3-Phenoxy- and 3-phenylthio-1-propynyl substituted derivatives of silicon and germanium

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Reactions of bromomagnesiopropargyl phenyl ethers and their isostructural sulfides $BrMgC{\equiv}CCH_2XPh$ (X = O, S) with $MeVinSiCl_2$, $Me(CH_2Cl)SiCl_2$, $EtSiHCl_2$, and Me_2SiHCl afforded the corresponding 3-phenoxy- and 3-phenylthio-1-propynyl substituted derivatives of silicon $(PhXCH_2C{\equiv}C)_2SiRR^1$ and $PhXCH_2C{\equiv}CSiHMe_2$ (X = O, S). Reactions of the above-mentioned Iotsitch reagents with $GeCl_4$ led to the corresponding germanium derivatives $(PhXCH_2C{\equiv}C)_4Ge$ (X = O, S).

Key words: 3-phenoxy- and 3-phenylthio-1-propynyl substituted derivatives of silicon and germanium; synthesis.

Carbofunctional organic compounds of silicon and germanium containing $—MC{\equiv}C—$ groups (M = Si, Ge) are of interest as intermediate products in fine organic synthesis, as possible biologically active substances, as corrosion inhibitors, as new monomers, *etc.*[1] Of this type of compounds,[2—5] (3-phenoxy- and 3-phenylthio-1-propynyl)silanes and their sulfur-containing analogs of the general formula $(PhXCH_2C{\equiv}C)_2SiRR^1$ as well as the corresponding monoacetylenic hydrosilanes $PhXCH_2C{\equiv}CSiHRR^1$ (X = O, S) and germanium derivatives containing these substituents have so far been unknown.

We prepared novel polyfunctional acetylenic derivatives of silicon and germanium (**3—11**) by the reaction of bromomagnesiopropargyl ethers (**1**) and isostructural sulfides (**2**) with organylsilanes $EtSiHCl_2$, $MeVinSiCl_2$, $Me(CH_2Cl)SiCl_2$, Me_2SiHCl, and tetrachlorogermane.

$$2PhXCH_2C{\equiv}CMgBr + RR^1SiCl_2 \rightarrow$$
$$\rightarrow (PhXCH_2C{\equiv}C)_2SiRR^1 + 2MgBrCl$$

X = O, S; R = H, Me; R^1 = Et, Vin, CH_2Cl

$$4PhXCH_2C{\equiv}CMgBr + GeCl_4 \rightarrow$$
$$\rightarrow (PhXCH_2C{\equiv}C)_4Ge + 4MgBrCl$$

X = O, S

The yields of the resulting compounds containing one to four propargyl groups were 79—91 %. All of them are thermally stable liquids (can be distilled *in vacuo*). Their physicochemical characteristics, IR spectral data, and the results of elemental analysis are summarized in Table 1.

The IR spectra of compounds **3—11** exhibit an intense absorption band at 2150—2190 cm^{-1} due to the stretching vibrations of the triple bond. The spectra of compounds **3**, **8**, and **9** display a weak band at 2120—2130 cm^{-1} which should be assigned[6] to vibrations of the Si—H bond. The stretching vibrations of the phenyl group account for the absorption in the region 1580—1600 cm^{-1}. It is likely that the stretching vibrations of the vinyl C=C bond in molecules **4** and **6** manifest themselves in the same region.

The structures of the compounds synthesized were confirmed as well by ^1H and ^{13}C NMR spectra (Table 2). The protons of the methyl group bonded with the silicon atom are responsible for the singlets at 0.24—0.30 ppm (compounds **4—7**) and doublets at 0.19 and 18 ppm (compounds **8** and **9** having Si—H bonds, respectively) in the ^1H NMR spectra of the tetraorganosilanes, while the proton of the Si—H bond in compounds **8** and **9** accounts for the doublets at 4.07 and 4.18 ppm, respectively. The multiplets in the region 7.03—7.30 ppm are associated with the phenyl protons. The singlets between 3.4 and 4.5 ppm correspond to the methylene group bonded with a hetero atom, O or S: 3.49—3.60 ppm for CH_2S and 4.38—4.50 ppm for CH_2O. In the spectra of silanehydrides **3**, **8**, and **9** these groups are exhibited as doublets at 4.60, 4.59, and 3.60 ppm, respectively. The different shielding of the OCH_2 and SCH_2 groups is due to the difference between the electronegativities of O and S atoms.

