selenium yields alkynylselenolates, which show significant interaction with the lithium counter ions, depending on solvent polarity and the electronic nature of the adjacent organic substituent. Likewise the dimerization behavior is different for alkyl- and aryl-substituted alkynylselenolates. From the latter, unsymmetrical 1,3-selenol is formed, the molecular structure of which was confirmed by X-ray structure analysis.* © 2005 Wiley Periodicals, Inc. Heteroatom Chem 16:169–174, 2005; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20088

INTRODUCTION

Alkynylchalcogenolates are known to show typical ambident nucleophilic behavior. For the heavier chalcogens of such compounds, the β-carbon atom represents the hard and the chalcogens atom the soft site of the unsaturated unit [1]. Therefore, addition of positively charged electrophiles gives rise to either organic chalcogenides (selenanes) or to chalcogenoketenes (Scheme 1). In the case of alkynylthiolates, this reactivity pattern has been successfully employed to generate thioketenes [1–5]. In contrast to the well-known ketenes and thioketenes, their heavier congeners, i.e. seleno and telluroketenes remain unknown up to now. Recent theoretical investigations suggest that in terms of reactivity thioketene is more similar to selenoketene than to ketene [4]. Nevertheless, experimental data to corroborate this hypothesis are not available for selenoketenes. Therefore, we were interested to investigate the reactivity of selenolates, due to their importance as potential precursors for the generation of selenoketenes.

RESULTS AND DISCUSSION

To investigate the ambident reactivity of alkynylselenolates, we prepared some hitherto unknown alkynylselenolates following an adapted approach of the general procedure by Brandsmaa [6,7]. The instability of ethynylselenolate earlier described by the same authors prompted us to consider substituents with different electronic properties. Therefore, we focused in our investigation on a comparison of phenyl- and pentyl-substituted alkynylchalcogenolates. 1-Heptyne and phenylacetylene were deprotonated with *n*-BuLi in THF solution at low temperature (−78°C) to the corresponding alkynyllithium derivatives, which subsequently were

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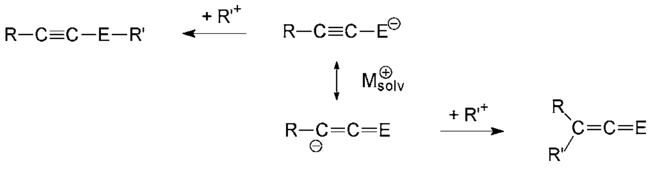
Contract grant sponsor: Fonds der Chemischen Industrie (Liebig Fellowship).
Contract grant sponsor: Ruhr-Universität Bochum (Anschubprogramm für den wissenschaftlichen Nachwuchs).



SCHEME 1 Reactivity pattern of alkynylchalcogenolates (E = chalcogens, M = alkali metal, R/R′ = organic substituent).

TABLE 1 Heteronuclear NMR Data for **2a** in Solvents of Different Polarity [8]

	C_6D_6	Et_2O	THF
Dipole moment	0	1.15	1.63
Dielectric constant	2.28	4.34	7.52
$\delta(^{77}Se)$	−15.1	−111.6	−114.6
$\delta(^{7}Li)$	−0.8	−1.7	−2.1

reacted without further purification with elemental gray selenium affording the respective alkynylselenolates **2a,b** in good yield (Scheme 2).

Besides ^{1}H and ^{13}C NMR, the resulting products have also been characterized by ^{7}Li and ^{77}Se NMR spectra. These heteronuclear NMR measurements show that the chemical shift values differ substantially with the polarity of the solvent and the substituent attached to the alkynyl group. For instance with R = pentyl, the ^{77}Se and ^{7}Li nuclei become more shielded going from lower to higher solvent polarity (Table 1).

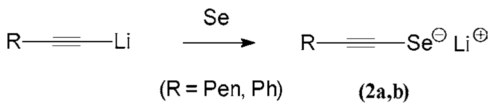
These findings may be caused by the influence of the solvent polarity on the separation of the ions in the lithium 1-heptynylselenolate. The observation that an increase in the solvent polarity leads to a shielding of the ^{77}Se and the ^{7}Li nuclei is in line with the assumption of a contact ion pair at lower solvent polarity, which becomes more separated the better the coordination properties of the solvent are (Scheme 3). This should increase the negative charge on the unsaturated CCSe unit and consequently on the selenium atom. Likewise the coordination number for the solvated lithium cation should increase, accompanied by a reduced positive charge on this metal ion.

