Synthesis of [3-(Trimethylsilyl)prop-2-yn-1-yl] Selenides

M. V. Musalov, M. V. Andreev, S. V. Amosova,* L. I. Larina, and V. A. Potapov

Favorskii Irkutsk Institute of Chemistry, Siberian Branch, Russian Academy of Sciences, ul. Favorskogo 1, Irkutsk, 664033 Russia *e-mail: amosova@irioch.irk.ru

Received May 30, 2017

Abstract—Efficient and selective methods have been developed for the synthesis of previously unknown organyl [3-(trimethylsilyl)prop-2-yn-1-yl] selenides, organyl prop-2-yn-1-yl selenides, and bis[3-(trimethylsilyl)prop-2-yn-1-yl] selenide by reactions of 3-bromo-1-(trimethylsilyl)prop-1-yne with the corresponding organylselenolates and sodium selenide generated from diorganyl diselenides or elemental selenium by the action of sodium tetrahydridoborate.

DOI: 10.1134/S1070428017100049

Unsaturated organoselenium compounds possess a high synthetic potential and are extensively used as intermediate products in organic synthesis [1-8]. Unsaturated diorganyl selenides can be synthesized by reactions involving generation of organylselenolate ions [1, 2, 9-11]. Organoselenium compounds exhibit biological activity; in particular, like glutathione peroxidase, they are capable of catalyzing peroxide reduction in mammalians [3, 4].

Propargyl selenides are important building blocks for the synthesis of organic compounds [12–17]. However, only alkynyl aryl selenides, mostly phenyl propargyl selenide [13, 16, 17], have been used so far. A number of unsaturated ketones and sesquiterpene 7-hydroxymyoporone were synthesized on the basis of phenyl propargyl selenide [13].

Published data on the synthesis of alkyl propargyl selenides are few in number [15–18]. We have recently synthesized previously unknown methyl propargyl selenide by reduction of dimethyl diselenide with sodium tetrahydridoborate to sodium methane-

selenolate and subsequent treatment with propargyl bromide [18]. Analogous reactions with diorganyl ditellurides afforded allenyl tellurides instead of propargyl tellurides [19]. Base-catalyzed prototropic rearrangement of methyl propargyl selenide gave allenyl methyl selenide [18].

We have synthesized organyl [3-(trimethylsilyl)prop-2-yn-1-yl] selenides 1-3 in 80–92% yield by reaction of the corresponding diorganyl diselenides with sodium tetrahydridoborate and 3-bromo-1-(trimethylsilyl)prop-1-yne (Scheme 1). The action of NaBH₄ on diorganyl diselenide generates *in situ* sodium organylselenolate which reacts with 3-bromo-1-(trimethylsilyl)prop-1-yne to give selenides 1-3; here, 1 mol of the initial diselenide gives rise to 2 mol of the product. It should be noted that no desilylation products were formed when the reaction was carried out in methanol or ethanol, so that compounds 1-3were obtained with high selectivity.

The reactions of dipropyl and dibenzyl diselenides with 3-bromo-1-(trimethylsilyl)prop-1-yne in methanol





at room temperature were accompanied by formation of up to 10% of bis[3-(trimethylsilyl)prop-2-yn-1-yl] selenide (4) as by-product. When these reactions were carried out in ethanol on cooling to -20° C, the yield of 4 was reduced to 2%. No selenide 4 was detected in the reaction with diphenyl diselenide. Presumably, selenide 4 is formed via side dealkylation of 2 and 3 by the action of phenylmethane- or propane-1-selenolate ion. We have synthesized selenide 4 in 81% yield by reaction of 3-bromo-1-(trimethylsilyl)prop-1-yne with sodium selenide in ethanol (Scheme 2).

Desilylation of 1-3 by the action of K_2CO_3 in ethanol afforded the corresponding organyl propargyl selenides 5–7 in high yields (90–94%; Scheme 3).



The reaction in ethanol at room temperature was chemoselective, and compounds 5-7 were the only products. Desilylation of 1 in methanol, other conditions being equal, gave 50% of propargyl selenide 7 and 45% of allenyl phenyl selenide 8 (Scheme 4).



