

LETTERS
TO THE EDITORAcetoxy(fluoro)(phenyl)silanes $C_6H_5Si(OCOCH_3)_nF_{3-n}$

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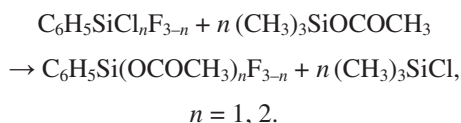
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Received July 31, 2008

DOI: 10.1134/S1070363209010319

Organyl(acetoxy)fluorosilanes have not yet been known. The only exception was acetoxy(difluoro)(vinyl)silane $CH_2=CHSi(OCOCH_3)F_2$ we earlier prepared by the reaction of difluoro(trimethylsilylamino)(vinyl)silane $CH_2=CHSi(NHSiMe_3)F_2$ with acetic acid but not studied in detail [1].

We have developed an original method of synthesis of acetoxy(fluoro)(phenyl)silanes $C_6H_5Si(OCOCH_3)_nF_{3-n}$ by the reaction of chloro(fluoro)(phenyl)silanes $C_6H_5SiCl_nF_{3-n}$ with acetoxytrimethylsilane at room temperature, according to the following scheme:



As can be seen, it is only the Si–Cl bond that is involved in reaction. As a result, $PhSiF_3$ ($n = 0$) does not react with acetoxytrimethylsilane even under reflux.

Earlier we reported [1] that the replacement of a fluorine atom at silicon by an alkoxy group in $(RO)_nSiF_{4-n}$ results in a downfield shift of the ^{29}Si and ^{19}F resonance up to 20 ppm and 6 ppm, respectively, and an increase of the ^{19}F – ^{29}Si coupling constants up to 20 Hz. However, in the case of alkoxy(fluoro)(phenyl)silanes $PhSi(OR)_nF_{3-n}$ the same replacement shifts the ^{29}Si resonance downfield (~10 ppm) and the ^{19}F resonance upfield (~1–2 ppm) and reduces the ^{19}F – ^{29}Si coupling constants (~5 Hz).

A similar variation of the chemical shifts is observed for acetoxy(fluoro)(phenyl)silanes $C_6H_5Si(OCOCH_3)_nF_{3-n}$ (see table), though the ^{19}F – ^{29}Si coupling constants slightly increase.

Below we present 1H , ^{19}F , and ^{29}Si NMR parameters for phenyl(acetoxy)fluorosilanes $C_6H_5Si(OCOCH_3)_nF_{3-n}$ (aromatic protons signals are observed at 7.30–7.65 ppm).

Compound	$PhSiF_2OAc$	$PhSiF(OAc)_2$
δ_H OAc, ppm	2.04	1.92
δ_{Si} , ppm	–65.9	–62.9
δ_F , ppm	–141.07	–142.21
J_{Si-F} , Hz	268.5	270.0

Mixed chloro(fluoro)(phenyl)silanes $C_6H_5SiCl_nF_{3-n}$ with $n = 1, 2$ were prepared by disproportionation of $PhSiF_3$ with $PhSiCl_3$ (cf. [3]).

Reaction of chloro(difluoro)(phenyl)silane with acetoxytrimethylsilane. A mixture of 1.8 g of chloro(difluoro)(phenyl)silane and 1.3 g of acetoxytrimethylsilane was kept at room temperature for 15–30 min and analyzed by 1H , ^{19}F , and ^{29}Si NMR spectroscopy.

The reaction of dichloro(fluoro)(phenyl)silane with acetoxytrimethylsilane was performed similarly. The obtained compounds are highly sensitive to heat and moisture.

The 1H , ^{19}F , and ^{29}Si NMR spectra were registered on a Bruker DPX 400 instrument (400 MHz) in $CDCl_3$, internal standards HMDS (1H , ^{29}Si) and $CFCl_3$ (^{19}F).

ACKNOWLEDGMENTS

This work was supported by the Council for Grants of the President of the Russian Federation (project no. NSh-4575.2006.3).

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