Regioselective Addition of Sulfur Dichloride and Selenium Tetrachloride to Diallyldimethylsilane as the Method of Preparation of Eight-Membered Heterocycles Containing Silicon and Chalcogens

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Received March 4, 2010

Abstract—The electrophilic additiob of sulfur dichloride and selenium tetrachloride to diallyldimethylsilane proceeds strictly according Markownikoff rule and results in the formation of previously unknown saturated silicon-containing heterocycles, 5,5-dimethyl-3,7-dichloro-1,5-thiasilacyclooctane and 5,5-dimethyl-1,1,3,7-tetrachloro-1,5-selena(IV)silacyclooctane. The structure of heterocycles obtained was confirmed by ¹H, ¹³C NMR spectra, in the case of selenium-containing heterocycle, by ⁷⁷Se NMR spectrum, among them the 2D HMBC spectrum.

DOI: 10.1134/S1070428010110114

The electrophilic addition of sulfur dichloride to diallyl systems like 1,5-hexadiene, diallyl sulfide and ether proceeds in pentane at 0°C as anti-Markownikoff addition at both allyl fragments with the formation of the corresponding five- and six-membered saturated heterocycles [1]. Analogously as anti-Markownikoff addition to the double bond of the allyl fragment the electrophilic reaction of sulfur dichloride occurs with diallyl ethers of glycols and mercaptophenols, allyl ethers of phenols and allyl aryl sulfides, resulting in sulfur-containing macrocyclic oxathia- and thiacrown ethers [2]. However with allylbenzenes the regioselectivity is opposite, and with a 100% selectivity only the products of Markownikoff addition are formed [2].

The electrophilic addition of selenium monochloride Se_2Cl_2 to 1,5-hexadiene and diallyl ether also proceeds against the Markownikoff rule and is accompanied with the elimination of one selenium atom. As a result with 1,5-hexadiene formed a five-membered saturated heterocycle, with diallyl ether, six-membered heterocycle. In both cases formed a single isomer that was assigned a *cis*-configuration as more feasible thermodynamically [3].

We established that unlike the known reactions of the diallyl systems the reactions of sulfur dichloride and selenium tetrachloride with diallyldimethylsilane at -20...-40°C in hexane or chloroform proceeded according to the Markownikoff rule and resulted in the formation of previously unknown saturated eight-membered heterocycles containing chalcogens and silicon, 5,5-dimethyl-3,7-dichloro-1,5-thiasilacyclooctane (I) in the case of SCl₂ and 5,5-dimethyl-1,1,3,7-tetrachloro-1,5-selena(IV) silacyclooctane (II) in the case of SeCl₄ (Scheme 1) in 77 and 98% yield, respectively.

The structure of obtained heterocycles was confirmed by the data of ¹H, ¹³C, ²⁹Si, ⁷⁷Se NMR spectra. ¹H NMR spectra of the heterocycles contain a multiplet signal of groups CHCl, two multiplet signals of nonequivalent



Scheme 1.

protons of groups CH_2Y (Y = S, SeCl₂), two multiplet signals of protons of groups CH₂Si, and singlet signals of the Me₂Si group. The presence of strong electronwithdrawing chlorine atoms in the SeCl₂ group of heterocycle II results in a sharp downfield shift of the proton signals of CHCl groups (by 0.8 ppm) and CH₂SeCl₂ groups (by 1.3 ppm) as compared to the signals of analogous protons in heterocycle I. The ¹³C NMR spectra of heterocycles I and II contain doublet signals of carbon atoms from CHCl groups, triplet signals from CH₂Y $(Y = S, SeCl_2)$ and CH_2Si groups, and a quartet from the dimethylsilyl group. The presence in the molecules of compounds I and II of CHCl and CH_2Y (Y = S, SeCl₂) groups is shown first of all by the characteristic values of the corresponding coupling constants ${}^{1}J_{CH}$ of carbon atoms, indicating the direct bonding of the carbon atom with a chlorine in the first case and with a chalcogen in the second [4]. The presence in the heterocycle II of the SeCl₂ group is seen from the ⁷⁷Se NMR spectrum where two multiplet selenium signals (δ 533.6 and 531.8 ppm) appear in the range characteristic of compounds RSeCl₂R [5]. The presence of two signals of ⁷⁷Se atoms shows that heterocycle II forms as two diastereomers owing to anti, anti- and anti, syn-addition of SeCl₄ to allyl fragments. It is also proved by the presence in the ¹³C NMR spectrum of two signals from the (CH₂)₂SeCl2. The Markownikoff structure of heterocycle II was confirmed by the 2D 1H-⁷⁷Se NMR spectrum HMBC where cross-peaks of atom ⁷⁷Se with protons of CH₂ groups at 4.20–4.33 ppm were observed.

In the ²⁹Si NMR spectra of heterocycles the silicon signal appears in the region 1.7–2.8 ppm.

1,1,3,7-Tetrachloro-1,5-selenasilacyclooctane (II) formed as yellowish fine-crystalline powder at storage at the room temperature within 24 h hydrolizes and decomposes, but at -20° C it can be stored for several weeks. The heating of heterocycle I and also its treatment with dehydrochlorinating reagents (*t*-BuOK in *t*-BuOH, Et₃N, DBU) leads to the dechlorination–desilylation with the cleavage of the ring and the formation of diallyl sulfide

(III) (Scheme 2) thus confirming the assumed structure of heterocycle I. Sulfide III was identified by the ¹H NMR spectrum identical to that of the standard sample. In the GC-MS spectrum of the reaction mixture the corresponding molecular ion was observed.