Besides the role of the solvent in the separation of the ion pair of alkynylselenolates **2a,b**, we also wanted to study the influence of the adjacent organic substituent on the negatively charged CCSe unit. In addition to the already mentioned pentyl- and phenyl-substituted alkynylselenolates **2a,b**, we also prepared the bulky 2,4,6-triisopropyl (=Tip) substituted congener **2c** [9]. All shifts have been measured in THF solution to maximize the negative charge on the anion. The ^{7}Li, ^{77}Se, and ^{13}C NMR data for the relevant CC-SeLi unit of alkynylselenolates **2a–c** are summarized in Table 2. The most pronounced difference is found for the ^{77}Se shifts of the aryl-substituted alkynylselenolates **2b,c** that appear to resonate generally at lower field than in the alkyl derivative. The ^{13}C resonances of the alkynyl carbon atoms do not differ by more than 10 ppm in all cases, and also the ^{13}C-^{77}Se-coupling constants (^{1}J and ^{2}J) are not significantly affected by substituents. On the first sight, from these spectroscopic data, no marked difference for the electron distribution for aryl- and alkyl-substituted alkynylselenolates would be deduced.

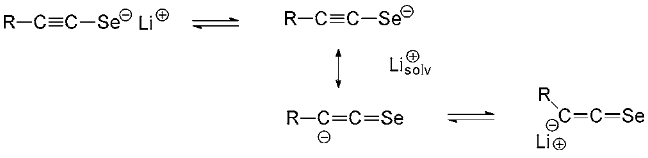
In contrast to this conclusion, we found substantial differences in the reactivity for alkyl- and aryl-substituted systems of this type. On protonation of the selenolates **2a,b** one would expect the formation of the corresponding selenols. However, these have not been isolated as the final products of this reaction. As we found out, the nature of the resulting product depends strongly on the nature of the substituent R in these selenolates. For instance, protonation of the pentyl-substituted alkynylselenolate **2a** results in the formation of the corresponding dialkynylselenide **3** (Scheme 4).

In contrast to this result, the protonation of the phenyl-substituted alkynylselenolate **2b** also leads to a dimeric product, however with a different structure. In the latter case, an unsymmetrically substituted 1,3-diselenole (**4**) is formed as the main product (Scheme 5).

To explain the formation of these products an initial protonation of the alkynylselenolate seems likely. For the resulting product, two tautomeric forms have to be considered: the alkynylselenol and the corresponding selenoketene. Since a direct nucleophilic displacement of an HSe^{-} group by a selenol or a selenolate appears highly unlikely at an sp-carbon center, the formation of **3** is more likely to involve a



SCHEME 2 Synthesis of alkynylchalcogenolates **2a,b**.



SCHEME 3 Equilibria of lithium alkynylchalcogenolates.

TABLE 2 Survey of NMR Data for the CCSe Unit of Lithium Alkynylchalcogenolates **2a–c** in the THF solution

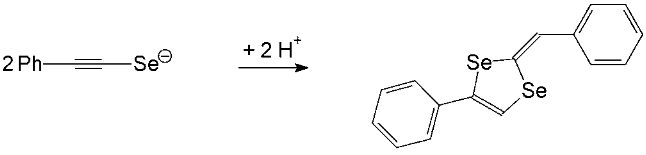
	R = Pentyl	*R = Phenyl*	*R = Tip*
δ(^{77}Se)	−114.6	−59.3	−64.6
δ(^{7}Li)	−2.1	−2.2	−0.8
δ(^{13}C), Se–$\underline{\text{C}}$≡C–	70.4	91.1	83.0
δ(^{13}C), Se–C≡$\underline{\text{C}}$–	78.5	81.6	84.6
$^{1}J_{\text{CSe}}$ (Hz)	219	231	–
$^{2}J_{\text{CSe}}$ (Hz)	34	32	–

selenoketene. Addition of either a selenol or a selenolate to the selenocarbonyl group of the selenoketene appears plausible. The resulting intermediate may then lose HSe^- or H_2Se giving the finally observed product **3** (Scheme 6).

With a phenyl-substituted alkynylselenolate in principle the same initial intermediates should be likely. In the second step, however the 1,3-dipolar cycloaddition of two selenoketene units would directly furnish the final product, which appears more likely than a stepwise addition mechanism.

We were able to obtain suitable crystals for an X-ray diffraction analysis of compound **4**. From this structure the constitution of the unsymmetrically substituted 1,3-diselenole is evident (Fig. 1). Actually, this is the first experimental proof for an unsymmetrical substituted 1,3-diselenole that had been postulated without any evidence in older work [10]. All rings as well as the exocyclic double bond of the molecule lie in one plane. Due to librational effects, the C=C bonds in and adjacent to the central ring appear shortened as was discussed by Dunitz earlier [11]. Otherwise, the relevant bond parameters and angles show no peculiarities and are summarized in Table 3. Details of the data collection and structure refinement are summarized in Table 4 and in the experimental section.

