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# Phenyl(acyloxy)fluorosilanes $C_6H_5Si(OCOR)_nF_{3-n}$ ($n = 1, 2$) and Phenyl(acyloxy)fluorochlorosilanes $C_6H_5Si(OCOR)FCl$

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**Abstract**—The method of synthesis of the hitherto unknown class of organosilicon compounds, phenyl(acyloxy)fluorosilanes $C_6H_5Si(OCOR)_nF_{3-n}$ ($n = 1, 2$) and phenyl(acyloxy)fluorochlorosilanes $C_6H_5Si(OCOR)FCl$ in up to 91% yield has been developed based on the reaction of phenyl(fluoro)chlorosilanes $C_6H_5SiCl_nF_{3-n}$ ($n = 1, 2$) with trimethylsilyl esters of carboxylic acids $Me_3SiOC(O)R$ [R = H, $CH_3$, $CF_3$, $CCl_3$, $ClCH_2$, $BrCH_2$, $CH_2=CHCH_3$, $CH_2=CHPh$, $CH(CH_3)=CH_2$, Ph].

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Phenyl(fluoro)chlorosilanes, $PhSiF_{3-n}Cl_n$ [$n = 1$ (**I**), 2 (**II**)] are known to react with trimethylacetoxysilane even at room temperature to form the earlier unknown phenyl(acetoxy)difluoro- and phenyl(diacetoxy)fluorosilanes in a quantitative yield [1]. It was also found that phenyltrifluorosilane behaves differently, and upon reflux for 7–14 h did not split the Si–O–C group in trimethylacyloxysilanes. However, phenyl(aciloxy)difluorosilanes are formed at keeping the reaction mixture for 2–4 weeks at 20°C, although in a very low yield (<5–8%).

In continuation of the investigation of reactions of phenyl(fluoro)chlorosilanes with trimethyl(acyloxy) silanes we have developed a preparative method of the synthesis of phenyl(acyloxy)fluorosilanes $C_6H_5Si\cdot(OCOR)_nF_{3-n}$ [R = H, $CH_3$, $CF_3$, $CCl_3$, $ClCH_2$, $BrCH_2$, $CH_2=CHCH_3$, $CH_2=CHPh$, $CH(CH_3)=CH_2$, Ph]) in 60–91% yield. Thus, the reaction of phenyl(difluoro)chlorosilane with trimethyl(acyloxy)silanes (molar ratio 1:1, 20°C, 0.5–1 h) affords phenyl(acyloxy)difluorosilanes, whereas in the reaction of phenyl(fluoro)dichlorosilane with trimethyl(acyloxy)silanes with the molar ratio 1:2 at 20°C for 7–8 h only phenyl(diacyloxy)fluoroilanes are formed.

$$\begin{tikzcd}
 & PhSiF_{3-n}Cl_n + n\,RC(O)OSiMe_3 \arrow[dl, "n = 1"'] \arrow[dr, "n = 2"] & \\
PhSiF_2OC(O)R + Me_3SiCl & & PhSiF[OC(O)R]_2 + 2\,Me_3SiCl
\end{tikzcd}$$

Carrying out the latter reaction with the molar ratio of the reagents of 1:1 at 20°C over 2–3 h leads mainly to the earlier unknown phenyl(acyloxy)fluorochlorosilanes possessing a chiral silicon atom. Phenyl(diacyloxy)fluorosilanes have also been identified.

$$PhSiFCl_2 + RC(O)OSiMe_3$$
$$\rightarrow PhSiFClOC(O)R + PhSiF[OC(O)R]_2 + Me_3SiCl.$$

Low-boiling trimethylchlorosilane formed in these reactions is easily removed from the reaction mixture by distillation.

From the GLC and $^{19}F$ NMR spectroscopy data, the rate of the reaction is determined by the number of chlorine atoms ($n$) in the starting phenyl(fluoro) chlorosilanes **I** and **II**, and it decreases in the series of compounds $PhSiF_2Cl > PhSiFCl_2 > PhSiCl_3$. This is indicative of an increased ionic character of the Si–Cl bond in $PhSiF_2Cl$ due to the presence of two fluorine atoms in the molecule.

The yield of the products depends on the nature of the acyloxy group in the starting trimethyl(acyloxy)silanes. In the reaction of $PhSiF_2Cl$ with $Me_3SiOCOR$ (R = Me, Ph, $CH_2Br$, H, $CH_2Cl$, $CCl_3$, $CF_3$) with the molar ratio 1:1 at 20°C the yield of the products after 52 h amounts to 92, 90, 76, 70, 61, 45, and 40%, respectively. The decrease in the yield is apparently due to the decrease in the nucleophilicity of the acyloxy group with the increase of electronegativity of substituent R in this order.

