Synthesis and Characterization of Allylic and Propargylic Selenols

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Allylic selenols (2-propene, 2-butene-, 3-methyl-2-butene-, and 2-methyl-2-propeneselenol) are formed by slow addition of *n*-Bu_3SnH to the corresponding diallylic diselenide diluted with tetraglyme or by a two-step reaction sequence involving the addition of the corresponding selenocyanate to LAH and subsequent treatment with an acid. The 2-propyne-, 3-butene-, and 3-butyneselenols have also been synthesized. β,γ-Unsaturated selenols are very unstable compounds at room temperature in the absence of a radical inhibitor. Characterization was performed by ^1H, ^{13}C, and ^{77}Se NMR spectroscopy and mass spectrometry.

Introduction

To the best of our knowledge, the first synthesis of the 2-propenethiol ($CH_2{=}CHCH_2SH$) was reported in 1857 by Cahours and Hofmann.[1] Before the end of the 19th century, several other preparations of this compound were published[2] and, for a long time, 2-propenethiol has been a commercially available compound. Although the synthesis of alkane-,[3] arene-,[4] and 1-alkeneselenols[5] has been reported, allylic and propargylic selenols have never been described in the literature. By comparison with the corresponding thiols, these β,γ-unsaturated selenols could be useful reagents in synthesis. However, the lack of a family of compounds in the literature is often explained by the thermodynamic instability or the kinetic reactivity of its members at room temperature. In the recent past, we have shown that numerous kinetically unstable compounds can be prepared using well-adapted experimental procedures.[5−7] The availability of such molecules allowed the determination of interesting physical properties.[8] We report herein the first preparation of allylic and propargylic selenols and their characterization by NMR spectroscopy and mass spectrometry. Radical and anionic reactions were independently used. Also described is the synthesis by similar approaches of a homoallylic and a homopropargylic selenol.

Results and Discussion

Selenols are usually prepared by the formation of the corresponding selenium salt followed by treatment with an acid,[4a] by nucleophilic substitution,[3a,4b] or by reduction of the corresponding selenocyanide[9] or diselenide.[3,10] Crich et al. have recently shown that a radical approach (the addition of small amounts of tri-*n*-butyltin hydride to a diarenediselenide) led to the detection of the corresponding areneselenol in the reaction mixture.[11] We applied this approach to the preparation of low-boiling 1-alkeneselenols,[5] and by analogy, we studied the reaction of diallylic diselenides with *n*-Bu_3SnH. On the other hand, we also attempted a preparation of allylic selenols through an anionic pathway.

Radical Route. Only one diallylic diselenide, the digeranyl diselenide, has been described in the literature.[12,13] It has been prepared by reaction of geranyl chloride with Na_2Se_2 in liquid ammonia and separated from about 30% of a byproduct, the digeranyl selenide, by chromatography on silica gel.[13] We synthesized di-2-propenyl (**1a**), di-2-butenyl (**1b**), and bis(3-methyl-2-butenyl) diselenides (**1c**) by reaction of the corresponding allylic halide with a dimetallic diselenide (Scheme 1). The best yields (∼40%) were obtained using Li_2Se_2, prepared by reaction of Super-Hydride ($Li(Et_3B)H$) with elemental selenium.[14] However, the formation of the corresponding diallylic monoselenides **2a**−**c** (47−62%)

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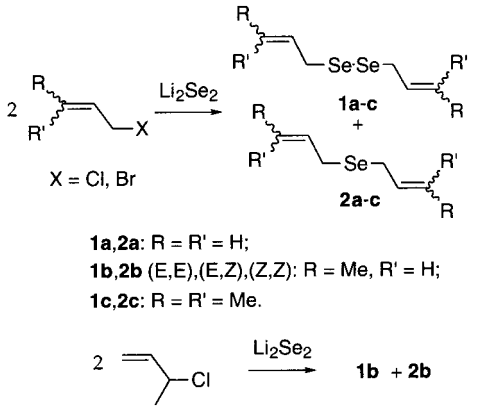
Scheme 1



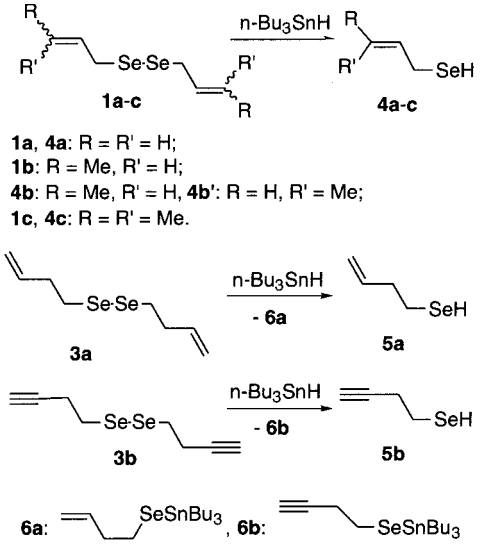
could not be avoided and we failed in our attempts to purify compounds **1a**−**c** by distillation or chromatography on silica gel. Very low yields were obtained in the preparation of the bis(2-methyl-2-propenyl) diselenide, and attempts to prepare the bis(1-methyl-2-propenyl) diselenide starting from 3-chloro-1-butene led to di-2-butenyl diselenide (**1b**), probably via a S_N2' reaction or by rearrangement of the expected product.[12,13] Similarly, the reaction of Li_2Se_2 with propargyl bromide gave a complex mixture of allenyl and propargyl derivatives. In contrast, γ,δ-unsaturated compounds, bis(3-butenyl) (**3a**)[15] and bis(3-butynyl) diselenides (**3b**),[15] were easily prepared by this approach in very good yield (>90%) and the presence of the corresponding monoselenide was not observed.

