



Note

Reactions of sodium selenide with ethynyl and bromoethynyl ketones: Stereo- and regioselective synthesis of functionalized divinyl selenides and 1,3-diselenetanes

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ABSTRACT

A method for the preparation of 2,4-dimethylene-1,3-diselenetanes based on the novel reaction of sodium selenide with bromoethynyl ketones has been developed. New functionalized divinyl selenides have been obtained by regio- and stereoselective addition of sodium selenide to ethynyl ketones.

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1. Introduction

Vinylic selenides are powerful tools in synthetic organic chemistry [1–5]. The data on diselenetanes synthesis are scarce in the literature. Only a few representatives of the 1,3-diselenetanes are known [6–10]. 2,4-Bis(methylene)-, bis(methylmethylene)- and bis(*tert*-butylmethylene)-1,3-diselenetanes have been synthesized from the corresponding selenoketenes generated from 1,2,3-selenadiazoles [6]. Hexafluoropropene reacted with selenium in DMF in the presence of CsF at 45–55 °C to give tetrakis(trifluoromethyl)-1,3-diselenetane in 50% yield [7]. The reaction of *tert*-butyl (*p*-methoxyphenyl)methylenetriphenylphosphorane tetrafluoroborate with elemental selenium afforded substituted 2,4-bis(*tert*-butyl)-2,4-bis(*p*-methoxyphenyl)-1,3-diselenetane in 24% yield [8]. The perfluorinated 1,3-diselenetanes have been prepared from selenocarbonyl compounds [9].

Previously, we have studied the reaction of selenourea with benzoylbromoacetylene and 2-thienoylbromoacetylene. The reaction proceeds in the presence of triethylamine affording *E*-2,4-bis(benzoylmethylene)-1,3-diselenetane and *E*-2,4-bis(2-thienoylmethylene)-1,3-diselenetane [10].

2. Results and discussion

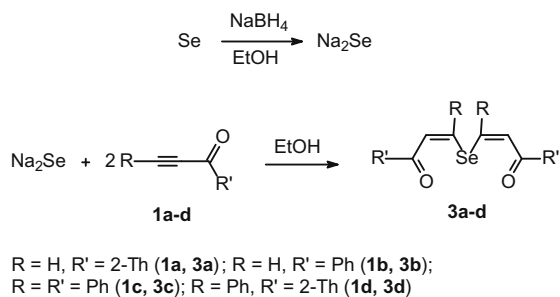
The synthesis of vinylic selenides and their reactions is a field of our continuous interest [11–22]. Earlier, we have developed efficient methods for the preparation of divinyl selenide and alkyl vinylic selenides [15–22]. Our thorough research of the reactions of various selenium reagents with acetylenes [15–28] led us to study the reactions of sodium selenide with ethynyl ketones **1a–d** and bromoethynyl ketones **2a,b**.

We have found that the reaction of sodium selenide with ethynyl ketones **1a–d** proceeds as regio- and stereoselective *anti*-addition to afford *Z,Z*-bis(acylvinylic) selenides **3a–d** in 47–76% yields (Scheme 1). Sodium selenide was prepared from elemental selenium and sodium borohydride in ethanol and used *in situ* for further reactions.

In the ¹H NMR spectra of selenide **3a**, signals of vinylic protons of the Se–CH=CH–CO group were observed as doublets at δ 7.79 and 8.55 ppm with ³J_{HH} = 9.5 Hz, that indicated *Z*-stereochemistry of the product. The methods of homonuclear (NOESY ¹H–¹H) and heteronuclear 2D NMR (Heteronuclear Single Quantum Correlation, Heteronuclear Multiple Bond Correlation) were used for the assignment. The cross peaks induced by dipole–dipole interaction between the vinylic proton at δ 7.79 ppm and the proton H-3 of the thiophene ring appeared in the 2D NOESY NMR spectra of selenide **3a** (Scheme 2). Therefore, the signal at δ 7.79 ppm was attributed to the proton of the =CH–CO group and a low-field signal at δ 8.55 ppm corresponded to the proton of the SeCH group.

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Scheme 1.

