Annulation of phenyl propargyl ether with selenium dichloride

M. V. Musalov, V. A. Potapov, and S. V. Amosova*

A. E. Favorsky Irkutsk Institute of Chemistry, Siberian Branch of the Russian Academy of Sciences, 1 ul. Favorskogo, 664033 Irkutsk, Russian Federation. Fax: +7 (395 2) 41 9346. E-mail: v_a_potapov@irioch.irk.ru

We are performing systematic studies aimed at the application of novel reagents, such as selenium dichloride and dibromide, in the chemistry of organoselenium compounds.[1—6] Although these reagents cannot be isolated in pure state and undergo disproportionation in solutions[7], it has been shown[1] that freshly prepared selenium dichloride and dibromide can be used as selective electrophilic reagents in the synthesis of organoselenium compounds. The reactions of selenium dichloride and dibromide with acetylene,[2] diphenylacetylene,[3] divinyl sulfide,[4] divinyl sulfone,[5] divinyl selenide,[6] propargyl alcohols,[8] 2,3-dimethoxybuta-1,3-diene[9] have been studied. In contrast to selenium tetrahalides, whose reactions with organic substances often afford mixtures of products[10], the reactions of selenium dihalides proceed selectively to afford the target compounds in high yields.[1—6,8,9]

The use of selenium dihalides for annulation of phenyl ethers containing unsaturated groups by combination of the addition to the unsaturated bond and electrophilic substitution in the *ortho*-position of the benzene ring is of the utmost interest. There are no data on annulation of phenyl propargyl ether with selenium halides.

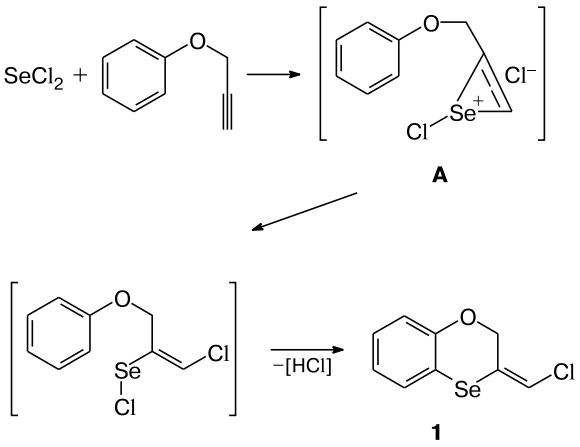
We studied the reaction of selenium dichloride with phenyl propargyl ether and found the conditions that allow selective preparation of previously unknown *E*-3-chloromethylidene-2,3-dihydro-1,4-benzoxaselenine (**1**). The highest yield of product **1** (80%) was obtained upon mixing reagents at low temperature (−60 °C) in chloroform followed by heating the reaction mixture to the boiling temperature of the solvent.

One can assume that the addition of selenium dichloride to the propargyl group occurs at low temperature and the second step, *viz.*, electrophilic aromatic substitution, requires heating of the reaction mixture.

The structure of product **1** was established by ^{1}H, ^{13}C (including JMOD), and ^{77}Se NMR spectroscopy and confirmed by the data from mass spectrometry and elemental analysis. The value of spin-spin coupling constant (100 Hz) between the selenium atom and the double-bond carbon atom having no protons corresponds to the C—Se direct constant ($^{1}J_{C-Se}$), which is evidence of the addition of the selenium atom to the central carbon atom of the propargyl group. The *E*-configuration of product **1** was established using the NOESY spectra.

The regio- and stereospecificity of the process can be explained by the fact that the reaction proceeds *via* the intermediate selenirenium ion **A**, which is attacked by the chloride ion at the sterically unshielded terminal carbon atom.

Thus, we showed for the first time the possibility of annulation of the selenium-containing heterocycles to the benzene ring based on the reaction of selenium dichloride with unsaturated organyl phenyl ethers, where the addition of selenium halides to the unsaturated bond of organyl phenyl ethers and electrophilic aromatic substitution is combined.