Compounds **1a**−**c** were characterized by ^{1}H, ^{13}C, and ^{77}Se NMR spectroscopy. The signals for the hydrogens on the α-carbon observed at δ_H ~3.6 ppm and those of the corresponding diallylic monoselenides **2a**−**c** at δ_H ~3.2 ppm are typical of these compounds.[12,16] Similarly, in the ^{77}Se NMR spectra,[17] the signals for diallylic diselenides **1a**−**c** were observed at δ_{Se} 340 ± 30 ppm and those for the monoselenides **2a**−**c** at δ_{Se} 230 ± 10 ppm.

The allylic selenols **4a**−**c** were prepared on a vacuum line by starting from the crude diselenides **1a**−**c** diluted in tetraglyme by very slow addition at room temperature of 1.5 equiv of *n*-Bu_3SnH. During the addition, selenols **4a**−**c** were continuously distilled off in vacuo from the reaction mixture and condensed at low temperature. The formation of the corresponding alkenes (10−30%) was also observed. The selective trapping of the allylic selenols in a cold trap (−80 °C) led to pure products in yields ranging between 43% (**4c**) and 75% (**4b**) (Scheme 2).

3-Buteneselenol (**5a**) and 3-butyneselenol (**5b**) were easily prepared in very good yield (>85%) starting from the corresponding diselenides **3a**,**b** by a similar approach. No butene or butyne was observed in the low-boiling products. In the reaction mixture, the formation of (3-butenylseleno)- (**6a**) and (3-butynylseleno)tributylstannanes (**6b**), respectively, was observed. This

Scheme 2



result is consistent with the formation of (alkylseleno)- or (arylseleno)stannane starting from dialkyl[3b] or diaryl diselenide.[11] An authentic sample of **6a**,**b** could be prepared by addition in diethyl ether of 2 equiv of Bu_3SnH to diselenide **3a** or **3b**, respectively; these compounds slowly decompose on silica gel, and only crude compounds were characterized by NMR spectroscopy and HRMS.

In contrast, no allylic selenostannane was observed in the reaction mixture of the diallylic compounds **1a**−**c** with Bu_3SnH. Attempts to detect them in an NMR tube by addition of Bu_3SnH to compound **1a** were unsuccessful. Although the reaction pathways are probably similar for the reaction of any diselenide with Bu_3SnH, we can confirm the very high reactivity of the allylic selenostannanes in the reaction mixture.

The addition of tin hydride to diallylic diselenides provides a radical route to synthesize allylic selenols. This approach is, however, limited by the small number of easily available precursors. Consequently, we looked for a more general approach to these compounds.

Anionic Route. We envisaged a two-step reaction involving the formation of the selenium salt and its acidification to form the expected allylic selenols. The nature of the precursor, the reaction used to form the salt, the choice of the acid, and the experimental conditions used to isolate the expected products were critical to find an anionic route to allylic selenols. In the case of alkane- or areneselenols, the reaction of a lithium or Grignard reagent with elemental selenium followed by acidification with aqueous hydrochloric acid is an efficient approach[4] which cannot be extended to kinetically unstabilized derivatives. We chose the selenocyanates as precursors and $LiAlH_4$ (LAH) as the reagent to form the selenolates.[18] 2-Propenyl[19] (**7a**), 2-butenyl (**7b**), 3-methyl-2-butenyl (**7c**), 2-methyl-2-propenyl (**7d**), 2-propynyl[20] (**7e**), 3-butenyl (**8a**), and 3-butynyl selenocyanates (**8b**) were prepared by starting

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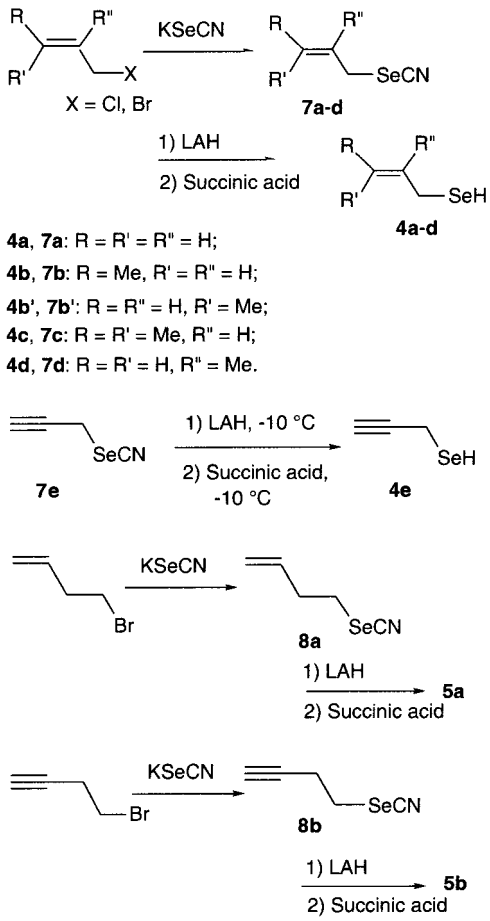
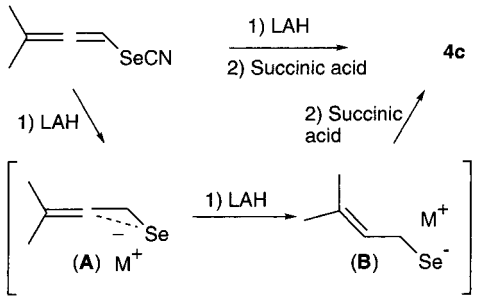
Scheme 3



from the corresponding halide and potassium selenocyanate (KSeCN) using the procedure reported by Sharpless and Lauer[12] (Scheme III). We failed in our attempts to prepare the 1-methyl-2-propenyl selenocyanate starting from 3-bromo-1-butene and KSeCN (small amounts of compound **7b** were obtained probably via a S_N2' reaction). Characterization of compounds **7b**−**d** and **8a**,**b** was performed by ^{1}H, ^{13}C, and ^{77}Se NMR spectroscopy, and the purity was determined by microanalysis.