In order to explain the difference in reactivity of alkyl- and aryl-substituted alkynylselenolates and to get an insight into the electron distribution within the CCSe unit, we performed quantum chemical calculations on DFT level. The results were obtained with the program package Gaussian 98 using a Becke–Lee–Yang–Parr hybrid functional and a 6-31G(d) basis set [12–14]. For the sake of simplicity, we replaced the pentyl group in **2a** with a methyl group (≡**2d**).



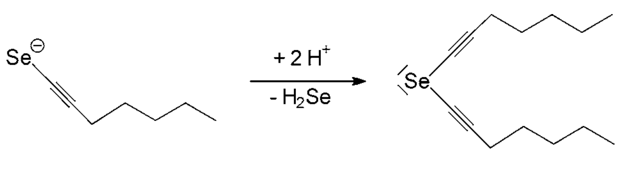
SCHEME 5 Synthesis of **4**.

In the case of the methyl-substituted alkynylselenolate, the charge distribution in terms of an NBO analysis shows that the negative charge is distributed over the whole molecule but still predominantly located on the selenium atom. Replacing methyl by phenyl results in a lowered charge density on the selenium atom as well as the alkynyl unit that in both cases seems to be rather unpolar (Fig. 2).

A more significant difference between these two substitution patterns can be derived from the MO coefficients of the HOMO. While the HOMO in the methyl-substituted case has the largest coefficient on the C_β atom. The largest HOMO coefficient of the phenyl-substituted system is found on the selenium atom. Since in orbital-controlled reactions an external electrophiles is likely to interact with the HOMO, these findings are is especially interesting with respect to the generation of a selenoketene from an alkynylselenolate. Moreover, in the case of the phenyl-substituted alkynylselenolate, the coefficients of the HOMO in the 1,3 positions of the CCSe unit are substantially larger than in the methyl derivative. This might be a one of the reasons for the increased reactivity of **2b** toward dimerization via 1,3-dipolar cycloaddition.

CONCLUSION

In summary, we investigated synthesis, characterization, and reactivity of alkyl versus aryl-substituted alkynylselenolates. We explored their dissociation



SCHEME 4 Formation of **3**.

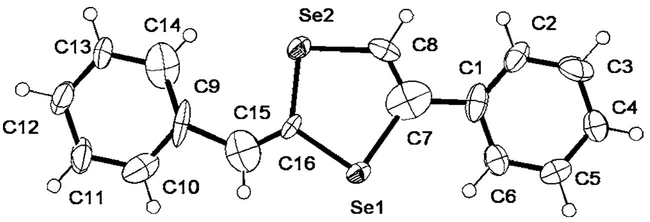
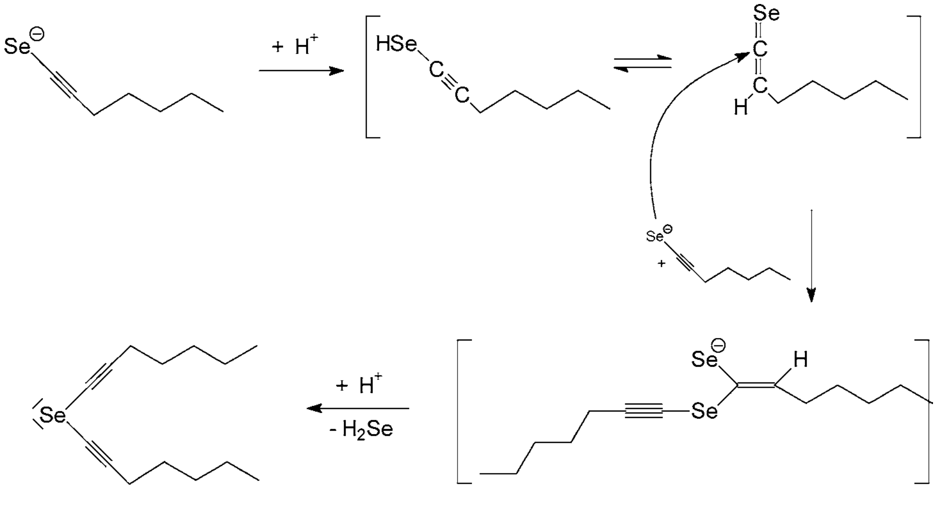


FIGURE 1 Molecular structure of **4** in the solid state.



