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Phenyl(trimethylsiloxy)fluorosiloxanes $PhSi(OSiMe_3)_nF_{3-n}$

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Abstract—The siloxane bond splitting reaction in hexamethyldisiloxanes $PhSiCl_nF_{3-n}$ was studied.

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Many examples of the siloxane bond splitting reaction induced by organylhalosilanes have been studied. As a rule, they proceed in the presence of a catalysts, at high temperature (200–250°C or higher) or increased pressure [1].

We investigated the reaction of splitting of the siloxane bond in hexamethyldisiloxanes $PhSiCl_nF_{3-n}$ (n = 0–3). The mixed phenyl(chloro)fluorosilanes with n = 1–2 were obtained by disproportionation of $PhSiF_3$ with $PhSiCl_3$ in the presence of aluminum halides.

$$PhSiF_3 + PhSiCl_3 \rightarrow PhSiClF_2 + PhSiCl_2F. \quad (1)$$

We have found that at room temperature hexamethyldisiloxane (HMDS) is not split by phenyltrichlorosilane. In contrast, phenyltrifluorosilane under the same conditions causes the rupture of the ≡Si–O–Si≡ group in HMDS in 6–8 h [2].

Noteworthy, phenyl(chloro)difluorosilane (PCDFS) splits the Si–O bond practically quantitatively in 30–60 min to afford trimethylchlorosilane and 1,1,1-trimethyl-3-phenyl-3,3-difluorosiloxane by the following scheme:

$$PhSiClF_2 + Me_3SiOSiMe_3 \rightarrow PhSi(OSiMe_3)F_2 + Me_3SiCl. \quad (2)$$

Reaction of PCDFS with excess HMDS (molar ratio 1:1.5 at 25°C) does not change the yield and composition of the products of reaction (2). This suggests that the formed fluorosiloxane (I) under these conditions does not split the ≡Si–O–Si≡ group (that is, no reaction occurs at the Si–F bond).

Reaction of phenyl(dichloro)fluorosilane (PDCFS) with HMDS (14 h, 25°C) leads to 1,1,1-trimethyl-3-phenyl-3-chloro-3-fluorosiloxane having an asymmetric silicon atom in 55–60% yield:

$$PhSiCl_2F + (Me_3Si)_2O \rightarrow PhSiClF(OSiMe_3) + Me_3SiCl. \quad (3)$$

The formation of 7–15% 1,1,1,5,5,5-hexamethyl-3-phenyl-3-fluorosiloxane is observed after 24–48 h at 25°C.

$$PhSiFCl(OSiMe_3) + (Me_3Si)_2O \rightarrow PhSiF(OSiMe_3)_2 + Me_3SiCl. \quad (4)$$

When performing the reaction of HMDS with the mixture of phenylfluorochlorosilanes $PhSiCl_nF_{3-n}$ (n = 1–2) (in the ratio of 1:1:1 at 25°C) it was found that $PhSiF_2Cl$ reacts at least 4-5 times faster than $PhSiFCl_2$, and that the reactivity of $PhSiFCl_2$ in this reaction is higher than that of $PhSiFCl(OSiMe_3)$ also 4–5 times; apparently, in the latter case it is due to steric effect of the trimethylsiloxy group.

No experimental evidences on participation of $PhSiF_3$ in splitting of the siloxane bond were obtained when performing the reaction of HMDS with the mixture of $PhSiF_2Cl$ and $PhSiF_3$, which suggests much higher reactivity of $PhSiF_2Cl$ relative to $PhSiF_3$ in this reaction.

The reaction of $PhSiF_2Cl$ with hexaethyldisiloxane (molar ratio 1:1 at 25°C, 48–72 h) leads to formation of 1,1,1-triethyl-3-phenyl-3,3-difluorosiloxane in 10–15% yield.

Note, that, while the ^1H, ^{13}C NMR spectroscopy is principally unsuitable for identification of the above and similar reaction mixtures, the ^{19}F, ^{29}Si NMR spectra are quite practical for this purpose, in

Table 1. ^{1}H, ^{19}F, ^{29}Si NMR spectra of phenyl(trimethylsiloxy)fluorosilanes $PhSi(OSiMe_3)_nF_{3–n}$ (CCl_4, 20% v/v; 20°C)[a]

Compound	δ_H, ppm	δ_{Si}, ppm		δ_F, ppm	$J_{Si–F}$, Hz
	Me_3SiO	PhSi	Me_3SiO		
$PhSiF_3$	–	–72.8	–	–140.94	267.0
$PhSiF_2Cl$	–	–42.9	–	–124.25	299.8
$PhSiFCl_2$	–	–18.8	–	–113.10	326.5
$PhSiFClOSiMe_3$	0.21	–50.5	16.1	–120.04	288.4
$PhSiF_2OSiMe_3$	0.19	–73.7	16.9	–136.23	256.3
$PhSiF(OSiMe_3)_2$	0.15	–75.2	11.6	–131.88	–247.2

[a] Aromatic protons resonate at 7.30–7.65 ppm.