We found that the addition of the selenocyanates **7a**−**e** and **8a**,**b** in tetraglyme to an excess of LAH in tetraglyme was effective in forming the corresponding selenolates. As an example, the 2-propeneselenolate with respect to the simplest derivative **4a** was characterized in the reaction mixture by ^{77}Se NMR spectroscopy (δ_{Se} −129.8 ppm). In the second step, the choice of the acid determines the yield: only traces of the expected products (**4a**−**e** and **5a**,**b**) were detected using a high-boiling monocarboxylic acid (decanoic acid), but better yields of these compounds were obtained using a diacid (succinic acid). The use of sulfuric acid diluted in tetraglyme led to **4a** or **5a**, but 1 equiv of hydrogen cyanide was also formed. A precise experimental procedure using a vacuum line was used to isolate the selenols: the tetraglyme solution containing the products formed in the reaction of the selenocyanate with LAH was slowly added to an excess of succinic acid diluted with tetraglyme. During and after the addition, selenols were continuously distilled in vacuo from the reaction mixture and condensed in a cold trap. The more

Scheme 4



unstable compounds **4d**,**e** were only obtained in moderate yields when the two reactions were performed at 0 °C. Byproducts corresponding to the reduction of the carbon−carbon double and triple bonds have never been observed.

This approach starting from the selenocyanates is effective in synthesizing allylic and propargylic selenols and presents the advantage of the facile preparation of various precursors in high yield. Nevertheless, it cannot be extended to the preparation of α,*β*-unsaturated selenols: the procedure applied to 3-methyl-1,2-butadienyl selenocyanate[21] only led to the allylic selenol **4c**. This result could be explained by the formation of the expected allylic selenolate (**A**)[21] followed by its reduction (**B**) before the acidolysis with succinic acid (Scheme 4). Similar reductions have already been observed in the preparation of primary α,*β*-unsaturated phosphines or arsines.[22] In the presence of a base, these compounds are known to easily rearrange[23] and this reaction could occur in the presence of LAH. In the case of the corresponding unsaturated silanes, germanes, or stannanes, for which the corresponding anion cannot be formed by LAH, the formation of α,*β*-saturated derivatives has never been observed.[7b]

Spectroscopic Characterization and Stability of Selenols 4a−e and 5a,b. The characterization of selenols **4a**−**e** and **5a**,**b** was performed by ^{1}H, ^{13}C, and ^{77}Se NMR spectroscopy and high-resolution mass spectrometry (HRMS). In the ^{1}H NMR spectra of allylic selenols **4a**−**d**, the signal corresponding to the hydrogen on the selenium atom is observed at δ_H ∼−0.3 ppm. These chemical shifts are observed between those of the 1-alkene- (δ_H ∼1.0 ppm) and alkaneselenols (δ_H ∼−0.6 ppm). The signal is shifted downfield (δ_H ∼0.4 ppm) for the 2-propyneselenol (**4e**). The difference between the chemical shift of 2-propeneselenol (**4a**) and 2-propyneselenol (**4e**) can be compared with those of the corresponding thiols, δ_H(S−H) 1.43 ($H_2C{=}CHCH_2SH$) and δ_H(S−H) 2.27 ppm ($HC{\equiv}CCH_2SH$), respectively. The signals for the hydrogens on the allylic carbon of **4a**−**d** are shifted upfield (δ_H ∼3.2 ppm) with respect to those of the corresponding diselenides **1a**−**c** and selenocyanates **7a**−**d**. The ^{77}Se NMR signals were observed around δ_{Se} ∼45 ppm. The coupling constants of selenols **4a**−**d**,

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$^1J_{SeH}$ = 44−45 Hz, are similar to those of alkyl derivatives.[17] The structures assigned to the allylic selenols were confirmed by the observation of the molecular ions by HRMS. The most important ion corresponds to the loss of the selenium atom. The products corresponding to an extrusion of selenium were also observed by NMR spectroscopy when samples were warmed to room temperature. For example, after a few minutes, 2-propeneselenol (**4a**) diluted with $CDCl_3$ quickly decomposes and propene is formed in about 90% yield. The presence of di-2-propenyl diselenide (**1a**) in the decomposition products has never been observed. The substituted compounds **4b**,**c** diluted with $CDCl_3$ decompose in a few hours with the formation of 1-butene and 3-methyl-1-butene, respectively, showing that the decomposition occurs via an allylic transposition reaction. We also demonstrated the radical pathway of this reaction: in the presence of a radical inhibitor, the half-life of selenols **4a**−**e** diluted with $CDCl_3$ increases from a few hours to several days. The comparison with allylic or propargylic arsines and phosphines,[6] germanes,[7] and silanes shows the particularly high reactivity of the corresponding selenols. This could be explained by the facile homolytic cleavage of the Se−H bond associated with an intramolecular radical allylic transposition. In contrast, in the NMR samples of 3-butene- (**5a**) and 3-butyneselenol (**5b**) diluted with $CDCl_3$, no decomposition was observed after several months at room temperature, and this can be explained because it was not possible for allylic transposition to occur with these compounds.

Conclusion

We have prepared allylic and 2-propyne selenols on a gram scale using particular experimental conditions. The dark period of almost 150 years which separates the first synthesis of allylic thiols from that of allylic selenols is easily explained by the high reactivity of these compounds in the condensed phase. The use of β,γ-unsaturated selenols (diluted in a solvent and stabilized by the presence of small amounts of a radical inhibitor) as reagents is currently in progress in our laboratory.

Experimental Section

Caution! Selenols, selenostannanes, selenocyanates, and diselenides are malodorous and potentially toxic compounds. All reactions and handling should be carried out in a well-ventilated hood.

