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# Phenyl(fluoro)chlorodisiloxanes

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**Abstract**—Cohydrolysis of phenyltrichlorosilane with phenyl(fluoro)dichloro- and phenyl(difluoro)-chlorosilanes and thermolysis of the formed siloxanes leading to the formation of phenyl(difluoro)chlorosilane are studied. The scheme of thermal decomposition of disiloxanes possessing fluorine atoms in the 1,3 positions is suggested. The scheme is based on the intermediate formation of an active four-membered cyclic complex closed by the fluorine bridge between the silicon atoms. In agreement with the scheme, no thermolysis of 1,3-diphenyl-1-fluoro-1,3,3-trichlorodisiloxane is observed under the studied conditions.

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Reactions of cohydrolysis of hydrocarbylchlorosilanes are well studied [1–6]. However, similar processes with participation of hydrocarbylhalosilanes containing two different halogen atoms at silicon have not been studied, and the hydrolysis of organosilicon monomers of this type ($PhSiF_2Cl$, $PhSiFCl_2$) is mentioned only in one publication [7].

To fill in this gap, we have studied cohydrolysis of phenyl(fluoro)chlorosilanes $PhSiF_{3-n}Cl_n$ ($n$ = 1, 2) with phenyltrichlorosilane ($n$ = 3). Starting $PhSiF_2Cl$ (**I**) and $PhSiFCl_2$ (**II**) were synthesized by Eq. (1), by disproportionation of equimolar mixture of phenyltrifluorosilane with phenyltrichlorosilane in the presence of aluminum halides ($AlX_3$, X = F, Cl, Br) (for X = Cl, cf. [7]).

$$\mathrm{PhSiF_3} + \mathrm{PhSiCl_3} \xrightleftharpoons{\mathrm{AlX_3}} \mathrm{PhSiF_2Cl} + \mathrm{PhSiFCl_2}. \quad (1)$$

We have found that cohydrolysis of phenyl(fluoro)-chlorosilane monomers **I** and **II** (molar ratio 1:1, 0.5–1 h) leads to the earlier unknown 1,3–diphenyl-1,3-difluoro-1,3-dichloro-disiloxane (**III**) and 1,3-diphenyl-1,1,3-trifluoro-3-chlorodisiloxane (**IV**), as well as to the earlier synthesized 1,3-diphenyltetrafluorodisiloxane (**V**) [7, 8].

Increase in the reaction duration to 7–8 h was followed by the formation, along with disiloxanes **III**–**V**, of oligosiloxane structures among which $PhSiF_2(OSiFPh)OF_2SiPh$, $(PhSiF_2OSiFPh)_2O$ and $(PhSiF_2O\cdot SiFPhO)_2FSiPh$ were detected by the $^{19}F$ and $^{29}Si$ NMR spectroscopy (see the table).

$$n\mathrm{PhSiF_2Cl} + m\mathrm{PhSiFCl_2} + \mathrm{H_2O}$$

$$\xrightarrow{n = 0,\, m = 2} \underset{\textbf{III}}{(\mathrm{PhSiFCl})_2\mathrm{O}} + 2\mathrm{HCl}, \quad (2)$$

$$\xrightarrow{n = 1,\, m = 1} \underset{\textbf{IV}}{\mathrm{PhSiF_2OSiFClPh}} + 2\mathrm{HCl}, \quad (3)$$

$$\xrightarrow{n = 2,\, m = 0} \underset{\textbf{V}}{(\mathrm{PhSiF_2})_2\mathrm{O}} + 2\mathrm{HCl}. \quad (4)$$

Cohydrolysis of $PhSiF_2Cl$ (**I**) and $PhSiCl_3$ gives rise to disiloxane **V**, as well as 1,3-diphenyltetra-chlorodisiloxane (**VI**) and 1,3-diphenyl-1,1-difluoro-3,3-dichlorodisiloxane (**VII**).

$$n\mathrm{PhSiF_2Cl} + m\mathrm{PhSiCl_3} + \mathrm{H_2O}$$

$$\xrightarrow{n = 2,\, m = 0} \underset{\textbf{V}}{(\mathrm{PhSiF_2})_2\mathrm{O}} + 2\mathrm{HCl}, \quad (5)$$

$$\xrightarrow{n = 0,\, m = 2} \underset{\textbf{VI}}{(\mathrm{PhSiCl_2})_2\mathrm{O}} + 2\mathrm{HCl}, \quad (6)$$

$$\xrightarrow{n = 1,\, m = 1} \underset{\textbf{VII}}{\mathrm{PhSiF_2OSiCl_2Ph}} + 2\mathrm{HCl}. \quad (7)$$

As the products of cohydrolysis of $PhSiFCl_2$ and $PhSiCl_3$, 1,3-diphenyl-1,3-difluoro-1,3-dichlorodisiloxane (**III**), 1,3-diphenyltetrachlorodisiloxane (**VI**) and 1,3-diphenyl-1-fluoro-1,3,3-trichlorodisiloxane (**VIII**) were identified.

