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LETTERS TO THE EDITOR

Regio- and Stereoselective Addition of Selenium Dihalogenides to Propargyl Halogenides

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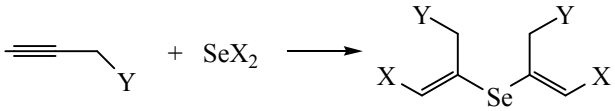
It is known that selenium dibromide and dichloride cannot be isolated in pure form and that in aprotic solvents the former exists in an equilibrium with Se_2Br_2 and bromine, and the latter with Se_2Cl_2 and $SeCl_4$ [1]. However, we have found that freshly prepared selenium dibromide and dichloride can be used as selective electrophilic reagents in the synthesis of organoselenium compounds [2–17]. The reactions of selenium halogenides with acetylene [2, 3], diethynylsilanes [4–6], diethynylgermanes [6, 7], divinyl sulfide [8–11], divinyl sulfone [12–14], and divinyl selenide [15–17] have been systematically studied.

Addition of selenium tetrahalogenides often results in a mixture of products [18]. According to [19, 20], the reaction of selenium dichloride and dibromide with propargyl alcohols proceeds as *syn*-addition with the formation of *Z,Z*-bis(1-halo-3-hydroxy-1-propenyl-2)-selenides.

In continuation of our systematic studies of electrophilic reactions of selenium dihalogenides [2–17], we have investigated the addition of selenium dichloride and dibromide to propargyl halogenides. The reaction was found to proceed stereo- and regioselectively as *anti*-addition with the formation of the anti-Markovnikov adducts, *E,E*-bis(1-bromo-3-chloro-1-propenyl-2)selenide (**I**) and *E,E*-bis(1-chloro-3-bromo-1-propenyl-2)selenide (**II**) in 98 and 62% yield, respectively.

The reaction with selenium dibromide generated from Se and Br_2 was carried out at room temperature in CCl_4, whereas the reaction with selenium dichloride prepared from Se and SO_2Cl_2, in $CHCl_3$ at –20°C. The



I, II

I: X = Br, Y = Cl; **II**: X = Cl, Y = Br.

structure of selenides **I** and **II** was proved by ^1H, ^{13}C, ^{77}Se NMR (including NOESY and *J*-modulation technique), their composition was confirmed by elemental analysis. The presence of the spin–spin coupling constant $^1J_{CSe}$ between the selenium atom and the carbon atom having no protons is indicative of the addition of selenium atom to the central carbon atom of propargyl halogenides. The *E*-configuration of the products was established by the 2D-NOESY spectra, in which the cross-peaks between the vinyl proton and protons of the CH_2Cl group are lacking, thus proving the *E*-configuration of selenides **I** and **II**.

Therefore, we have demonstrated the possibility of the synthesis, based on selenium dichloride and dibromide, of compounds of the same molecular formula but with different location of the halogen atoms in the molecule. As distinct from the reaction with propargyl alcohols [19, 20], the reactions of selenium dihalogenides with propargyl halogenides proceeds as *anti*-addition. It can be assumed that the reaction with propargyl halogenides proceeds via the selenirenium cations [18], which after nucleophilic attack of halogenide anions give rise to the products of the *E*-configuration.

***E,E*-Bis(1-bromo-3-chloro-1-propenyl-2)selenide (I)**. ^{1}H NMR spectrum, δ, ppm: 4.54 s (4H, CH_2Cl), 7.29 s (2H, =CHBr). ^{13}C NMR, δ, ppm: 44.07 (CH_2Cl), 119.13 (=CHBr, $^2J_{CSe}$ 10 Hz), 131.10 (=CSe, $^1J_{CSe}$ 134 Hz). ^{77}Se NMR, δ, ppm: 495. Found, %: C 18.93; H 1.73; Cl 17.96; Br 40.84; Se 20.67. $C_6H_6Cl_2Br_2Se$. Calculated, %: C 18.58; H 1.56; Cl 18.28; Br 41.21; Se 20.36.

***E,E*-Bis(1-chloro-3-bromo-1-propenyl-2)selenide (II).** ^{1}H NMR spectrum, δ, ppm: 4.30 s (4H, CH_2Br), 6.70 s (2H, =CHCl). ^{13}C NMR, δ, ppm: 29.98 (CH_2Br), 126.96 (=CHCl, $^2J_{CSe}$ 23.6 Hz); 128.10 (=CSe, $^1J_{CSe}$ 113 Hz). ^{77}Se NMR, δ, ppm: 439. Found, %: C 18.99; H 2.00; Cl 17.78; Br 41.11; Se 20.42. $C_6H_6Cl_2Br_2Se$. Calculated, %: C 18.58; H 1.56; Cl 18.28; Br 41.21; Se 20.36.