General Considerations. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded on a Bruker ARX400 spectrometer and ^{77}Se (52.7 MHz) and ^{119}Sn (112 MHz) NMR on a Bruker AC 300C spectrometer. Chemical shifts are given in ppm (δ) relative to tetramethylsilane (^{1}H), solvent (^{13}C, $CDCl_3$, δ 77.0 ppm), external Me_2Se (^{77}Se NMR), and external Me_4Sn (^{119}Sn NMR). The NMR spectra were recorded using $CDCl_3$ as solvent. High-resolution mass spectra (HRMS) were obtained on a Varian MAT 311 instrument. To record the mass spectra, the selenols **4a**−**e** and **5a**,**b** were directly introduced from a cooled cell into the ionization chamber of the spectrometer. The yields and half-lives ($\tau_{1/2}$) of the unstable derivatives were determined by ^{1}H NMR with an internal reference.

Preparation of Diallylic Diselenides (1a−c). Gray selenium (319 mg, 4.04 mmol) was added portionwise to 4.2 mL of $Li(C_2H_5)_3BH$ solution (4.2 mmol) with magnetic stirring. Gas evolution occurred, and the suspension turned dark brown-red. The Li_2Se_2 thus formed was stirred for at least 20 min. Allylic halide (4.0 mmol) in 5 mL of THF was added dropwise to this cooled solution (−40 °C) of Li_2Se_2 (2.0 mmol) suspended in 0.5 mL (5.3 mmol) of *tert*-butyl alcohol and 10 mL of THF. The solution was then warmed to room temperature and stirred for 6 h. The reaction mixture was taken up in diethyl ether/water. After separation, the aqueous layer was extracted twice with ether (2 × 30 mL). The organic phases were combined and dried over $MgSO_4$. After filtration, the solvent was removed under vacuum. Attempts to purify diselenides **1a**−**c** by distillation in vacuo or chromatography on silica gel were unsuccessful, and the purity never exceeded 80%.

Di-2-propenyl Diselenide (1a). Yield: 27% (crude). ^{1}H NMR ($CDCl_3$): δ 3.56 (d, 2H, $^3J_{HH}$ = 7.9 Hz, CH_2); 5.10 (d, 1H, $^3J_{HH,cis}$ = 9.7 Hz, C=CH(*H*)); 5.12 (d, 2H, $^3J_{HH}$ = 16.8 Hz, C=C*H*(H)); 5.88 (ddt, 1H, $^3J_{HH}$ = 16.8 Hz, $^3J_{HH,cis}$ = 9.7 Hz, $^3J_{HH}$ = 7.9 Hz, H_2C=C*H*). ^{13}C NMR ($CDCl_3$): δ 31.9 (t, CH_2); 117.1 (t, C=*C*H_2); 134.7 (d, H_2C=*C*H). ^{77}Se NMR ($CDCl_3$): δ 355.3. IR (KBr): 3081 (m, $\nu_{C=C-H}$), 2961 (s), 2922 (s), 1631 (s, $\nu_{C=C}$), 1428 (s), 1174 (s), 986 (s), 910 (s), 693 (s) cm^{-1}.

Di-2-butenyl Diselenide (1b; Mixture of *E*,*E*, *E*,*Z*, and *Z*,*Z* Compounds). (E:Z/80:20) Yield: 34% (crude). *E* moiety: ^{1}H NMR ($CDCl_3$) δ 1.66 (d, 3H, $^3J_{HH}$ = 5.6 Hz, CH_3), 3.51 (d, 2H, $^3J_{HH}$ = 6.6 Hz, CH_2), 5.57 (m, 1H, $^3J_{HH,trans}$ = 13.4 Hz, $^3J_{HH}$ = 6.6 Hz, C*H*CH_2), 5.63 (m, 1H, $^3J_{HH}$ = 13.4 Hz, $^3J_{HH}$ = 5.6 Hz, MeC*H*); ^{13}C NMR ($CDCl_3$) δ 17.8 (q, CH_3), 31.6 (t, $^1J_{SeH}$ = 64.3 Hz (d), CH_2), 127.0 (d, *C*HCH_2), 127.9 (d, *C*H−CH_3). *Z* moiety: ^{1}H NMR ($CDCl_3$) δ 1.66 (d, 3H, $^3J_{HH}$ = 5.9 Hz, CH_3), 3.56 (d, 2H, $^3J_{HH}$ = 6.4 Hz, CH_2), 5.51 (m, 1H, C*H*CH_2), 5.60 (m, 1H, MeC*H*); ^{13}C NMR ($CDCl_3$) δ 12.8 (q, CH_3), 33.0 (t, CH_2), 127.6 (d, *C*H−CH_2), 128.0 (d, *C*H−CH_3). ^{77}Se NMR ($CDCl_3$): δ 352.1 (major (*E*,*E*)), 320.0 (minor (*E*,*Z*)). IR (KBr): 3019 (m, $\nu_{C=C-H}$), 2962 (s), 2932 (s), 1662 and 1630 (m, $\nu_{C=C}$), 1376 (s), 1261 (s), 962 (s), 801 (s) cm^{-1}.

Bis(3-methyl-2-butenyl) Diselenide (1c). Yield: 43% (crude). ^{1}H NMR ($CDCl_3$): δ 1.71 (s, 3H); 1.75 (s, 3H); 3.63 (d, 2H, $^3J_{HH}$ = 8.4 Hz, CH_2); 5.36 (tsept, 1H, $^3J_{HH}$ = 8.4 Hz, $^4J_{HH}$ = 1.5 Hz, =CH). ^{13}C NMR ($CDCl_3$): δ 17.8 (q, CH_3), 25.7 (q, CH_3), 27.7 (t, $^1J_{SeH}$ = 62.6 Hz (d), CH_2), 120.9 (d, C=*C*H_2), 136.5 (s, Me_2C). ^{77}Se NMR ($CDCl_3$): δ 346.4. IR (KBr): 3020 (w, $\nu_{C=C-H}$), 2968 (s), 2926 (s), 1661 (m, $\nu_{C=C}$), 1447 (s), 1377 (s), 1168 (s), 841 (s) cm^{-1}.