Usually protons of the SeCH group in vinylic selenides revealed signals at 6.0–6.9 ppm [2,3,22]. A down-field shift of the vinylic proton was obviously due to electron withdrawing effect of the carbonyl group leading to appearance of partly positive charge on the β-carbon atom of the CH=CH-CO group. This can be demonstrated with the help of mesomeric structures (Scheme 2). Analogously, in the NOESY spectra of selenide 3b, the proton of the =CH-CO group showed cross peaks with the *ortho*-proton of the phenyl ring (Scheme 2). Based on this observation we assumed that favorable conformations of the fragments Th-CO-CH=CH-Se and Ph-CO-CH=CH-Se in compounds 3a and 3b were close to plane.

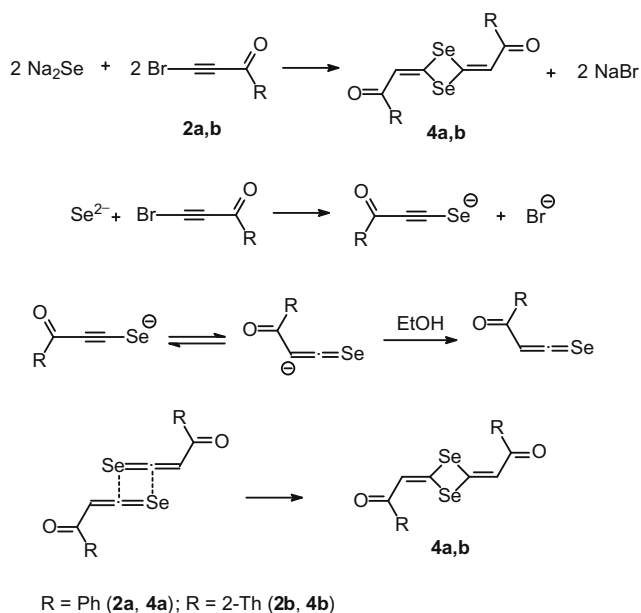
The ⁷⁷Se spectra of selenides 3a and 3b were characterized by the coupling constants ²J_{SeH} (8.1 and 8.4 Hz) and ³J_{SeH} (5.5 and 5.3 Hz, *trans*-position of the vinylic proton and the selenium atom).

In the NOESY spectra of selenide 3c, the vinylic proton at δ 7.59 showed cross peaks with the *ortho*-proton of the phenyl ring of the benzoyl group (Scheme 2). This indicated the Ph-CO-CH= structure and therefore addition of selenide anion occurred to the β-carbon of ethynyl ketone 1c. Similar trends were observed in the case of selenide 3d. The NOESY spectra of selenide 3d were characterized by cross peaks with the vinylic proton at δ 7.36 with the proton H-3 of the thiophene ring (Scheme 2). This revealed the Th-CO-CH= structure and addition of selenide anion to the β-carbon of ethynyl ketone 1d. Thus, the addition of selenide anion to the β-carbon of ethynyl ketones 1c,d was favorable in comparison with the addition to the α-carbon. The electron withdrawing

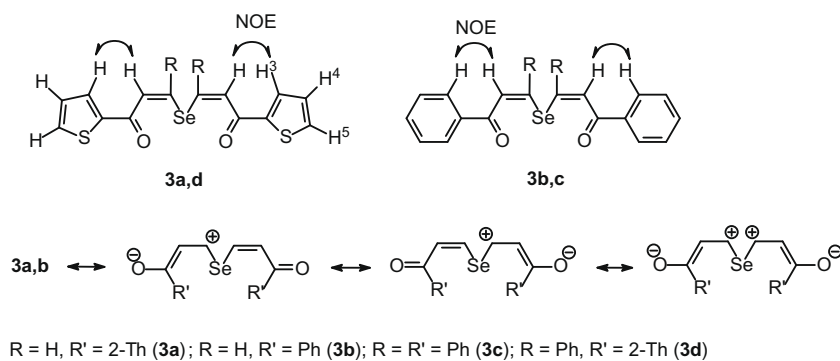
effect of benzoyl or 2-thienoyl groups is significantly higher than that of phenyl group and carbanion 5 is energetically preferable in comparison with intermediate 6 (Scheme 3).

The ⁷⁷Se spectra of selenides 3c and 3d were characterized by the coupling constants ³J_{SeH} = 6.3 Hz, that pointed to *trans*-position of the vinylic proton and the selenium atom and indicated *Z*-stereochemistry.