$$n\mathrm{PhSiFCl_2} + m\mathrm{PhSiCl_3} + \mathrm{H_2O}$$

$$\xrightarrow{n = 2,\, m = 0} \underset{\textbf{III}}{(\mathrm{PhSiFCl})_2\mathrm{O}} + 2\mathrm{HCl}, \qquad (8)$$

$$\xrightarrow{n = 0,\, m = 2} \underset{\textbf{VI}}{(\mathrm{PhSiCl_2})_2\mathrm{O}} + 2\mathrm{HCl}, \qquad (9)$$

$$\xrightarrow{n = 1,\, m = 1} \underset{\textbf{VIII}}{\mathrm{PhSiFClOSiCl_2Ph}} + 2\mathrm{HCl}. \qquad (10)$$

The main product of hydrolysis of $\mathrm{PhSiFCl_2}$ (**II**) is 1,3-diphenyl-1,3-difluoro-1,3-dichloro-disiloxane **III**.

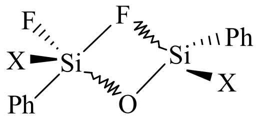
In all of the above reactions the mixed phenyl-(fluoro)chlorosilanes show enhanced reactivity manifested in the predominant formation of symmetric fluorocontaining disiloxanes.

Analysis of the $^{19}$F NMR spectra has shown the absence of any cyclic structures or linear trisiloxanes or higher homologs after short-term passing of atmospheric air through the reaction mixture for 1–2 h, as proved by the absence of signals at –131 to –132 ppm in the studied spectra.

Earlier we have shown that thermolysis of 1,3-diphenyltetrafluorodisiloxane (**V**) leads to cyclic and linear phenylfluorosiloxanes and phenyltrifluorosilane [8].

$$(n + m)(\mathrm{PhF_2Si})_2\mathrm{O} \rightarrow (\mathrm{PhFSiO})_n + \mathrm{PhF_2SiO(PhFSiO)}_m\mathrm{SiF_2Ph} + (n + m)\mathrm{PhSiF_3}, \qquad (11)$$

$$n = 3\text{–}4,\ m = 1\text{–}2.$$



Formation of phenyltrifluorosilane upon heating of disiloxane **V** was noticed earlier [7].

Interestingly, an attempt to isolate disiloxanes **III–V, VII** by vacuum distillation at 1 mm Hg leads to their decomposition with the formation of phenyltrifluoro- and -(difluoro)chlorosilanes.

$$\mathrm{PhSiF_2OSiFClPh} \rightarrow \mathrm{PhSiF_3} + [\mathrm{PhClSi{=}O}], \qquad (12)$$

$$\mathrm{PhSiFClOSiFClPh} \rightarrow \mathrm{PhSiF_2Cl} + [\mathrm{PhClSi{=}O}], \qquad (13)$$

$$\mathrm{PhSiF_2OSiF_2Ph} \rightarrow \mathrm{PhSiF_3} + [\mathrm{PhFSi{=}O}], \qquad (14)$$

$$\mathrm{PhSiF_2OSiCl_2Ph} \rightarrow \mathrm{PhSiF_2Cl} + [\mathrm{PhClSi{=}O}]. \qquad (15)$$

A tentative mechanism of reactions (12)–(14) may include the formation of four-membered complex containing the fluorine bridge between the two silicon atom of the Si–O–Si group.

Decomposition of hexafluorodisiloxane [8] and diphenyltetrafluorodisiloxane [9], apparently, follows the same route.

$$\mathrm{SiF_3OSiF_3} \rightarrow \mathrm{SiF_4} + [\mathrm{F_2Si{=}O}]. \qquad (16)$$

Decomposition by scheme (15) is apparently feasible due to the presence of strong acceptors at the silicon atom ($\mathrm{PhSiF_2}$) which facilitate the intramolecular interaction.

$^{19}$F, $^{29}$Si NMR parameters ($\mathrm{CCl_4}$, 20% v/v; 25°C)