Preparation of Allylic, 2-Propynyl, 3-Butenyl, and 3-Butynyl Selenocyanates (7a−e, 8a,b). The procedure reported for the preparation of the geranyl selenocyanate[12,13] has been applied to the preparation of compounds **7a**−**e** and **8a**,**b**. In a 100 mL two-necked flask equipped with a stirring bar and a nitrogen inlet were introduced the halide (20 mmol), dry acetone or acetonitrile (50 mL), and potassium selenocyanate (2.88 g, 20 mmol). After the mixture was stirred for 3 h at room temperature (**7a**−**e**) or at 60 °C (**8a**,**b**), the precipitated potassium chloride was filtered and the solvent was removed in vacuo. Selenocyanates **7a**−**e** and **8a**,**b** were purified by distillation in vacuo.

Selenocyanic Acid, 2-Butene Ester (*Z* and *E* Isomers; 7b). Yield: 83%. Bp: 48 °C (0.1 mmHg). *E*/*Z* = 4/1. *E* isomer: ^{1}H NMR ($CDCl_3$) δ 1.75 (d, 3H, $^3J_{HH}$ = 6.6 Hz, CH_3), 3.64 (d, $^3J_{HH}$ = 7.9 Hz, $^2J_{SeH}$ = 22.3 Hz (d), CH_2), 5.65 (dt, 1H, $^3J_{HH,trans}$ = 15.0 Hz, $^3J_{HH}$ = 7.9 Hz, *C*HCH_2), 5.77 (dq, $^3J_{HH,trans}$ = 15.0 Hz, $^3J_{HH}$ = 6.6 Hz, MeCH).; ^{13}C NMR ($CDCl_3$) δ 17.7 (q, CH_3), 31.4 (t, $^1J_{SeC}$ = 41.0 Hz (d), H_2C), 102.0 (s, CN), 124.5 (d, HC= *C*Me), 132.9 (d, H*C*=CMe); ^{77}Se NMR ($CDCl_3$) δ 258.0. *Z* isomer: ^{1}H NMR ($CDCl_3$) δ 1.74 (d, 3H, $^3J_{HH}$ = 8.4 Hz, CH_3), 3.78 (d, $^3J_{HH}$ = 8.1 Hz, $^2J_{SeH}$ = 22.7 Hz (d), CH_2), 5.58 (dt, 1H, $^3J_{HH,cis}$ = 11.7 Hz, $^3J_{HH}$ = 8.4 Hz, *C*HCH_2), 5.78 (dt, 1H, $^3J_{HHcis}$ = 11.7 Hz, $^3J_{HH}$ = 8.1 Hz, MeCH); ^{13}C NMR ($CDCl_3$) δ 12.7 (q, CH_3), 25.5 (t, $^1J_{SeC}$ = 45.0 Hz (d)), 101.9 (s, CN), 123.1 (d, HC= *C*Me), 131.3 (d, H*C*=CMe); ^{77}Se NMR ($CDCl_3$) δ 244.0. Anal.

Calcd for C_5H_7NSe: C, 37.52; H, 4.41. Found: C, 37.2; H, 4.19. HRMS: calcd for C_5H_7NSe, 160.9743; found, 160.975. IR (KBr): 3027 (s, $\nu_{C=CH}$), 2967 (s), 2930 (s), 2149 (vs, ν_{CN}), 1660 (s, $\nu_{C=C}$), 1450 (s), 1192 (s), 964 (s) cm^{-1}.

Selenocyanic Acid, 2-Methyl-2-butene Ester (7c). Yield: 92%. Bp: 63 °C (0.1 mmHg). ^1H NMR ($CDCl_3$): δ 1.73 (s, 3H, CH_3); 1.77 (s, 3H, CH_3); 3.78 (d, 2H, $^3J_{HH}$ = 8.3 Hz, $^2J_{SeH}$ = 13.8 Hz, CH_2); 5.42 (t, 1H, $^3J_{HH}$ = 8.3 Hz, CH). ^{13}C NMR ($CDCl_3$): δ 17.8 (q, CH_3); 25.8 (t, $^1J_{SeC}$ = 43.5 Hz (d), CH_2); 27.8 (q, CH_3); 102.2 (s, CN); 117.6 (d, CH); 141.3 (s, Me_2C). ^{77}Se NMR ($CDCl_3$): δ 237.5. Anal. Calcd for C_6H_9NSe: C, 41.39; H: 5.21. Found: C, 41.67; H, 5.31. HRMS: calcd for C_6H_9NSe, 174.9900; found, 174.990. IR (KBr): 2975 (s), 2915 (s), 2149 (s, ν_{CN}), 1661 (s, $\nu_{C=C}$), 1449 (s), 1379 (s), 1190 (s), 840 (s) cm^{-1}.

Selenocyanic Acid, 2-Methyl-2-propene Ester (7d). Yield: 83%. Bp: 46 °C (0.1 mmHg). ^1H NMR ($CDCl_3$): δ 1.86 (s, 3H, CH_3); 3.63 (s, 2H, $^2J_{SeH}$ = 17.5 Hz, CH_2); 4.96 (s, 1H, HC=C); 5.04 (s, 1H, HC=C). ^{13}C NMR ($CDCl_3$): δ 26.2 (q, CH_3); 36.6 (t, $^1J_{SeC}$ = 47.3 Hz (d), CH_2); 101.7 (s, CN); 116.8 (t, H_2C=C); 139.1 (s, CMe). ^{77}Se NMR ($CDCl_3$): δ 240.9. Anal. Calcd for C_5H_7NSe; C, 37.52; H, 4.41. Found: C, 37.75; H, 4.66. HRMS: calcd for C_5H_7NSe, 160.9743; found, 160.974. IR (KBr): 3084 (s, $\nu_{C=CH}$), 2978 (s), 2942 (s), 2919 (s), 2150 (s, ν_{CN}), 1644 (s, $\nu_{C=C}$), 1443 (s), 1378 (s), 905 (s) cm^{-1}.