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SCHEME 6 Tentative mechanism for the formation of **3**.

behavior in solvents of different polarity, their spectroscopic properties, their different dimerization behavior, as well as their different electronic situation on the basis of ab initio calculations. As a result, we found a substantial difference caused by the different electronic interaction of the CCSe unit with adjacent substituents. This leads to a marked contrast in the dimerization behavior for **2a,b**, which in both cases might involve selenoketene intermediates. Moreover, we report the first experimental evidence for an unsymmetrically substituted 1,3-diselenole, for which we present a crystal structure.

EXPERIMENTAL

The chemical experiments were performed in an argon atmosphere and solvents were freshly distilled prior to use. NMR spectra were recorded on a Bruker DPX 250 and referenced using tetramethylsilane ($^1H/^{13}C$), LiCl/H$_2$O (^7Li), and H_2SeO_3/H_2O (^{77}Se) as external standards. Mass spectra were recorded on a VG Instruments Autospec/EBEE-geometry.

TABLE 3 Selected Bond Lengths and Angles of **4** in degrees and Å

Se(1)–C(16)	1.872(14)	C(16)–Se(1)–C(7)	90.4(8)
Se(1)–C(7)	2.03(3)	C(16)–Se(2)–C(8)	94.0(7)
Se(2)–C(16)	1.821(17)	C(7)–C(8)–Se(2)	117.7(14)
Se(2)–C(8)	1.96(2)	C(16)–C(15)–C(9)	129(2)
C(1)–C(7)	1.56(2)	C(15)–C(16)–Se(2)	122.4(15)
C(7)–C(8)	1.28(3)	C(15)–C(16)–Se(1)	118.7(15)
C(9)–C(15)	1.56(2)	Se(2)–C(16)–Se(1)	118.8(9)
C(15)–C(16)	1.24(3)		

Synthesis of Lithium 1-Heptynylselenolate **2a**

To a solution of 0.96 g (10 mmol) of 1-heptyne in 40 mL of the THF cooled to −78°C, a solution of *n*-BuLi (11 mmol) in hexane is slowly added while stirring. Stirring is continued for 90 min at this temperature, after which the mixture is warmed to room temperature resulting in a yellow solution. This solution is again cooled to −78°C and gray selenium powder (0.79 g, 10 mmol) is added in small portions. Stirring is continued and the reaction mixture is warmed to room temperature over night upon

TABLE 4 Crystal Data and Structure Refinement for **4**

Formula	$C_{16}H_{12}Se_2$
Formula weight	362.18
Temp. (K)	203(2)
Wavelength	0.71073
Crystal system	Orthorhombic
Space group	*Pca2*(1)
Unit cell dimensions	
a (Å)	8.2207(16)
b (Å)	5.7511(12)
c (Å)	27.936(6)
α (°)	90
β (°)	90
γ (°)	90
Volume (Å^3)	1320.8(5)
Z	4
Density (calcd.) (mg/m^3)	1.821
μ (mm^{-1})	5.576
θ range for data collection (deg)	2.92–25.18
goodness-of-fit on F^2	1.122
*R*1 (observed data)	0.0826
*wR*2 (all data)	0.2113

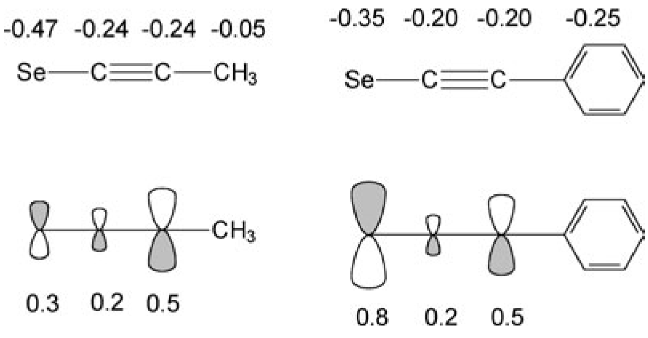

FIGURE 2 Natural charges derived from an NBO analysis (upper section) and illustration of the MO coefficients of the π-system (lower section) of **2b** and **2d**.

which the selenium is dissolved completely. Evaporation of the solvent in vacuum furnishes a orange-brown viscous oil, which is washed twice with 10 mL of pentane. Yield: 1.71 g (94%). ^{1}H: 0.8 (3H), 1.1–1.5 (6H), 2.0 (2H). ^{13}C (C_6D_6): 14.15 (CH_3), 21.86 (CH_2), 22.77 (CH_2), 30.72 (CH_2), 31.54 (CH_2), 70.35 ($^1J_{\mathrm{CSe}} = 219$ Hz, Se-$\underline{\mathrm{C}}$C), 78.45($^2J_{\mathrm{CSe}} = 34$ Hz, Se-C$\underline{\mathrm{C}}$). ^{77}Se (C_6D_6): −15.1. ^{7}Li (C_6D_6): −0.8. MS (FAB): 176, M$^+$, 20%; 133, M$^+$-propyl, 30%; 95, propyl$^+$, 55%.