Yields, $^{19}$F, $^{29}$Si NMR spectral parameters of phenyl(acyloxy)fluorosilanes ($CCl_4$, 20 v/v%, 20°C), and p$K_a$ values of acids RCOOH

| $PhSiHlg_2OC(O)R$ | Yield, % | p$K_a$ RCOOH | $\delta_{Si}$, ppm | $\delta_F$, ppm | $J_{SiF}$, Hz |
|---|---|---|---|---|---|
| $PhSiF_2OC(O)H$ | 69.7 | 3.45 | –65.6 | –140.07 | 271.2 |
| $PhSiF_2OC(O)CH_3$ | 91.2 | 4.75 | –65.9 | –141.07 | 268.5 |
| $PhSiF_2OC(O)C(CH_3)_3$ | – | 5.05 | – | –141.10 | – |
| $PhSiF_2OC(O)Ph$ | 89.8 | 4.19 | –64.5 | –140.62 | 268.6 |
| $PhSiF_2OC(O)CH_2Cl$ | 61.2 | 2.85 | –66.0 | –140.49 | 272.0 |
| $PhSiF_2OC(O)CH_2Br$ | 75.6 | 2.90 | –66.1 | –140.59 | 271.5 |
| $PhSiF_2OC(O)CCl_3$ | 45.3 | 0.70 | –66.2 | –140.19 | 276.4 |
| $PhSiF_2OC(O)CF_3$ | 40.1 | 0.23 | –66.0 | –139.96 | 276.6 |
| $PhSiF_2OC(O)CCH_3{=}CH_2$ | 74.0 | 4.66 | –65.1 | –140.90 | 268.0 |
| *(E)*-$PhSiF_2OC(O)CH{=}CHCH_3$ | 73.3 | 4.69 | –64.9 | –140.71 | 266.9 |
| *(E)*-$PhSiF_2OC(O)CH{=}CHPh$ | 73.0 | 4.44 | –64.8 | –140.67 | 267.4 |
| $PhSiFClOC(O)H$ | 44.1 | 3.45 | –39.3 | –128.55 | 298.7 |
| $PhSiFClOC(O)CH_3$ | 44.2 | 4.75 | –39.8 | –129.98 | 296.4 |
| $PhSiFClOC(O)C(CH_3)_3$ | – | 5.05 | – | –130.09 | – |
| $PhSiFClOC(O)Ph$ | 35.7 | 4.19 | –38.2 | –129.61 | 296.0 |
| $PhSiFClOC(O)CH_2Cl$ | 40.1 | 2.85 | –39.2 | –129.30 | 298.7 |
| $PhSiFClOC(O)CH_2Br$ | 36.3 | 2.90 | –39.3 | –129.30 | 298.7 |
| $PhSiFClOC(O)CCl_3$ | 27.0 | 0.70 | –38.4 | –128.39 | 304.0 |
| $PhSiFClOC(O)CF_3$ | 19.9 | 0.23 | –38.0 | –128.57 | 303.4 |
| $PhSiFClOC(O)CCH_3{=}CH_2$ | 58.7 | 4.66 | –38.9 | –129.81 | 295.4 |
| (*E*)-$PhSiFClOC(O)CH{=}CHCH_3$ | 40.7 | 4.69 | –38.9 | –129.83 | 294.9 |
| (*E*)-$PhSiFClOC(O)CH{=}CHPh$ | 40.1 | 4.44 | –38.7 | –129.75 | 294.5 |
| $PhSiF(OC(O)H)_2$ | 75.8 | 3.45 | –61.7 | –140.72 | 274.3 |
| $PhSiF[OC(O)CH_3]_2$ | 92.1 | 4.75 | –62.9 | –142.21 | 270.0 |
| $PhSiF[OC(O)Ph]_2$ | 81.2 | 4.19 | –59.9 | –141.70 | 270.0 |
| $PhSiF[OC(O)CH_2Cl]_2$ | 72.3 | 2.85 | –62.5 | –141.43 | 275.5 |
| $PhSiF[OC(O)CH_2Br]_2$ | 73.4 | 2.90 | –62.5 | –141.51 | 275.5 |
| $PhSiF[OC(O)CCl_3]_2$ | 41.9 | 0.70 | –61.4 | –140.69 | 265.0 |
| $PhSiF[OC(O)CCH_3{=}CH_2]_2$ | 75.1 | 4.66 | –61.3 | –142.06 | 269.3 |
| (*E*)-$PhSiF[OC(O)CH{=}CHCH_3]_2$ | 71.2 | 4.69 | –61.1 | –142.04 | 268.2 |
| (*E*)-$PhSiF[OC(O)CH{=}CHPh]_2$ | 71.2 | 4.44 | –60.8 | –141.75 | 269.0 |

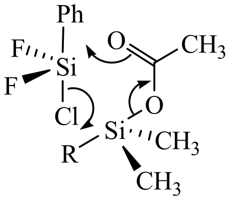
Yields, parameters of NMR spectra of phenyl(acyloxy)fluorosilanes, and p$K_a$ values of the corresponding acids are given in the table.