Selenocyanic Acid, 3-Butene Ester (8a). Yield: 84%. Bp: 53 °C (0.1 mmHg). ^1H NMR ($CDCl_3$): δ 2.64 (dt, 2H, $^3J_{HH}$ = 7.1 Hz, $^3J_{HH}$ = 6.8 Hz, $SeCH_2$); 3.11 (t, 2H, $^3J_{HH}$ = 7.1 Hz, =CCH_2); 5.14 (dd, 1H, $^3J_{HHcis}$ = 10.2 Hz, $^2J_{HH}$ = 1.3 Hz, =C(*H*)H); 5.16 (dd, 1H, $^3J_{HH,trans}$ = 17.1 Hz, $^2J_{HH}$ = 1.5 Hz, =C(H)*H*); 5.78 (ddt, 1H, $^3J_{HH,trans}$ = 17.1 Hz, $^3J_{HH,cis}$ = 10.2 Hz, $^3J_{HH}$ = 6.8 Hz, CH_2Se). ^{13}C NMR ($CDCl_3$): δ 28.3 (t, $^1J_{SeC}$ = 50.6 Hz (d), Se−CH_2); 34.4 (t, =$CHCH_2$); 101.5 (s, CN); 117.9 (dd, =CH_2); 134.5 (d, H*C*=C). ^{77}Se NMR ($CDCl_3$): δ 207.0. Anal. Calcd for C_5H_7NSe: C, 37.52; H, 4.41. Found: C, 37.45; H, 4.36. HRMS: calcd for C_5H_7NSe, 160.9743; found, 160.975. IR (KBr): 3081 (s, $\nu_{C=CH}$), 2981 (s), 2934 (s), 2151 (vs, ν_{CN}), 1641 (s, $\nu_{C=C}$), 1437 (s), 1264 (s) cm^{-1}.

Selenocyanic Acid, 3-Butyne Ester (8b). Yield: 83%. Bp: 51 °C (0.1 mmHg). ^1H NMR ($CDCl_3$): δ 2.17 (t, 1H, $^4J_{HH}$ = 2.5 Hz, C≡CH); 2.82 (td, 2H, $^3J_{HH}$ = 6.9 Hz, $^4J_{HH}$ = 2.5 Hz, CH_2C≡C); 3.19 (t, 2H, $^3J_{HH}$ = 6.9 Hz, $SeCH_2$). ^{13}C NMR ($CDCl_3$): δ 20.7 (t, *C*H_2C≡C); 27.2 (t, $^1J_{SeC}$ = 53.8 Hz (d), CH_2Se), 71.3 (d, C≡*C*H); 80.5 (s, *C*≡CH); 100.9 (s, CN). ^{77}Se NMR ($CDCl_3$): δ 221.9. Anal. Calcd for C_5H_5NSe: C, 37.99; H, 3.19. Found: C, 37.68; H, 2.89. HRMS: calcd for C_5H_5NSe, 158.9587; found, 158.959. IR (KBr): 3292 (s, $\nu_{C≡CH}$), 2990 (s), 2939 (s), 2236 (w, $\nu_{C≡C}$), 2154 (m, ν_{CN}), 1415 (s), 1360 (s), 1235 (s), 977 (m) cm^{-1}.

Preparation of Allylic Selenols (4a−c), 3-Buteneselenol (5a), and 3-Butyneselenol (5b) (Method A). The apparatus already described for the preparation of allylic arsines was used.[6] The flask containing the crude diallylic diselenides **1a**−**c** and **3a**,**b** (2 mmol) diluted with tetraglyme (5 mL) was attached to a vacuum line and degassed. Bu_3SnH (3 mmol) was then slowly added (30 min) at room temperature with a syringe through the septum. During and after the addition, selenols **4a**−**c** and **5a**,**b** were distilled off in vacuo (10^{-1} mbar) from the reaction mixture. The first cold trap (−40 °C) removed selectively the less volatile products, and compounds **4a**−**c** and **5a**,**b** were condensed in a second trap cooled at −80 °C. At the end of the reaction, the second trap was warmed to room temperature and the products were condensed on a cold finger (−196 °C) connected at the bottom to a flask or an NMR tube immersed in liquid nitrogen. A cosolvent can be added at this step. After disconnection from the vacuum line by stopcocks, the apparatus was filled with dry nitrogen; liquid nitrogen was subsequently removed. The products were collected in a Schlenk flask or an NMR tube and kept at low temperature (<−50 °C) before analysis. Yields were determined by ^1H NMR spectroscopy using an internal reference.

Preparation of Allylic Selenols (4a-d), 2-Propyneselenol (4e), 3-Buteneselenol (5a), and 3-Butyneselenol (5b) with the Corresponding Selenocyanates as Starting Materials (Method B). The apparatus was similar to the one used above. A 50 mL two-necked flask containing succinic acid (10 mmol) diluted with tetraglyme (10 mL) was immersed in a 0 °C cold bath, attached to a vacuum line, and degassed. In a 25 mL two-necked flask equipped with a stirring bar and a nitrogen inlet were introduced LAH (100 mg, 2.4 mmol) and tetraglyme (5 mL). The flask was immersed in a bath cooled at 0 °C, and the selenocyanate (2 mmol) diluted with tetraglyme (1 mL) was slowly added. After 10 min of stirring, this solution was then slowly added (10 min) with a syringe through the septum in the flask containing the succinic acid. During and after the addition, selenols **4a**−**e** and **5a**,**b** were distilled off in vacuo (10^{-1} mbar) from the reaction mixture. The first cold trap (−40 °C) removed selectively the less volatile products, and compounds **4a**−**e** and **5a**,**b** were condensed in a second trap cooled at −80 °C. At the end of the reaction, the second trap was warmed to room temperature and the products were condensed on a cold finger (−196 °C) connected at the bottom to a flask or an NMR tube immersed in liquid nitrogen. A cosolvent can be added at this step. After disconnection from the vacuum line by stopcocks, the apparatus was filled with dry nitrogen; liquid nitrogen was subsequently removed. The products were collected in a Schlenk flask or an NMR tube and kept at low temperature (<−50 °C) before analysis. Yields were determined by ^1H NMR spectroscopy using an internal reference.

