Reaction of selenium dichloride with trimethylpropargylsilane

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The addition of compounds containing the selenium—halogen bond (SeX_4, Se_2X_2, SeX_2, RSeX, X = Cl, Br) to alkynes results usually in *E*-products.[1,2] The fact that these reactions proceed as the *anti* addition is explained by the formation of intermediate selenirenium ions.[1] Selenium dichloride and dibromide add to acetylene to form *E,E*-bis-(2-halovinyl) selenides.[2] The reactions of selenium dichloride and dibromide with propargyl alcohols have also been described[3], which afford the anti-Markovnikov *syn* addition products, *viz.*, *Z,Z*-bis(1-halo-3-hydroxyprop-1-en-2-yl) selenides.[3] The *Z*-stereospecificity was rationalized assuming the involvement of the hydroxy group in this reaction, which reacts with the selenirenium ion.[3]

We are studying intensively the synthetic potential of novel electrophilic reagents, such as selenium dichloride[4,5] and selenium dibromide[5,6], whose addition to alkenes, alkynes, and their derivatives results in the organoselenium compounds unknown previously.

We obtained an unexpected result when studying the reaction of selenium dichloride with trimethylpropargylsilane. The reaction proceeds regio- and stereospecifically to form the Markovnikov *Z,E*-adduct, *viz.*, *Z,E*-bis(2-chloro-3-trimethylsilylprop-1-enyl) selenide (**1**), in quantitative yield.

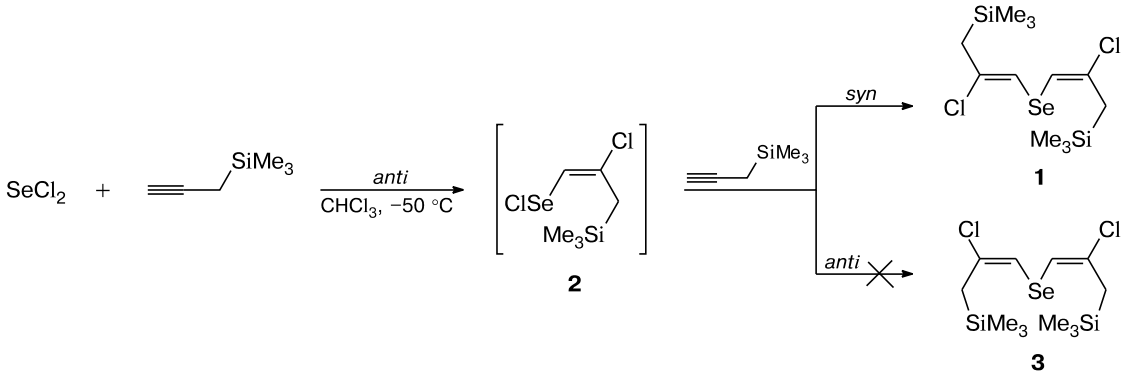
Presumably, the *anti* addition of $SeCl_2$ to one trimethylpropargylsilane molecule is followed by the *syn* addition of intermediate **2** to the second trimethylpropargylsilane molecule. The *syn* addition at the second step seems to be energetically more favorable than the *anti* addition due to a strong steric effect of the trimethylsilyl groups, which makes the formation of the expected product **3** improbable.

The reaction is carried out by addition of a solution of $SeCl_2$ in chloroform to a cooled to −50 °C solution of trimethylpropargylsilane in chloroform (the molar ratio of trimethylpropargylsilane to $SeCl_2$ is 2 : 1) followed by stirring the reaction mixture for 2 h at −50 °C.

The structure of compound **1** was confirmed by ^1H, ^{13}C, ^{29}Si, and ^{77}Se NMR spectroscopy and elemental analysis. The values of two spin-spin coupling constants between the selenium atom and two olefinic carbon atoms each correspond to the values of the C—Se direct constants ($^1J_{C-Se}$)[3,5], which is evidence of the addition of the selenium atom to the terminal carbon atoms of two propargyl groups. The ^{77}Se NMR spectrum displays one signal at δ 309; however, in the ^1H, ^{13}C, and ^{29}Si NMR spectra, two 2-chloro-3-trimethylsilylprop-1-enyl groups have different signals, whose integration in the ^1H NMR spectrum affords the 1 : 1 ratio. The NOESY spectrum displays the interaction of the olefinic proton at δ 5.91 with the protons of the $SiCH_2$ group at δ 1.97, which allows assignment of these signals to the *Z*-2-chloro-3-trimethylsilylprop-1-enyl group. There is no interaction of analogous protons in the propenyl group of the *E*-structure.

Thus, we found an example of the regio- and stereospecific reaction, which affords quantitatively the *Z,E*-product through the assumed *anti-syn* addition.

***Z,E*-Bis(2-chloro-3-trimethylsilylprop-1-enyl) selenide (1).** ^1H NMR ($CDCl_3$), δ: 0.12 (s, 9 H, $SiMe_3$); 0.15 (s, 9 H, $SiMe_3$);



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1.97 (s, 2 H, $SiCH_2$); 2.10 (s, 2 H, $SiCH_2$); 5.91 (s, 1 H, =CHSe); 6.22 (s, 1 H, =CHSe). ^{13}C NMR ($CDCl_3$), δ: 0.52 ($SiMe_3$); 0.94 ($SiMe_3$); 30.94 ($SiCH_2$); 33.28 ($SiCH_2$); 111.19 (=CHSe, $^1J_{C-Se}$ = 101 Hz); 114.36 (=CHSe, $^1J_{C-Se}$ = 102 Hz); 135.47 (=CCl); 136.65 (=CCl). ^{29}Si NMR ($CDCl_3$), δ: 1.50; 2.94. ^{77}Se NMR ($CDCl_3$), δ: 309. Found (%): C, 38.86; H, 6.65; Cl, 19.32; Si, 14.68; Se, 20.74. $C_{12}H_{24}Cl_2Si_2Se$. Calculated (%): C, 38.50; H, 6.46; Cl, 18.94; Si, 15.00; Se, 21.09.

NMR spectra were recorded on a Bruker DPX-400 instrument at 400.13 (^1H, HMDS), 100.61 (^{13}C, HMDS), 79.49 (^{29}Si, HMDS), and 76.30 MHz (^{77}Se, Me_2Se).

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