In the spectra of compounds **9** and **8** a long-range spin-spin coupling constant (0.9 Hz) of the CH_2 and SiH protons is observed, which attests to an interaction between π-electrons and the $H_2C—C$ and C—SiH σ-bonds. The protons of the vinyl groups of compounds **4** and **6** are exhibited as multiplets at 5.94 and 5.92 ppm. The singlets at 2.73 ppm (compound **5**) and 2.69 ppm (compound **7**) correspond to the CH_2Cl group. Para-

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Table 1. 3-Phenoxy- and 3-phenylthio-1-propynyl substituted silanes and germanes

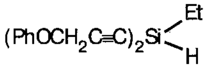
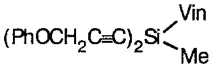
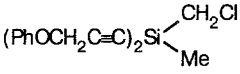
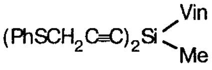
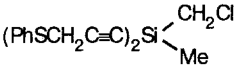
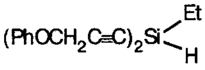
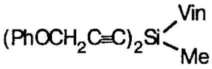
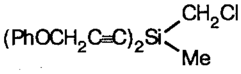
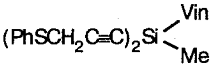
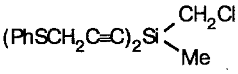
Compound		Yield (%)	B.p./°C (p/Torr)	n_D^{20}	IR (ν/cm^{-1})	Found / Calculated (%)					Molecular formula
						C	H	S	Si or Ge	Cl	
 $(PhOCH_2C{\equiv}C)_2Si{<}^{Et}_{H}$	**(3)**	85.6	200—201 (0.3)	1.5432	2150 (Si—H); 2180 (C≡C)	83.08 83.27	6.61 6.90	—	10.08 9.73	—	$C_{20}H_{20}O_2Si$
 $(PhOCH_2C{\equiv}C)_2Si{<}^{Vin}_{Me}$	**(4)**	80.0	210 (1)	1.5650	1590 (CH=CH$_2$); 2180 (C≡C)	75.70 75.86	6.45 6.44	—	8.71 8.44	—	$C_{21}H_{20}O_2Si$
 $(PhOCH_2C{\equiv}C)_2Si{<}^{CH_2Cl}_{Me}$	**(5)**	78.0	194 (5)	1.5870	2190 (C≡C)	67.15 67.67	5.96 5.39	—	7.18 7.91	9.59 10.0	$C_{20}H_{19}O_2SiCl$
 $(PhSCH_2C{\equiv}C)_2Si{<}^{Vin}_{Me}$	**(6)**	72.0	Oil		1600 (CH=CH$_2$); 2180 (C≡C)	58.57 58.33	4.31 4.70	29.47 29.91	6.20 6.55	—	$C_{21}H_{20}S_2Si$
 $(PhSCH_2C{\equiv}C)_2Si{<}^{CH_2Cl}_{Me}$	**(7)**	75.3	225—227 (2)	1.5650	2150 (C≡C)	62.00 62.03	4.61 4.94	16.22 16.56	7.00 7.25	8.97 9.17	$C_{20}H_{19}S_2SiCl$
$PhOCH_2C{\equiv}CSi(Me)_2H$	**(8)**	91.9	84—85 (0.5)	1.5176	2130 (Si—H); 2170 (C≡C)	69.61 69.42	7.40 7.40	—	14.38 14.75	—	$C_{11}H_{13}OSi$
$PhSCH_2C{\equiv}CSi(Me)_2H$	**(9)**	77.8	99—100 (0.5)	1.5530	2120 (Si—H); 2160 (C≡C)	64.60 64.03	6.25 6.84	15.33 15.31	13.01 13.61	—	$C_{11}H_{13}SSi$
$(PhOCH_2C{\equiv}C)_4Ge$	**(10)**	74.2	Oil		2190 (C≡C)	72.73 72.39	5.17 4.73	—	12.38 12.15	—	$C_{36}H_{28}O_4Ge$
$(PhSCH_2C{\equiv}C)_4Ge$	**(11)**	86.6	Oil		2180 (C≡C)	65.10 65.36.	4.10 4.26	19.11 19.38	10.31 10.97	—	$C_{36}H_{28}S_4Ge$