Table 2. Comparison of ^{19}F, ^{29}Si NMR spectra parameters for derivatives of phenyltrifluorosilanes $PhSiF_{3–n}X_n$

X	*n*	δ_{Si}, ppm	δ_F, ppm	$J_{Si–F}$, Hz
OEt	0	–72.6	–140.9	267.3
	1	–67.0	–140.7	265.0
	2	–61.4	–142.4	262.0
OAc	0	–72.6	–140.9	267.3
	1	–65.9	–141.1	268.5
	2	–62.9	–142.2	270.0
$OSiMe_3$	0	–72.6	–140.9	267.3
	1	–73.7	–136.2	256.3
	2	–75.2	–131.9	247.2

Table 3. Mass-spectra

Ion	*m/z* (intensity, % to maximum)		
	$PhSiF_2OSiMe_3$	$PhSiF(OSiMe_3)_2$	$PhSiF_2OSiEt_3$
$[M]^+$	232(5)	–	274(1)
$[M – R]^+$	217(100)	287(67)	245(100)
$[M – R – RH]^+$	201(13)	271(2)	215(3)
$[M – 3R]^+$	187(4)	257(1)	187(19)
$[M – OSiR_3]^+$	143(5)	213(2)	143(15)
$[PhSiFR]^+$	139(4)	139(3)	–
$[PhSiR_2]^+$	135(2)	135(100)	–
$[Ph]^+$	77(11)	77(9)	77(13)

particular, the (^{19}F–^{29}Si) coupling constant along with the earlier reported [3] trends for chemical shifts of these nuclei for the series of the alkoxy and acetoxysubstituted phenylfluorosilanes.

It is evident from Table 2 that, unlike alkoxy and acetoxy derivatives, replacement of fluorine atoms in phenyltrifluorosilanes by trimethylsiloxy group results in an increase of the shielding of ^{29}Si (2–14 ppm), downfield shift (up to 10 ppm) of the fluorine signals, and a significant decrease of the (^{19}F–^{29}Si) coupling constant (up to 20 Hz).

EXPERIMENTAL

IR spectra were taken on a Specord IR-75 spectrometer in thin layer in the range of 400–4000 cm$^{–1}$. ^{1}H, ^{19}F and ^{29}Si NMR spectra were registered on a Bruker DPX 400 spectrometer at working frequencies 400 (^{1}H), 376.47 (^{19}F) and 79.49 MHz (^{29}Si) in CCl_4, internal standard for ^{1}H, ^{29}Si (HMDS), for ^{19}F ($CFCl_3$). Electron impact (70 eV) mass spectra were obtained on a SHIMADZU GCMS-QP5050A chromatomass spectrometer, gas-carrier helium, temperature of injector 200–250°C, temperature of detector 200°C, quadrupole mass analyzer.

Mixed phenyl(chloro)fluorosilanes $PhSiCl_nF_{3–n}$ with $n = 1–2$ were obtained by disproportionation of $PhSiF_3$ with $PhSiCl_3$ (cf. [4]).

Reaction of phenyl(chloro)difluorosilane with hexamethyldisiloxane. Mixture of 1.80 g (0.01 mol) of phenyl(chloro)difluorosilane and 1.62 g (0.01 mol) of hexamethyldisiloxane was kept at room temperature for 15–30 min and analyzed by the method of ^{1}H, ^{19}F and ^{29}Si NMR spectroscopy (Tables 1–2). After distillation of 0.9 g (98%) of trimethylchlorosilane with bp 57°C and vacuum distillation of the residue, 2.15 g (92.0%) of phenyl(trimethylsiloxy)difluorosilane with bp 60–62°C (5 mm Hg) was isolated, n_D^{20} 1.4260. IR spectrum (ν, cm$^{–1}$): $PhSiF_2OSiMe_3$: 3075, 3055 ν_{sym}(C–H), $\nu(C_6H_5)$; 2965, 2895 ν_{asym}(C–H), $\nu(CH_3)$; 1590, 1490 ν(C=C), $\nu(C_6H_5)$; 1420, 1130 $\nu(Si–C_{ar})$, $\nu(Si–C_6H_5)$; 1250 δ(Si–C), $\delta(Si-CH_3)$; 1090 ν_{asym}(Si–O); 905, 870 ν(Si–F), $\nu(SiF_2)$; 830, 745 ν(Si–C), $\nu[Si(CH_3)_3]$; 730; 690 δ_1(C–H), $\delta_1(C_6H_5)$; 640 ν_{sym}(Si–O).

The reactions of phenyl(chloro)difluorosilane with hexaethyldisiloxane and of phenyl(dichloro)fluorosilane with hexamethyldisiloxane were performed similarly. The obtained compounds are very sensitive to heating and air moisture.

The data of mass spectrometry analysis of phenyl(trimethylsiloxy)fluorosiloxanes $PhSi(OSiMe_3)_nF_{3-n}$ are summarized in Table 3. IR spectrum (ν, cm^{-1}): $PhSiFCl(OSiMe_3)$: 3075, 3055 ν_{sym}(C–H), $\nu_{sym}(C_6H_5)$; 2965, 2895 ν_{asym}(C–H), $\nu_{asym}(CH_3)$; 1590, 1490 ν(C=C), $\nu(C_6H_5)$; 1420, 1120 $\nu(Si\text{-}C_{ar})$, $\nu(Si–C_6H_5)$; 1250 δ(Si–C), $\delta(Si–CH_3)$; 1060 ν_{asym}(Si–O); 895 ν(Si–F); 835, 750 ν(Si–C), $\nu[Si(CH_3)_3]$; 730; 690 δ_1(C–H), $\delta_1(C_6H_5)$; 610 ν_{sym}(Si–O); 535 ν(Si–Cl).

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