The structure of the synthesized compounds was confirmed by ¹H, ¹³C, ²⁸Si, and ⁷⁷Se NMR spectra and elemental analyses. Signals in the ¹³C NMR spectra were assigned using HMBC technique.

Thus, we have proposed efficient and selective methods for the preparation of previously unknown propargyl selenides that are promising as intermediate products in organic synthesis.

EXPERIMENTAL

The NMR spectra were recorded from solutions in CDCl₃ on a Bruker DPX-400 spectrometer operating at 400.13 (¹H), 100.61 (¹³C), 79.5 (²⁹Si), or 76.3 MHz (⁷⁷Se); the ²⁹Si and ⁷⁷Se chemical shifts were measured relative to hexamethyldisiloxane and dimethyl selenide, respectively. The solvents used were preliminarily dried and distilled. The elemental analyses were obtained on a Thermo Flash EA1112 analyzer.

Phenyl [3-(trimethylsilyl)prop-2-yn-1-yl] selenide (1). Sodium tetrahydridoborate, 100 mg (2.63 mmol), was added in small portions under argon to a solution of 200 mg (0.64 mmol) of diphenyl diselenide and 260 mg (1.36 mmol) of 3-bromo-1-(trimethylsilyl)prop-1-yne in 7 mL of methanol. The mixture was stirred for 4 h at room temperature in a closed vessel, diluted with degassed water (10 mL), and extracted with carbon tetrachloride $(3 \times 10 \text{ mL})$. The extract was dried over Na₂SO₄ and filtered, the solvent was distilled off from the filtrate on a rotary evaporator, and the residue was dried under reduced pressure. Yield 315 mg (92%), yellowish liquid. ¹H NMR spectrum, δ, ppm: 0.13 s (9H, Me₃Si), 3.52 s (2H, CH₂, ${}^{2}J_{\text{Se-H}} = 13.5$ Hz), 7.29–7.31 m (3H, *p*-H, *m*-H), 7.61–7.63 m (2H, *o*-H). {}^{13}\text{C} NMR spectrum, δ_{C} , ppm: 0.02 (CH₃Si), 13.86 (CH₂), 88.88 (SiC≡), 102.70 $(\equiv \mathbf{CCH}_2), 127.88 (\mathbf{C}^p), 129.05 (\mathbf{C}^m), 129.58 (\mathbf{C}^i),$ 134.10 (C^o). ²⁹Si NMR spectrum: δ_{Si} –18.2 ppm. ⁷⁷Se NMR spectrum: δ_{Se} 381.0 ppm. Found, %: C 53.85; H 6.14; Se 29.83; Si 10.35. C₁₂H₁₆SeSi. Calculated, %: C 53.92; H 6.03; Se 29.54; Si 10.51.

Compounds 2 and 3 were synthesized in a similar way.

Benzyl [3-(trimethylsilyl)prop-2-yn-1-yl] selenide (2). Yield 83%, yellowish liquid. ¹H NMR spectrum, δ, ppm: 0.22 s (9H, Me₃Si), 3.11 s (2H, CH₂C≡, ${}^{2}J_{Se-H} =$ 14.8 Hz), 3.98 s (2H, CH₂Ph, ${}^{2}J_{Se-H} =$ 13.9 Hz). ¹³C NMR spectrum, δ_C, ppm: 0.22 (CH₃Si), 8.63 (CH₂C≡), 27.56 (CH₂Ph), 88.60 (SiC≡), 102.76 (≡CCH₂), 126.96 (C^{*p*}), 128.68 (C^{*m*}), 129.04 (C^{*o*}), 138.99 (C^{*i*}). ²⁹Si NMR spectrum: δ_{Si} –18.2 ppm. ⁷⁷Se NMR spectrum: δ_{Se} 345.2 ppm. Found, %: C 55.74; H 6.65; Se 27.83; Si 10.14. C₁₃H₁₈SeSi. Calculated, %: C 55.50; H 6.45; Se 28.07; Si 9.98.

