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LETTERS TO THE EDITOR

Acetoxy(fluoro)(phenyl)silanes $C_6H_5Si(OCOCH_3)_nF_{3-n}$

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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)(phenylsilanes $C_6H_5Si\cdot Cl_nF_{3-n}$ with acetoxytrimethylsilane at room temperature, according to the following scheme:

$$C_6H_5SiCl_nF_{3-n} + n\,(CH_3)_3SiOCOCH_3 \rightarrow C_6H_5Si(OCOCH_3)_nF_{3-n} + n\,(CH_3)_3SiCl,$$
$$n = 1, 2.$$

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 $(RO)_n\cdot SiF_{4-n}$ 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 ^{1}H, ^{19}F, and ^{29}Si NMR parameters for phenyl(acetoxy)fluorosilanes $C_6H_5Si\cdot(OCOCH_3)_nF_{3-n}$ (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 ^{1}H, ^{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 ^{1}H, ^{19}F, and ^{29}Si NMR spectra were registered on a Bruker DPX 400 instrument (400 MHz) in $CDCl_3$, internal standards HMDS (^{1}H, ^{29}Si) and CFCl (^{19}F).

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