***E*-3-Chloromethylidene-2,3-dihydro-1,4-benzoxaselenine (1).** ^{1}H NMR ($CDCl_3$), δ: 4.39 (s, 2 H, CH_2O); 6.30 (s, 1 H, =CHCl); 6.80—7.10 (m, 4 H, C_6H_4). ^{13}C NMR ($CDCl_3$), δ: 66.87 (OCH_2); 113.97 (=CHCl); 115.01 (SeC_{arom}, $^{1}J_{C-Se}$ = 65 Hz); 119.25 (C_{arom}); 123.57 (C_{arom}); 126.94 (C_{arom}); 128.49 (C_{arom}); 131.40 (=CSe, $^{1}J_{C-Se}$ = 100 Hz); 154.65 (OC_{arom}). ^{77}Se NMR ($CDCl_3$), δ: 495. MS (EI, 70 eV), *m/z* (I_{rel} (%)): 246 $[M]^{+\cdot}$ (66), 211 $[M - Cl]^{+}$ (28), 183 $[M - C_2H_4Cl]^{+}$ (10), 166 $[M - Se]^{+\cdot}$ (84), 144 $[M - OSeH_2]^{+\cdot}$ (70), 131 $[OSeCl]^{+}$ (100), 118 $[SeC_3H_2]^{+\cdot}$ (35), 91 $[PhCH_2]^{+}$ (12), 63 $[C_2H_4Cl]^{+}$ (92), 50 $[CH_3Cl]^{+\cdot}$ (25). Found (%): C, 43.67; H, 2.69; Cl, 14.82; Se, 31.87. C_9H_7OClSe. Calculated (%): C, 44.02; H, 2.87; Cl, 14.44; Se, 32.15.

NMR spectra were recorded on a Bruker DPX-400 instrument at 400.13 (^{1}H, HMDS), 100.61 (^{13}C, HMDS), and 76.30 MHz (^{77}Se, Me_2Se). The mass spectrum was obtained on a GCMS-QP5050A (Shimadzu, 70 eV) chromato-mass spectrometer.

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References

1. (a) V. A. Potapov, S. V. Amosova, O. V. Belozerova, A. I. Albanov, O. G. Yarosh, M. G. Voronkov, *Khim. Geterotsikl. Soedin.*, 2003, 633 [*Chem. Heterocycl. Compd.* (*Engl. Transl.*), 2003, **39**, 549]; (b) V. A. Potapov, S. V. Amosova, *Zh. Org. Khim.*, 2003, **39**, 1449 [*Russ. J. Org. Chem.* (*Engl. Transl.*), 2003, **39**, 1373].
2. (a) V. A. Potapov, O. I. Khuriganova, M. V. Musalov, L. I. Larina, S. V. Amosova, *Zh. Obshch. Khim.,* 2010, **80**, 513 [*Russ. J. Gen. Chem.* (*Engl. Transl.*), 2010, **80**, 541]; (b) V. A. Potapov, M. V. Musalov, O. I. Khuriganova, L. I. Larina, S. V. Amosova, *Zh. Org. Khim.,* 2010, **46**, 758 [*Russ. J. Org. Chem.* (*Engl. Transl.*), 2010, **46**, 753].
3. V. A. Potapov, O. I. Khuriganova, S. V. Amosova, *Zh. Org. Khim.*, 2010, **46**, 1417 [*Russ. J. Org. Chem.* (*Engl. Transl.*), 2010, **46**, 1421].
4. (a) S. V. Amosova, M. V. Penzik, A. I. Albanov, V. A. Potapov, *Tetrahedron Lett.*, 2009, **50**, 306; (b) S. V. Amosova, M. V. Penzik, A. I. Albanov, V. A. Potapov, *J. Organomet. Chem.*, 2009, **694**, 3369; (c) V. A. Potapov, V. A. Shagun, M. V. Penzik, S. V. Amosova, *J. Organomet. Chem.*, 2010, **695**, 1603.
5. (a) V. A. Potapov, E. O. Kurkutov, M. V. Musalov, S. V. Amosova, *Tetrahedron Lett.*, 2010, **51**, 5258; (b) V. A. Potapov, E. O. Kurkutov, S. V. Amosova, *Zh. Org. Khim.,* 2010, **46**, 1098 [*Russ. J. Org. Chem.* (*Engl. Transl.*), 2010, **46**, 1099].
6. V. A. Potapov, S. V. Amosova, K. A. Volkova, M. V. Penzik, A. I. Albanov, *Tetrahedron Lett.*, 2010, **51**, 89.
7. M. Lamoureux, J. Milne, *Polyhedron*, 1990, **9**, 589.
8. (a) S. Braverman, R. Jana, M. Cherkinsky, H. E. Gottlieb, M. Sprecher, *Synth. Lett.*, 2007, 2663; (b) S. Braverman, M. Cherkinsky, R. Jana, Y. Kalendar, M. Sprecher, *J. Phys. Org. Chem.*, 2010, **23**, 1114.
9. A. Patra, Y. H. Wijsboom, S. S. Zade, M. Li, Y. Sheynin, G. Leitus, M. Bendikov, *J. Am. Chem. Soc.*, 2008, **130**, 6734.
10. (a) T. G. Back, In *Organoselenium Chemistry*, Ed. D. Liotta, John Wiley & Sons, New York, 1987, p. 1; (b) Yu. V. Migalina, S. V. Galla-Bobik, S. M. Khripak, V. I. Staninets, *Khim. Geterotsikl. Soedin.*, 1982, 911 [*Chem. Heterocycl. Compd.* (*Engl. Transl.*), 1982, **18**, 690].

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