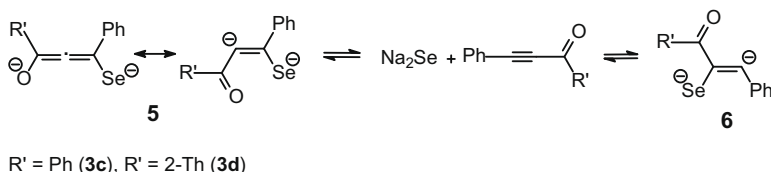
Unexpectedly, the reaction of sodium selenide with bromoethynyl ketones 2a,b gave *E*-2,4-bis(benzoylmethylene)- and *E*-2,4-bis(2-thienoylmethylene)-1,3-diselenetanes 4a,b in 79% and 77% yields, respectively. A reaction pathway was suggested to involve the formation of selenoketenes, which underwent [2+2] cycloaddition to form diselenetanes 4a,b (Scheme 4). It is noteworthy that dimerisation of thiocarbonyl compounds to 1,3-dithietanes is a known process [29].



Scheme 4.



Scheme 2.



Scheme 3.

The structural assignment of compounds **4a,b** was made by ^1H , ^{13}C and ^{77}Se NMR spectroscopy and GC–MS. In the mass spectra of compounds **4a,b**, the molecular ions (420 for **4a** and 432 for **4b**) were observed. The choice between the structures of the *Z*- and *E*-isomers of 1,3-diselenetanes **4a,b** was made based on the ^{77}Se spectra, which contained only one signal. The selenium atoms are chemically equivalent in the *E*-isomers, which give one signal in the ^{77}Se spectra, whereas the *Z*-isomers having two different selenium atoms should show two signals in the ^{77}Se spectra. The coupling constants $^3J_{\text{SeH}}$ (10.5 Hz for **4a** and 11.5 Hz for **4b**) correspond to *cis*-position of the selenium atom and the vinylic proton. Spectral characteristics of diselenetanes **4a,b** are in accordance with those of known samples which we previously obtained from bromoacetylene **2a,b** and selenourea [10].

The method represents simple and efficient approach to 2,4-dimethylene-1,3-diselenetanes. We expect that this method can be also used for generation of selenoketenes, which would then be used for further reactions, e.g., addition reactions on the double bond of selenoketenes [6].

In conclusion, new functionalized divinyl selenides have been synthesized by regio- and stereoselective addition of sodium selenide to ethynyl ketones. A novel method for the preparation of 2,4-dimethylene-1,3-diselenetanes based on the novel reaction of sodium selenide with bromoethynyl ketones has been developed.

3. Experimental

3.1. General

^1H (400.1 MHz), ^{13}C (100.6 MHz) and ^{77}Se (76.3 MHz) NMR spectra were recorded on a Bruker DPX-400 spectrometer in 5–10% solution in DMSO- d_6 , referenced to TMS (^1H and ^{13}C NMR, internal) and Me_2Se (^{77}Se NMR, external). GC–MS spectra were recorded on a Shimadzu QP5050A spectrometer at an electron energy of 70 eV.

3.2. *Z,Z*-Bis[2-(2-thienoylviny)] selenide (**3a**)