To record the mass spectra using method A or B, the second cold trap was disconnected from the vacuum line and fitted on the ionization chamber of the mass spectrometer.

2-Propeneselenol (4a). Yield: 67% (method A) and 74% (method B). Bp: ∼−65 °C (0.1 mmHg). $t_{1/2}$ (room temperature, 2% in $CDCl_3$): ∼10 min in the absence of a radical inhibitor and 1 day in the presence of small amounts of duroquinone. ^1H NMR ($CDCl_3$, −40 °C): δ −0.33 (t, 1H, $^3J_{HH}$ = 6.4 Hz, $^1J_{SeH}$ = 45.0 Hz (d), Se−H); 3.25 (dd, 2H, $^3J_{HH}$ = 7.1 Hz, $^3J_{HH}$ = 6.4 Hz, CH_2); 4.93 (d, 1H, $^3J_{HH,cis}$ = 9.7 Hz, C=CH(*H*)); 5.10 (d, 2H, $^3J_{HH,trans}$ = 16.8 Hz, C=C*H*(H)); 6.03 (ddt, 1H, $^3J_{HH,trans}$ = 16.8 Hz, $^3J_{HH,cis}$ = 9.7 Hz, $^3J_{HH}$ = 7.1 Hz, H_2C=C*H*). ^{13}C NMR ($CDCl_3$, −40 °C): δ 20.4 (t, $^1J_{SeC}$ = 43.4 Hz (d), CH_2); 115.3 (t, C=CH_2); 137.5 (d, H_2C=*C*H). ^{77}Se NMR ($CDCl_3$): δ 46.9. HRMS: calcd for C_3H_6Se, 121.9634; found, 121.964. MS (*m*/*z* (%)): 124 (5.0), 122 (24.4), 120 (11.3), 119 (3.8), 118 (4.5), 93 (5.8), 41 (100), 39 (52.2), 38 (8.5).

2-Buteneselenol (4b). Yield: 75% (method A) and 72% (method B). Bp: ∼−40 °C (0.1 mmHg). $t_{1/2}$ (room temperature, 3% in $CDCl_3$): 6 h in the absence of a radical inhibitor and 4 days in the presence of duroquinone. *E*/*Z* = 9/1. E isomer: ^1H NMR ($CDCl_3$, −40 °C) δ −0.37 (t, 1H, $^3J_{HH}$ = 6.4 Hz, $^1J_{SeH}$ = 45.3 Hz (d), SeH), 1.69 (d, 3H, $^3J_{HH}$ = 6.4 Hz, CH_3), 3.21 (dd, 2H, $^3J_{HH}$ = 6.8 Hz, $^3J_{HH}$ = 6.4 Hz, CH_2), 5.53 (dq, 1H, $^3J_{HH,trans}$ = 15.0 Hz, $^3J_{HH}$ = 6.4 Hz, C*H*CH_3), 5.66 (dt, 2H, $^3J_{HH,trans}$ = 15.0 Hz, $^3J_{HH}$ = 6.8 Hz, C*H*CH_2); ^{13}C NMR ($CDCl_3$, −40 °C) δ 17.9 (q, CH_3), 19.8 (t, $^1J_{SeC}$ = 42.6 Hz (d), CH_2), 126.7 (d, *C*HCH_2), 130.1 (d, *C*H−CH_3); ^{77}Se NMR ($CDCl_3$, −40 °C) δ 47.5. *Z* isomer: ^1H NMR ($CDCl_3$, −40 °C) δ −0.36 (t, 1H, $^3J_{HH}$ = 6.4 Hz, $^1J_{SeH}$ = 44.3 Hz (d), SeH), 1.67 (d, 3H, $^3J_{HH}$ = 6.4 Hz, CH_3), 3.28 (dd, 2H, $^3J_{HH}$ = 6.4 Hz, $^3J_{HH}$ = 7.1 Hz, CH_2), 5.46 (dq, 1H, $^3J_{HH,cis}$ = 11.7 Hz, $^3J_{HH}$ = 7.1 Hz, C*H*CH_3), 5.69 (dt, 2H, $^3J_{HH,cis}$ = 11.7 Hz, $^3J_{HH}$ = 6.4 Hz, C*H*CH_2); ^{13}C NMR ($CDCl_3$, −40 °C) δ 12.4 (q, CH_3), 13.6 (t, $^1J_{SeC}$ = 41.0 Hz (d), CH_2), 125.4 (d, *C*HCH_2), 128.9 (d, *C*HCH_3); ^{77}Se NMR ($CDCl_3$, −40 °C) δ 42.6. HRMS: calcd for C_4H_8Se, 135.9791; found, 135.978.