Synthesis of Lithium Phenylalkynylselenolate **2b**

2b was prepared similar to **2a**. Starting from of 1.02 g (10 mmol) of phenylacetylene 1.65 g (88%) of lithium phenylalkynylselenolate **2b** was obtained. ^{1}H (THF-d^8): 6.9–7.5 (m). ^{13}C (THF-d^8): 81.6 ($^1J_{\mathrm{CSe}} = 31.5$ Hz, Se-C$\underline{\mathrm{C}}$), 91.1 ($^1J_{\mathrm{CSe}} = 231$ Hz, Se-$\underline{\mathrm{C}}$C), 122.9 (p-CH), 127.9 (CH), 130.6 (Cq), 131.0 (CH). ^{77}Se (THF-d^8): −59.2. ^{7}Li (THF-d^8): −2.18. MS (EI): 187, M$^+$, 2%; 98, M$^+$-H_2Se, 17%, 60, 100%.

Synthesis of Di(1-heptynyl)selenide **3**

In a schlenk flask, **2a** (0.5 g, 2.8 mmol) is dissolved in 50 mL of ether and subsequently treated with 10 mL of half-concentrated aqueous hydrochloric acid. The mixture is stirred for 30 min and then the layers are separated, and the aqueous layer is extracted twice with 20 mL of pentane. The combined organic layers are dried over magnesium sulfate, filtered, and the solvents are removed in vacuum. **3** is obtained as an orange pasty residue (0.27g, 72%).

^{1}H: 0.92 (3H), 1.31 (6H), 2.20 (2H). ^{13}C (C_6D_6): 14.32 (CH_3), 20.65 (CH_2), 22.65 (CH_2), 28.58 (CH_2), 31.38 (CH_2), 55.1 (Se-$\underline{\mathrm{C}}$C), 101.8 (Se-C$\underline{\mathrm{C}}$). ^{77}Se (C_6D_6): 358.1. MS(EI): 266.091357 found (.0913601) calcd. (M$^+$, 4%), 78 (Se$^+$, 100%).

*Synthesis of 2-Benzylidene-4-phenyl-1,3-diselenole (***4***)*

In a schlenk flask, **2a** (0.5 g, 2.7 mmol) is dissolved in 50 mL of ether and subsequently treated with 10 mL of half-concentrated aqueous hydrochloric acid. The mixture is stirred for 30 min and then the layers are separated, and the aqueous layer is extracted twice with 20 mL of pentane. The combined organic layers are dried over magnesium sulfate, filtered, and the solvents are removed in vacuum. **4** is obtained as orange pasty residue that can be recrystallized from MTBE/toluene (0.32 g, 64%).

^{1}H: 7.5–7.2 (m). ^{13}C: 138.6, 137.5, 136.0, 129.3 (CH), 129.0 (CH), 128.2, 127.2 (CH), 126.9 (CH), 126.2, 125.9, 121.8, 126.3. ^{77}Se: 684 (s), 544 (s). MS (FAB): 363.9, M$^+$, 73%; 182, M$^+$/2, 20%. $C_{16}H_{12}Se_2$: calcd.:C: 53.06, H: 3.34; found: C: 52.67, H: 3.08.

Crystallographic Details for **4**

A colorless crystal of **5** with dimensions 0.1 × 0.2 × 0.2 mm was coated in paraffin oil, mounted on a glass fiber, and placed under a cold stream of nitrogen. All the measurements were performed using graphite-monochromatized Mo K_α radiation at 203 K. A total of 4983 reflections were collected ($\Theta_{\max} = 25°$), from which 2220 were unique ($R_{\mathrm{int}} = 0.0740$). Additional experimental details are given in Table 4. The structure was solved by direct methods (SHELXS-97) and refined by full-matrix least-squares techniques against F^2 (SHELXL-97) [15,16]. The non-hydrogen atoms were refined with anisotropic displacement parameters without any constraints. For 140 parameters, final R indices of $R = 0.0826$ and $wR2 = 0.2113$ (GOF = 1.122) were obtained.

ACKNOWLEDGMENT

The authors would like to thank Prof. Matthias Driess for helpful discussions.

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