In the reaction of $PhSiF_2Cl$ with trimethylsilyl esters of α,β-unsaturated carboxylic acids $Me_3SiOCOR$ [R = C(Me)=$CH_2$, CH=CHMe, CH=CHPh] under similar conditions the yield of the formed phenyl(acyloxy)fluorosilanes is practically identical (73–74%), in agreement with their p$K_a$ values (4.66; 4.69; 4.44).

In the reaction of $PhSiFCl_2$ with $Me_3SiOCOR$ [R = C(Me)=$CH_2$, H, CH=CHMe, CH=CHPh, $CH_2Cl$, Ph, $CH_2Br$, $CCl_3$] with the molar ratio of the reagents 1:1

at 20°C phenyl(diacyloxy)fluorosilanes were identified. Trimethylsilyl ester of trifluoroacetic acid does not acylate phenyl(fluoro)dichlorosilane.

In the reactions with trimethyl(pivaloyloxy)silane, acyloxysilanes $C_6H_5Si(OCOCMe_3)F_2$ and $C_6H_5Si\cdot(OCOCMe_3)FCl$ are formed only in trace amounts, and the products of substitution of two chlorine atoms in $PhSiFCl_2$ were not detected, although pivalic acid is weaker than acetic acid (p$K_a$ 5.05 and 4.75, respectively). Therefore the rate and the course of the reaction are affected not only by electronegativity but also by the volume of substituent R since the values of $E_s$ for R = Me and $CMe_3$ are equal to 0.00 and –1.54, respectively.



The mechanism of the studied reactions apparently includes the formation of the transition state in which the silicon atom is pentacoordinate.

The synthesized phenyl(acyloxy)difluorosilanes disproportionate after long standing at room temperature or at heating. The effect of the nature of the alkyl or haloalkyl substituent R on the rate of this reaction is negligible. Phenyl(diacyloxy)fluorosilanes are more stable and only partly disproportionate at the vacuum distillation.

The structure of all synthesized compounds is proved by the data of $^1H$, $^{13}C$, $^{19}F$, $^{29}Si$ NMR spectroscopy.

As in the case of phenyl(alkoxy)fluorosilanes $PhSi(OR)_nF_{3-n}$ [2], the replacement of the fluorine atoms by acyloxy group [$PhSiF_2OAc \rightarrow PhSiF(OAc)_2$] also results in some shielding of the silicon atom (by 3–5 ppm) and shielding of the fluorine atom (by ~1 ppm), and to the increase in the coupling constant ($^{29}Si–^{19}F$) by 1–11 Hz. These changes of the NMR parameters are parallel to those caused by the decrease in the contribution of the intra– and intermolecular interactions F–Si←O=C in going from difluorides to monofluorides.

The replacement of the fluorine atom of phenyl(acyloxy)difluorosilane by chlorine atom expectedly results in strong deshielding of the silicon atom (25–27 ppm), fluorine atom (11 ppm) and the increase in the coupling constant $^{29}Si–^{19}F$ (27–28 Hz).

Earlier a reciprocal relationship between the value of $J_{SiF}$ and electronegativity of the substituent was suggested [3–4]. However, the values of $J_{SiF}$ in the series of the obtained compounds do not obey this relationship since the largest coupling constant is observed for acyloxyfluorochlorosilanes rather than diacyloxyfluorosilanes.

## EXPERIMENTAL

$^1H$, $^{19}F$, $^{29}Si$ NMR spectra were recorded on a Bruker DPX 400 (400 MHz) instrument in $CCl_4$, internal reference for $^1H$, $^{29}Si$ TMS, for $^{19}F$ $CFCl_3$.

Mixed phenyl(chloro)fluorosilanes $C_6H_5SiCl_nF_{3-n}$ ($n$ = 1–2) were obtained by conproportionation of $PhSiF_3$ with $PhSiCl_3$ [5]. Trimethylsilyl esters of the corresponding acids were obtained by the known procedure [6].

**Reaction of phenyl(chloro)difluorosilane with trimethylacetoxysilane.** The mixture of 1.8 g (0.01 mol) of phenyl(chloro)difluorosilane and 1.3 g (0.01 mol) of trimethylacetoxysilane was kept at room temperature for 15–30 min. The formed trimethylchlorosilane was distilled off under reduced pressure (10 mm Hg), the residue was analyzed by $^1H$, $^{19}F$ and $^{29}Si$ NMR spectroscopy (see the table).

The reactions of phenyl(chloro)difluorosilane and phenyl(dichloro)fluorosilane with trimethylsilyl esters of carboxylic acids $Me_3SiOCOR$ [R = H, $CH_3$, $CF_3$, $CCl_3$, $ClCH_2$, $BrCH_2$, $CH_2$=$CHCH_3$, $CH_2$=CHPh, $CH(CH_3)$=$CH_2$, Ph] were performed similarly (see the table). The obtained compounds are very sensitive to heating and air moisture.

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