Table 2. Parameters of ^{1}H NMR spectra of 3-phenoxy- and 3-phenylthio-1-propynyl substituted silanes and germanes

Compound		δ				J/Hz	
		SiMe (Et)	SiR	XCH$_2$	Ph	HSiMe(Et)	CH$_2$SiH
 $(PhOCH_2C{\equiv}C)_2Si{<}^{Et}_{H}$	**(3)**	0.27 m; 0.94 t	4.26 t	4.60 s	7.07 m	3.2	—
 $(PhOCH_2C{\equiv}C)_2Si{<}^{Vin}_{Me}$	**(4)**	0.29 s	5.94 m	4.50 s	7.04 m	—	—
 $(PhOCH_2C{\equiv}C)_2Si{<}^{CH_2Cl}_{Me}$	**(5)**	0.30 s	2.73 s	4.48 s	7.03 m	—	—
 $(PhSCH_2C{\equiv}C)_2Si{<}^{Vin}_{Me}$	**(6)**	0.24 s	5.92 m	3.52 s	7.30 m	—	—
 $(PhSCH_2C{\equiv}C)_2Si{<}^{CH_2Cl}_{Me}$	**(7)**	0.26 s	2.69 s	3.49 s	7.29 m	—	—
$PhOCH_2C{\equiv}CSi(Me)_2H$	**(8)**	0.19 d	4.07 d	4.59 d	7.09 m	3.7	0.9
$PhSCH_2C{\equiv}CSi(Me)_2H$	**(9)**	0.18 d	4.18 d	3.60 d	7.32 m	4.2	0.9
$(PhOCH_2C{\equiv}C)_4Ge$	**(10)**	—	—	4.38 s	7.05 m	—	—
$(PhSCH_2C{\equiv}C)_4Ge$	**(11)**	—	—	3.34 s	7.50 m	—	—

meters of the ^{13}C NMR spectrum were determined only for compound **4**, δ: 1.50 (Me); 56.24 (OCH_2); 86.79 and 102.78 (C=C); 114.78, 121.36, 129.24, 157.49 (Ph); 135.5 and 135.55 (C≡C). The chemical shift of the methyl carbon atom is negative, which is normal for methylvinylsilanes.[7]

The data on the biological activity of these compounds will be published separately.

Experimental

^1H and ^{13}C NMR spectra were recorded on Jeol FX 900 and Tesla BS 567 A spectrometers for 5 % solutions in $CDCl_3$. IR spectra were measured on a UR-20 spectrophotometer.

50 mL of a 0.1 *M* solution of propargyl phenyl ether or propargyl phenyl sulfide in anhydrous Et_2O was slowly added to a Grignard reagent (0.1 *M* Mg and 0.1 *M* EtBr in 50 mL of anhydrous Et_2O). The reaction mixture was refluxed for 1.5 h, then a calculated amount of an ethereal solution of silane or $GeCl_4$ was added, and the mixture was boiled for an additional 2 h. After cooling, an aqueous solution of 0.1 *M* of NH_4Cl was added, and the ethereal layer was separated, washed with water, and dried with $MgSO_4$. The solvent was removed and the residue was distilled *in vacuo*. Characteristics of the resulting compounds are given in Tables 1 and 2.

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