NMR spectra were registered on a Bruker DPX 400 spectrometer in $CDCl_3$ at working frequencies of 400.13 (^{1}H, HMDS), 100.61 (^{13}C, HMDS), and 76.30 MHz (^{77}Se, Me_2Se).

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REFERENCES

1. Lamoureux, M. and Milne, J., *Polyhedron*, 1990, vol. 9, no. 4, p. 589.
2. Potapov, V.A., Khuriganova, O.I., Musalov, M.V., Larina, L.I., and Amosova, S.V., *Russ. J. Gen. Chem*., 2010, vol. 80, no. 3, p. 541.
3. Potapov, V.A., Musalov, M.V., Khuriganova, O.I., Larina, L.I., and Amosova, S.V., *Russ. J. Org. Chem.,* 2010, vol. 46, no. 5, p. 753.
4. Potapov, V.A., Amosova, S.V., Belozerova, O.V., Albanov, A.I., Yarosh, O.G., and Voronkov, M.G., *Chem. Heterocycl. Comp*., 2003, vol. 39, no. 4, p. 549.
5. Potapov, V.A. and Amosova, S.V., *Russ. J. Org. Chem*., 2003, vol. 39, no. 10, p. 1373.
6. Amosova, S.V. and Martynov, A.V., *Mini-Rev. Org. Chem*., 2010, vol. 7, no. 1, p. 23.
7. Amosova, S.V., Penzik, M.V., Martynov, A.V., Makhaeva, N.A., Yarosh, N.O., and Voronkov, M.G., *J. Organometal. Chem*., 2008, vol. 693, nos. 21–22, p. 3346.
8. Amosova, S.V., Penzik, M.V., Albanov, A.I., and Potapov, V.A., *Tetrahedron Lett*., 2009, vol. 50, no. 3, p. 306.
9. Amosova, S.V., Penzik, M.V., Albanov, A.I., and Potapov, V.A., *J. Organomet. Chem*., 2009, vol. 694, no. 20, p. 3369.
10. Potapov, V.A., Shagun, V.A., Penzik, M.V., and Amosova, S.V., *J. Organometal. Chem*., 2010, vol. 695, nos. 10–11, p. 1603.
11. Amosova, S.V., Penzik, M.V., Potapov, V.A., and Albanov, A.I., *Russ. Chem. Bull. Int. Ed*., 2008, vol. 57, no. 6, p. 1323.
12. Potapov, V.A., Kurkutov, E.O., Albanov, A.I., and Amosova, S.V., *Russ. J. Org. Chem*., 2008, vol. 44, no. 10, p. 1547.
13. Potapov, V.A., Kurkutov, E.O., and Amosova, S.V., *Russ. J. Org. Chem*., 2010, vol. 46, no. 7, p. 1099.
14. Potapov, V.A., Kurkutov, E.O., Musalov, M.V., and Amosova, S.V., *Tetrahedron Lett*., 2010, vol. 51, no. 40, p. 5258.
15. Potapov, V.A., Amosova, S.V., Volkova, K.A., Penzik, M.V., and Albanov, A.I., *Tetrahedron Lett*., 2010, vol. 51, no. 1, p. 89.
16. Potapov, V.A., Volkova, K.A., Penzik, M.V., Albanov, A.I., and Amosova, S.V., *Russ. J. Org. Chem.,* 2008, vol. 44, no. 10, p. 1556.
17. Potapov, V.A., Volkova, K.A., Penzik, M.V., Albanov, A.I., and Amosova, S.V., *Russ. J. Gen. Chem*., 2008, vol. 78, no. 10, p. 1990.
18. Back, TG., in *Organoselenium Chemistry,* Liotta, D., Ed., New York: Wiley, 1987, p. 1.
19. Braverman, S., Jana, R., Cherkinsky, M., Gottlieb, H.E., and Sprecher, M., *Synlett*, 2007, no. 17, p. 2663.
20. Braverman, S., Cherkinsky, M., Jana, R., Kalendar, Y., and Sprecher, M., *J. Phys. Org. Chem*., 2010, vol. 23, no. 11, p. 1114.