3-Methyl-2-buteneselenol (4c). Yield: 43% (method A) and 82% (method B). Bp: ∼−20 °C (0.1 mmHg). $t_{1/2}$ (room temperature, 3% in $CDCl_3$): 5 h. ^1H NMR ($CDCl_3$, −40 °C): δ −0.41 (t, 1H, $^3J_{HH}$ = 6.1 Hz, $^1J_{SeH}$ = 41.2 Hz (d), SeH); 1.67 (s, 3H, CH_3); 1.74 (s, 3H, CH_3); 3.24 (dd, 2H, $^3J_{HH}$ = 6.1 Hz, $^3J_{HH}$

= 7.0 Hz, CH_2); 5.42 (tsept, 1H, $^3J_{HH}$ = 7.0 Hz, $^4J_{HH}$ = 1.3 Hz, =CH). ^{13}C NMR ($CDCl_3$, −40 °C): δ 15.2 (t, $^1J_{SeC}$ = 40.2 Hz (d), CH_2); 17.2 (q, CH_3); 25.7 (q, CH_3); 123.4 (d, H*C*=C); 134.2 (s, C=*C*Me_2). ^{77}Se NMR ($CDCl_3$, −40 °C): δ 39.6. HRMS: calcd for $C_5H_{10}Se$, 149.9947; found, 149.995.

2-Methyl-2-propeneselenol (4d). Yield: 50% (method B). Bp: ∼−40 °C (0.1 mmHg). $t_{1/2}$ (room temperature, 3% in $CDCl_3$): 1 h. ^{1}H NMR ($CDCl_3$): δ −0.26 (t, 1H, $^3J_{HH}$ = 7.1 Hz, $^1J_{SeH}$ = 45.0 Hz, SeH); 1.87 (s, 3H, CH_3); 3.24 (d, 2H, $^3J_{HH}$ = 7.1 Hz, CH_2); 4.74 (s, 1H, H−C=C); 4.90 (s, 1H, H−C=C). ^{13}C NMR ($CDCl_3$): δ 20.8 (q, CH_3); 24.9 (t, $^1J_{SeC}$ = 45.0 Hz (d), CH); 112.2 (t, H_2*C*=C); 145.0 (s, *C*Me). ^{77}Se NMR ($CDCl_3$): δ 30.9. HRMS: calcd for C_4H_8Se, 135.9791; found, 135.979.

2-Propyneselenol (4e). Yield: 32% (method B). Bp: ∼−70 °C (0.1 mmHg). $t_{1/2}$ (room temperature, 3% in $CDCl_3$): 1 h. ^{1}H NMR ($CDCl_3$): δ 0.34 (t, 1H, $^3J_{HH}$ = 7.1 Hz, $^1J_{SeH}$ = 41.3 Hz, SeH); 2.28 (t, 1H, $^4J_{HH}$ = 2.5 Hz, CH); 3.23 (d, 2H, $^3J_{HH}$ = 6.9 Hz, $^4J_{HH}$ = 2.5 Hz, CH_2). ^{13}C NMR ($CDCl_3$): δ 12.3 (t, CH_2); 82.4 (s, *C*≡CH); 71.1 (d, C≡*C*H). ^{77}Se NMR ($CDCl_3$): δ 90.1. HRMS: calcd for C_3H_4Se, 119.9478; found, 119.947.

3-Buteneselenol (5a). Yield: 87%. (method A and B). Bp: ∼−40 °C (0.1 mmHg). No decomposition after several weeks at room temperature. ^{1}H NMR ($CDCl_3$): δ −0.56 (t, 1H, $^3J_{HH}$ = 6.9 Hz, SeH, $^1J_{SeH}$ = 45.6 Hz); 2.47 (dt, 2H, $^3J_{HH}$ = $^3J_{HH}$ = 6.9 Hz, $SeCH_2$); 2.64 (dt, 2H, $^3J_{HH}$ = $^3J_{HH}$ = 6.9 Hz, =CCH_2); 5.07 (d, 1H, $^3J_{HH,cis}$ = 10.2 Hz, =C(*H*)H); 5.09 (dd, 1H, $^3J_{HH,trans}$ = 18.6 Hz, $^2J_{HH}$ = 1.5 Hz, =C(H)*H*); 5.77 (ddt, 1H, $^3J_{HH,trans}$ = 18.6 Hz, $^3J_{HH,cis}$ = 10.2 Hz, $^3J_{HH}$ = 6.9 Hz, CH_2Se). ^{13}C NMR ($CDCl_3$): δ 16.6 (t, $^1J_{SeC}$ = 49.0 Hz (d), $SeCH_2$); 37.9 (t, =*C*CH_2); 116.4 (dd, C=*C*H_2); 136.8 (d, HC=C). ^{77}Se NMR ($CDCl_3$): δ −19.3. HRMS: calcd for $C_4H_8{}^{78}Se$, 133.9799; found, 135.979.

3-Butyneselenol (5b). Yield: 85% (method A) and 91% (method B). Bp: ∼−40 °C (0.1 mmHg). No decomposition after several weeks at room temperature. ^{1}H NMR ($CDCl_3$): δ −0.24 (t, 1H, $^3J_{HH}$ = 7.1 Hz, SeH, $^1J_{SeH}$ = 46.3 Hz); 2.10 (t, 1H, $^4J_{HH}$ = 2.5 Hz, C≡C*H*); 2.67 (td, 2H, $^3J_{HH}$ = 5.9 Hz, $^4J_{HH}$ = 2.5 Hz, ≡CCH_2); 2.73 (dt, 1H, $^3J_{HH}$ = 7.1 Hz, $^3J_{HH}$ = 5.9 Hz, CH_2Se). ^{13}C NMR ($CDCl_3$): δ 15.7 (t, $SeCH_2$); 23.7 (t, ≡*C*CH_2); 69.8 (d, C≡*C*H); 82.7 (s, HC≡*C*). ^{77}Se NMR ($CDCl_3$): δ −0.17. HRMS: calcd for C_4H_6Se, 133.9634; found, 133.964.

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Supporting Information Available: Text giving NMR data for selenides **2b**,**c**, selenostannanes **6a**,**b**, and selenocyanates **7a**,**e** and figures giving ^{1}H and ^{13}C NMR spectra of selenides **2b**,**c**, selenols **4a**−**e** and **5a**,**b**, and selenocyanates **7b**-**d** and **8a**,**b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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