Propyl [3-(trimethylsilyl)prop-2-yn-1-yl] selenide (3). Yield 80%, yellowish liquid. ¹H NMR spectrum, δ, ppm: 0.16 s (9H, Me₃Si), 1.02 t (3H, CH₃), 1.72 m (2H, CH₂), 2.75 t (2H, SeCH₂), 3.22 s (2H, (≡CCH₂). ¹³C NMR spectrum, δ_C, ppm: 0.18 (CH₃Si), 7.84 (SeCH₂), 14.87 (CH₃), 23.68 (CH₂), 26.89 (CH₂), 88.57 (SiC≡), 102.78 (≡CCH₂). ²⁹Si NMR spectrum: δ_{Si} –18.2 ppm. Found, %: C 46.05; H 8.02; Se 34.15; Si 11.85. C₉H₁₈SeSi. Calculated, %: C 46.34; H 7.78; Se 33.85; Si 12.04.

Bis[3-(trimethylsilyl)prop-2-yn-1-yl] selenide (4). Sodium tetrahydridoborate, 70 mg (1.85 mmol), was added in small portions under argon to a mixture of 50 mg (0.63 mmol) of selenium and 5 mL of methanol until the mixture became colorless. A solution of 210 mg (1.1 mmol) of 3-bromo-1-(trimethylsilyl)prop-1-yne in 1 mL of methanol was added, and the mixture was stirred for 4 h at room temperature in a closed vessel. The mixture was then diluted with degassed water (15 mL) and extracted with carbon tetrachloride $(3 \times 15 \text{ mL})$. The extract was dried over Na₂SO₄ and filtered, the solvent was distilled off from the filtrate on a rotary evaporator, and the residue was dried under reduced pressure. Yield 135 mg (81%), yellowish liquid. ¹H NMR spectrum, δ, ppm: 0.16 s (18H, Me₃Si), 3.41 s (4H, CH₂, ${}^{2}J_{Se-H} = 14.0$ Hz). ${}^{13}C$ NMR spectrum, δ_{C} , ppm: 0.16 (CH₃Si), 9.57 (CH₂, ${}^{1}J_{CH} =$ 147.9 Hz), 88.58 (SiC=), 102.00 (=CCH₂). ²⁹Si NMR spectrum: δ_{si} –18.1 ppm. ⁷⁷Se NMR spectrum: δ_{Se} 339.6 ppm. Found, %: C 48.07; H 7.53; Se 25.92; Si 18.34. C₁₂H₂₂SeSi₂. Calculated, %: C 47.81; H 7.36; Se 26.19; Si 18.63.

Benzyl prop-2-yn-1-yl selenide (5). Potassium carbonate, 828 mg (6 mmol), was added to a solution of 281 mg (1 mmol) of selenide 2 in 15 mL of anhydrous ethanol, and the mixture was stirred for 24 h at room temperature under argon. The mixture was diluted with cold degassed water (30 mL) and extracted with carbon tetrachloride $(3 \times 15 \text{ mL})$. The extract was washed with water and dried over Na₂SO₄, the solvent was removed on a rotary evaporator, and the residue was dried under reduced pressure. Yield 196 mg (94%), yellowish liquid. ¹H NMR spectrum, δ , ppm: 2.15 t (1H, ${}^{4}J$ = 2.7 Hz), 2.85 d (2H, SeCH₂, ${}^{4}J$ = 2.7 Hz), 3.69 s (2H, PhCH₂), 7.05-7.19 m (Ph). ¹³C NMR spectrum, δ_{C} , ppm: 7.76 (SeCH₂), 28.10 (PhCH₂), 72.21 (CH), 81.63; 127.41, 129.00, 129.58, 139.22 (Carom). Found, %: C 57.27; H 4.65; Se 38.04. C₁₀H₁₀Se. Calculated, %: C 57.43; H 4.82; Se 37.75.

Compounds 6 and 7 were synthesized in a similar way.

Propyl prop-2-yn-1-yl selenide (6). Yield 90%, yellowish liquid. ¹H NMR spectrum, δ , ppm: 1.02 t (3H, CH₃), 1.69 m (2H, CH₂), 2.08 t (1H, CH, ⁴*J* = 2.6 Hz), 2.68 t (2H, SeCH₂), 3.08 d (2H, SeCH₂, ⁴*J* = 2.6 Hz). ¹³C NMR spectrum, $\delta_{\rm C}$, ppm: 6.83 (SeCH₂), 14.93 (CH₃), 23.66 (CH₂), 26.98 (CH₂), 71.39 (=CH), 81.17 (=C). Found, %: C 44.57; H 6.43; Se 48.76. C₆H₁₀Se. Calculated, %: C 44.73; H 6.26; Se 49.01.