Sodium borohydride (0.25 g, 6.5 mmol) was added portion wise to a mixture of elemental selenium (0.25 g, 3.2 mmol) and absolute ethanol (20 ml) for 0.5 h at room temperature under argon atmosphere. A solution of acetylene **1a** (0.89 g, 6.5 mmol) in diethyl ether (20 ml) was added to the reaction mixture and stirred for 2 h at room temperature under argon. Precipitation of a yellow solid was observed. The reaction mixture was cooled to 0 °C for 1 h and the precipitated yellow solid was filtered off, washed progressively with water, ethanol and diethyl ether and dried *in vacuo* to give 0.65 g (58% yield) of selenide **3a** as a light-yellow solid. M.p. 197–198 °C (from methanol). IR (KBr): 1585 (C=C), 1660 (C=O) cm^{-1} . ^1H NMR (DMSO- d_6): δ 7.28 dd (2H, $^3J = 3.7$, $^3J = 4.7$ Hz, $\text{C}_4\text{H}_3\text{S}$, H^4), 7.79 d (2H, CO–CH, $^3J = 9.5$ Hz), 8.06 (2H, $^3J = 4.7$ Hz, $\text{C}_4\text{H}_3\text{S}$, H^5), 8.16 d (2H, $^3J = 3.7$ Hz, $\text{C}_4\text{H}_3\text{S}$, H^3), 8.55 d (2H, Se–CH, $^3J = 9.5$ Hz). ^{13}C NMR (DMSO- d_6): δ 122.92 ($\text{C}_4\text{H}_3\text{S}$, C^4), 129.74 (CO–CH, 1J 171.0) 133.75 ($\text{C}_4\text{H}_3\text{S}$, C^3), 136.24 ($\text{C}_4\text{H}_3\text{S}$, C^5), 145.12 ($\text{C}_4\text{H}_3\text{S}$, C^2), 153.27 (SeCH=, $^1J_{\text{SeC}} = 175.0$ Hz), 182.90 (C=O). ^{77}Se NMR (DMSO- d_6): δ 592 ($^2J_{\text{SeH}} = 8.1$, $^3J_{\text{SeH}} = 5.5$ Hz). Anal. Calc. for $\text{C}_{14}\text{H}_{10}\text{O}_2\text{S}_2\text{Se}$: C, 47.59; H, 2.53; S, 18.13; Se, 22.37. Found: C, 47.49; H, 2.83; S, 18.28; Se, 22.63%.

3.3. *Z,Z*-Bis(2-benzoylviny)] selenide (**3b**)

Selenide **3b** was prepared analogously to **3a** from elemental selenium (0.25 g, 3.2 mmol), sodium borohydride (0.25 g, 6.5 mmol) and acetylene **1b** (0.85 g, 6.5 mmol) to yield 0.51 g (47%) of selenide **3b** as a light-yellow solid. M.p. 203–204 °C (from

dioxane). IR (KBr): 1575 (C=C), 1640 (C=O) cm^{-1} . ^1H NMR (DMSO- d_6): δ 7.57 dd (4H, Ph, *meta*), 7.66 t (2H, Ph, *para*), 7.92 d (2H, CO–CH, $^3J = 9.5$ Hz), 8.09 d (4H, Ph, *ortho*), 8.63 d (2H, SeCH, $^3J = 9.5$ Hz). ^{13}C NMR (DMSO- d_6): δ 122.31 (CH–CO), 128.33 (Ph, *ortho*), 129.04 (Ph, *meta*), 133.35 (Ph, *para*), 137.04 (Ph, *ipso*), 154.20 (SeCH=), 189.59 (C=O). ^{77}Se NMR (DMSO- d_6): δ 600 ($^2J_{\text{SeH}} = 8.4$, $^3J_{\text{SeH}} = 5.3$ Hz). GC–MS, *m/z* (rel. int.): 342 (39) $[\text{M}]^+$, 286 (35), 262 (28), 211 (75), 157 (25), 105 (100), 77 (95). Anal. Calc. for $\text{C}_{18}\text{H}_{14}\text{O}_2\text{Se}$: C, 63.34; H, 4.10; Se, 23.16. Found: C, 63.25; H, 4.12; Se, 23.00.

3.4. *Z,Z*-Bis(2-benzoyl-1-phenylviny)] selenide (**3c**)

Selenide **3c** was prepared analogously to **3a** from elemental selenium (0.25 g, 3.2 mmol), sodium borohydride (0.25 g, 6.5 mmol) and acetylene **1c** (1.23 g, 6 mmol) to yield 1.06 g (72%) of selenide **3c** as a light-yellow solid, m.p. 171–173 °C. IR (KBr): 1585 (C=C), 1640 (C=O) cm^{-1} . ^1H NMR (DMSO- d_6): δ 7.05 dd (4H, Ph, *meta*), 7.19 t (2H, Ph, *para*), 7.59 dd (4H, PhCO, *meta*), 7.59 s (2H, CH–CO), 7.68 t (2H, PhCO, *para*), 8.11 d (4H, PhCO, *ortho*), 8.67 d (4H, Ph, *ortho*). ^{13}C NMR (DMSO- d_6): δ 126.67 (=CH–CO), 128.07 (*meta*, Ph), 128.14 (*ortho*, Ph), 128.64 (*meta*, Ph), 128.64 (*ortho*, PhCO), 129.17 (*meta*, PhCO), 133.47 (*para*, PhCO), 137.26 (PhCO, *ipso*), 141.36 (Ph, *ipso*), 158.32 (SeC), 189.20 (C=O). ^{77}Se NMR (DMSO- d_6): δ 593 ($^3J_{\text{SeH}} = 6.3$ Hz). Anal. Calc. for $\text{C}_{30}\text{H}_{22}\text{O}_2\text{Se}$: C, 73.02; H, 4.46; Se, 16.32. Found: C, 73.15; H, 4.33; Se, 16.02.