The formation of the diallyl sulfide may be ascribed to the ready desilylation of the relatively weak C–Si bond of the intermediately formed carbocation containing in the vicinal position a silyl group. The C–Si bond is even more destabilized due to the hyperconjugation with the positive charge [6] (the so-called β -effect [7–9]).

EXPERIMENTAL

¹H (400.13 MHz), ¹³C (100.61 MHz), ²⁹Si (79.50 MHz), ⁷⁷Se (76.31 MHz) NMR spectra were registered on spectrometers Bruker DPX-400 and AV-400 frpm 5–10% solutions in CDCl₃. For heterocycle **II** a ⁷⁷Se NMR spectrum was obtained by the use of 2D NMR, method HMBC GP ¹H-⁷⁷Se. GC-MS spectrum was obtained on an instrument Shimadzu QP5050A at the energy of ionizing electrons 70 eV, capillary colun SPB-5, 60 m × 0.25 mm, 0.25 µm, vaporizer temperature 260°C, oven temperature 50–220°C. Diallyldimethylsilane was synthesized from 3-chloropropene and trimethylchlorosilane by Grignard reaction [10]. SCl₂ was prepared by chlorination of S₂Cl₂ [11].

5,5-Dimethyl-3,7-dichloro-1,5-thiasilacycloctane (I). To a solution of 2.13 g (15.2 mmol) of diallyldimethylsilane in 60 ml of hexane at -20° C within 25 min was added a solution of 1.56 g (15.2 mmol) of SCl₂ in 15 ml of hexane. The reaction mixture was stirred for 3 h gradually warming it to room temperature, and it was left overnight. The reaction mixture separated in two colorless layers. The upper hexane layer was decanted, the bottom layer was treated with chloroform. After removal of solvent from the extract we obtained 2.12 g of heterocycle I as a colorless viscous fluid. The residue after removal of the solvent from the hexane solution weighed 1.50 g and contained according the ¹H NMR

Scheme 2.



data 47% of heterocycle I together with the products of its decomposition, including diallyl sulfide (III). Overall yield of heterocycle I 77%. ¹H NMR spectrum, δ , ppm: 0.20 s [6H, (CH₃)₂Si], 1.27–1.25 m, 1.49–1.46 m [4H, (CH₂)₂Si], 2.91–2.89 m, 3.00 m [4H, (CH₂)₂S], 4.17 m (2H, 2CHCl). ¹³C NMR spectrum, δ , ppm: –1.70 q [(CH₃)₂Si, ¹J_{CH} 119.5 Hz], –1.50 q [(CH₃)₂Si, ¹J_{CH} 118.3 Hz], 25.65 t (CH₂Si, ¹J_{CH} 118.1 Hz), 45.09 t (CH₂S, ¹J_{CH} 142.3 Hz), 60.27 d (2CHCl, ¹J_{CH} 155.9 Hz). ²⁹Si NMR spectrum, δ , ppm: 1.7. Found, %: C 38.97; H 6.50; C128.60; S 13.68; Si 11.37. C₈H₁₆Cl₂SSi. Calculated, %: C 39.50; H 6.63; Cl 29.15; S 13.18; Si 11.55.

To 0.208 g (0.85 mmol) of heterocycle I was added 0.260 g (1.71 mmol) of DBU in 8 ml of Et₂O, and the mixture was stirred for 6 h. Then the reaction mixture was washed with water, the solvent was removed in a vacuum. We obtained 0.118 g of a mixture that contained according to the ¹H NMR data initial heterocycle I and diallyl sulfide (III) in a ratio 78:23. GC-MS spectrum of compound III, m/z (I_{rel} , %): 114 (33) [M]⁺, 73 (100) [M-CH₂CH=CH₂]⁺.

5,5-Dimethyl-1,1,3,7-tetrachloro-1,5-selena(IV) silacyclooctane (II). To 0.617 g (2.79 mmol) freshly prepared SeCl₄ synthesized from selenium and SO₂Cl₂ in CHCl₃ by procedure [12] in 30 ml of CHCl₃ at -40°C under argon was quickly added 0.392 g (2.79 mmol) of diallyldimethylsilane in 5 ml of CHCl₃, the mixture was stirred at the same temperature for 1.5 h, then it was gradually warmed to room temperature, and the stirring was continued for 8 h. On removing the solvent the yield of the product 0.985 g (98%), light-yellow fine crystalline powder, mp 59-60°C (hexane). ¹H NMR spectrum, δ, ppm: 0.25 s [6H, (CH₃)₂Si], 1.37–1.40 m, 1.50-1.57 m [4H, (CH₂)₂Si], 4.20 m, 4.28-4.33 m [4H, (CH₂)₂SeCl₂], 4.98 m (2H, 2CHCl). ¹³C NMR spectrum, δ , ppm: -1.79 q [(CH₃)₂Si, ¹J_{CH} 119.3 Hz], 26.09 t (CH₂Si, ¹J_{CH} 117.6 Hz), 54.79 d (2CHCl, ¹J_{CH} 157.1 Hz), 70.75 t (CH₂SeCl₂, ¹J_{CH} 150.4 Hz), 70.91 t

(CH₂SeCl₂, ${}^{1}J_{CH}$ 147.6 Hz). 29 Si NMR spectrum, δ , ppm: 2.8. 77 Se NMR spectrum, δ , ppm: 533.6 m, 531.8 m (1:1). Found, %: C 25.90; H 4.52; Cl 39.01; Se 21.60; Si 7.44. C₈H₁₆Cl₄SeSi. Calculated, %: C 26.61; H 4.47; Cl 39.28; Se 21.87; Si 7.78.

ACKNOWLEDGMENTS

The study was carried out under the financial support of the Presidium of the Russian Academy of Sciences (grant 18.19) and of the Russian Foundation for Basic Research (grant 10-03-00-543a).

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