Phenyl prop-2-yn-1-yl selenide (7). Yield 93%, yellowish liquid.

Allenyl phenyl selenide (8). Potassium carbonate, 828 mg (6 mmol), was added to a solution of 267 mg (1 mmol) of selenide 1 in 15 mL of anhydrous methanol, and the mixture was stirred for 24 h at room temperature under argon. The mixture was diluted with cold degassed water (30 mL) and extracted with carbon tetrachloride (3×15 mL). The extract was washed with water and dried over Na₂SO₄, the solvent was removed on a rotary evaporator, and the residue was dried under reduced pressure. The product was 185 mg of a mixture of selenides 7 (98 mg, 50%) and 8 (87 mg, 45%) which were separated by column chromatography on silica gel (hexane–chloroform, 6:1). Compounds 7 and 8 were described previously [13, 16, 17].

The spectral studies were performed using the facilities of the Baikal Joint Analytical Center, Siberian Branch, Russian Academy of Sciences.

REFERENCES

- 1. Wirth, T., Organoselenium Chemistry: Synthesis and Reactions, Weinheim: Wiley-VCH, 2011.
- 2. Perin, G., Lenardão, E.J., Jacob, R.G., and Panatieri, R.B., *Chem. Rev.*, 2009, vol. 109, p. 1277.
- Bhabak, K. and Mugesh, G., Acc. Chem. Res., 2010, vol. 43, p. 1408.
- 4. Back, T., Can. J. Chem., 2009, vol. 87, p. 1657.
- 5. Potapov, V.A., Amosova, S.V., and Kashik, A.S., *Tetrahedron Lett.*, 1989, vol. 30, p. 613.
- Bagnoly, L., Casini, S., Marini, F., Santi, C., and Testaferri, L., *Tetrahedron*, 2013, vol. 69, p. 481.
- 7. Braverman, S., Pechenick-Azizi, T., Gottlieb, H., and Sprecher, M., *Synthesis*, 2011, p. 577.
- Braverman, S., Cherkinsky, M., Kalendar, Yu., Jana, R., Sprecher, M., and Goldberg, I., *Synthesis*, 2014, vol. 46, p. 119.
- 9. Zeni, G., Formiga, H.B., and Comasseto, J.V., *Tetrahedron Lett.*, 2000, vol. 41, p. 1311.

RUSSIAN JOURNAL OF ORGANIC CHEMISTRY Vol. 53 No. 10 2017

- Bhasin, K.K., Singh, N., Kumar, R., Deepali, D.G., Mehta, S.K., Klapoetke, T.M., and Crawford, M.-J., *J. Organomet. Chem.*, 2004, vol. 689, p. 3327.
- Potapov, V.A. and Amosova, S.V., *Phosphorus, Sulfur Silicon Relat. Elem.*, 1993, vol. 79, p. 277.
- Hirabayashi, K., Shibagaki, K., and Shimizu, T., *Phosphorus, Sulfur Silicon Relat. Elem.*, 2016, vol. 191, p. 268.
- 13. Reich, H.J., Shah, S.K., Gold, P.M., and Olson, R.E., *J. Am. Chem. Soc.*, 1981, vol. 103, p. 3112.
- 14. Bao, W., Zheng, Y., Zhang, Y., and Zhou, J., *Tetrahedron Lett.*, 1996, vol. 37, p. 9333.

- 15. Rong, M., Huang, R., You, Y., and Weng, Z., *Tetrahedron*, 2014, vol. 70, p. 8872.
- 16. Ma, S., Hao, X., Meng, X., and Huang, X., J. Org. Chem., 2004, vol. 69, p. 5720.
- Ma, S., Hao, X., and Huang, X., Chem. Commun., 2003, p. 1082.
- Potapov, V.A., Panov, V.A., Musalov, M.V., Musalova, M.V., and Amosova, S.V., *Russ. J. Org. Chem.*, 2016, vol. 52, p. 1054.
- Musalova, M.V., Musalov, M.V., Potapov, V.A., and Amosova, S.V., *Russ. J. Org. Chem.*, 2012, vol. 48, p. 1569.