3.5. Bis[2-(2-thienoyl)-1-phenylviny)] selenide (**3d**)

Selenide **3d** was prepared analogously to **3a** from elemental selenium (0.25 g, 3.2 mmol), sodium borohydride (0.25 g, 6.5 mmol) and acetylene **1d** (1.35 g, 6.4 mmol) to yield 1.15 g (76%) of selenide **3d** as a light-yellow solid. M.p. 169–170 °C. IR (KBr): 1580 (C=C), 1635 (C=O) cm^{-1} . ^1H NMR (DMSO- d_6): δ 6.66 dd (2H, $\text{C}_4\text{H}_3\text{S}$, H^4 , $^3J = 1.6$, $^3J = 3.6$ Hz), 6.83 d (4H, Ph, *ortho*), 7.05 dd (4H, Ph, *meta*), 7.16 t (2H, Ph, *para*), 7.36 s (2H, CH–CO), 7.69 d (2H, $\text{C}_4\text{H}_3\text{S}$, H^3 , $^3J = 3.6$ Hz), 8.06 d (2H, $\text{C}_4\text{H}_3\text{S}$, H^5 , $^3J = 1.6$ Hz). ^{13}C NMR (DMSO- d_6): δ 113.15 ($\text{C}_4\text{H}_3\text{S}$, C^4), 119.27 ($\text{C}_4\text{H}_3\text{S}$, C^3), 125.48 (=CH), 128.05 (Ph, *ortho*), 128.18 (Ph, *meta*), 128.70 (Ph, *para*), 141.42 (SeC), 148.45 ($\text{C}_4\text{H}_3\text{S}$, C^5), 152.92 ($\text{C}_4\text{H}_3\text{S}$, C^2), 158.51 (Ph, *ipso*), 175.75 (C=O). ^{77}Se NMR (DMSO- d_6): δ 599 ($^3J_{\text{SeH}} = 6.3$ Hz). GC–MS, *m/z* (rel. int.): 506 (11) $[\text{M}]^+$, 290 (11), 277 (75), 264 (44), 238 (47), 214 (52), 126 (71), 111 (18), 105 (100), 83 (70), 77 (62).

3.6. *E*-2,4-bis(benzoylmethylene)-1,3-diselenetane (**4a**)

Sodium borohydride (0.25 g, 6.5 mmol) was added portion wise to a mixture of elemental selenium (0.25 g, 3.2 mmol) and absolute ethanol (20 ml), for 0.5 h at room temperature under argon atmosphere. Bromoacetylene **2a** (0.81 g, 4 mmol) was added to the reaction mixture and stirred for 3 h at room temperature under argon. Precipitation of a yellow solid was observed. The reaction mixture was cooled to 0 °C for 1 h and the precipitated yellow solid was filtered off, washed progressively with water, ethanol and diethyl ether and dried *in vacuo* to give 0.53 g (79% yield) of diselenetane **4a** as a light-yellow solid. M.p. 203–204 °C. Spectral characteristics of diselenetane **4a** correspond to those of known sample obtained from bromoacetylene **2a** and selenourea [10].

3.7. *E*-2,4-bis(2-thienoylmethylene)-1,3-diselenetane (**4b**)

Diselenetane **4b** was prepared analogously to **4a** from elemental selenium (0.25 g, 3.2 mmol), sodium borohydride (0.25 g, 6.5 mmol) and bromoacetylene **2b** (1.33 g, 6 mmol) to yield 0.5 g

(77%) as a light-yellow solid. M.p. 274–275 °C. Spectral characteristics of diselenetane **4b** correspond to those of known sample obtained from bromoacetylene **2b** and selenourea [10].

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