| Compound | $\delta_F$, ppm | $\delta_{Si}$, ppm | $J_{SiF}$, Hz | $\delta_F$, ppm | $\delta_{Si}$, ppm | $J_{SiF}$, Hz |
|---|---|---|---|---|---|---|
| | PhSiF | | | PhSiF | | |
| $\mathrm{PhSiCl_3}$ | – | –1.1 | – | – | – | – |
| $\mathrm{PhSiFCl_2}$ | –113.16 | –18.8 | 326.5 | – | – | – |
| $\mathrm{PhSiF_2Cl}$ | –124.25 | –42.9 | 299.8 | – | – | – |
| $\mathrm{PhSiF_3}$ | –140.94 | –72.8 | 267.0 | – | – | – |
| $\mathrm{PhSiF_2–O–SiCl_2Ph}$ | –136.56 | –73.9 | 256.35 | – | –28.6 | – |
| $\mathrm{PhSiF_2–O–SiFClPh}$ | –136.79 | –74.0 | 260.93 | –121.11 | –48.7 | 291.40 |
| PhSiFCl–O–SiFClPh | –121.00 | –48.7 | 293.00 | –121.03 | –48.7 | 293.00 |
| $\mathrm{PhSiFCl–O–SiCl_2Ph}$ | –120.84 | –48.6 | 296.70 | – | –28.6 | – |
| $\mathrm{PhSiF_2–O–SiF_2Ph}$ | –137.00 | –74.1 | 263.90 | –137.00 | –74.1 | 263.90 |
| $\mathrm{PhSiF_2–O–SiFPh–O–F_2SiPh}$ | –136.94 | – | 263.55 | –132.90 | – | – |
| $\mathrm{(PhSiF_2–O–SiFPh–)_2O}$ | –136.94 | – | 263.55 | –132.77 | – | – |
| $\mathrm{(PhSiF_2–O–SiFPh–O–)_2FSiPh}$[a] | –136.93 | – | 263.55 | –132.75 | – | – |

[a] $\delta_F$ = –132.56 ppm.

We did not observe thermal decomposition of 1,3-diphenyl-1-fluoro-1,3,3-trichlorodisiloxane (**VIII**) nor of the synthesized by us 1,1,1-trimethyl-3-phenyl-3,3-difluorodisiloxane under the studied conditions.

The synthesized phenyl(fluoro)chlorodisiloxanes were identified by $^{19}$F, $^{29}$Si NMR spectroscopy (see the table).

In the IR spectra of compounds **III–VIII** the bands in the region 1060–1100 cm$^{-1}$ characteristic of the Si–O–Si antisymmetric stretching vibrations, at 895, 920 cm$^{-1}$ characteristic of the $SiF_2$ and SiF fragments, 695–700, 715–720, 1110–1130, 1415, 1590 cm$^{-1}$ (bending and stretching vibrations of the Si–$C_6H_5$ bond), and bands at 450–470 and 500–570 cm$^{-1}$ belonging to the C–Cl bond vibrations are present. The position of the absorption maxima corresponding to vibrations of these bonds is constant in frequency and independent on the substituents at the silicon atom (chlorine or fluorine atoms) [10].

## EXPERIMENTAL

$^{19}$F and $^{29}$Si NMR spectra were registered on a Bruker DPX 400 instrument with working frequencies 376.47 ($^{19}$F) and 79.49 MHz ($^{29}$Si) in $CCl_4$, internal reference for $^{29}$Si, TMS, for $^{19}$F, $CFCl_3$. IR spectra were recorded on a Specord IR 75 spectrometer in the range of 400–4000 cm$^{-1}$ from thin film. Electron ionization mass spectra were taken on a SHIMADZU GCMS-QP5050A mass spectrometer, injector temperature 200–250°C, gas-carrier helium, detector temperature 200°C, quadruple mass analyzer, energy of electrons 70 eV.

Mixed phenyl(fluoro)chlorosilanes $PhSiCl_nF_{3-n}$ with $n = 1, 2$ were prepared by disproportionation of $PhSiF_3$ with $PhSiCl_3$ in the presence of aluminum halides (cf. [7]). $PhSiFCl_2$: bp 163–166ºC, $n_D$ 1.4854 [cf. 13–15]. Mass spectrum, $m/z$ ($I$, %) ion: 194 (100) $[M]^{\bullet+}$; 175 (1) $[M - F]^+$; 159 (92) $[M - Cl]^+$; 158 (23); 133 (3); 131 (6); 117 (41) $[M - Ph]^+$; 112 (30) $[PhCl]^{\bullet+}$; 107 (7); 82 (9) $[SiClF]^+$; 77 (83) $[Ph]^+$; 76 (26); 75 (16); 74 (25); 63 (9) $[SiCl]^+$; 51 (99); 50 (88); 47 (72) $[SiF]^+$; 39 (20); 38 (17).

**Mild cohydrolysis of phenyl(fluoro)chlorosilanes (I, II).** Through the mixture of 1.80 g (0.01 mol) of phenyl(difluoro)chlorosilane and 1.95 g (0.01 mol) of phenyl(fluoro)dichlorosilane atmospheric air was bubbled during 30 min and the mixture was analyzed by the $^{19}$F and $^{29}$Si NMR method (see the table).

Reactions of phenyl(difluoro)chlorosilane and phenyl(fluoro)dichlorosilane with phenyltrichlorosilane were performed similarly.

Thermolysis of phenyl(fluoro)chlorodisiloxanes was performed in sealed ampules in the argon atmosphere at 175–225ºC during 1.5–2 h. The formed phenyltrifluorosilane $PhSiF_3$, bp 100–101.5ºC, $n_D$ 1.4110 (cf. [11]) and phenyl(difluoro)chlorosilane $PhSiF_2Cl$, bp 132–135ºC, $n_D$ 1.4579 (cf. [12–14]) were distilled off and identified by the $^{19}$F and $^{29}$Si NMR (see the table).

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