ELIMINATION AND REARRANGEMENT REACTIONS
IN SYNTHESIS OF TRIALKYL(FLUOROMETHYL)SILANES

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The methods for the synthesis of triorganyl(halomethyl)silanes $R_nSiCH_2X$ ($X = Cl$, Br, I) and their chemical properties have been studied well [1]. However, the analogous compounds with $X = F$ are difficultly available. They could be obtained only via the corresponding organomercury compounds [2, 3]. In a search for a convenient synthesis of alkyl(fluoromethyl)silanes we studied the exchange reaction of the chloromethyl- and iodomethylsilanes with anhydrous KF in various solvents. The analogous reaction between KF and a (halomethyl) silane $XCH_2SiH_3$ ($X = Cl$, I) led to decomposition products, and specifically $SiF_4$ and $CH_2F_2$ [4].

Only the chlorine atoms, attached to silicon, exchange when (chloromethyl)chlorosilanes are reacted with KF in nitrobenzene medium.

$$Cl_{3-n}(CH_3)_nSiCH_2Cl \xrightarrow{KF} F_{3-n}(CH_3)_nSiCH_2Cl$$

$n = 0, 2$

This reaction, which gives the corresponding $F_{3-n}(CH_3)_nSiCH_2Cl$ in 50–70% yield, proceeds only in the presence of traces of moisture. The starting chlorosilanes are regenerated in a completely anhydrous medium, even when the reaction is carried out in an autoclave (solvent = nitromethane, 10 atm. 150°C).

Exchange of the halogen atoms in the halomethyl radical also fails to occur when the reaction is run with triorganyl(halomethyl)silanes. Thus, the reaction of triethyl(chloromethyl)silane with KF in DMFA medium gave triethylfluorosilane and diethyl–n-propylfluorosilane in low yield. Triethyl(iodomethyl)silane proves to be more reactive here, but only to give the indicated reaction products in larger yield.

$$2(C_2H_5)_3SiCH_2X + 2KF_{DMFA} \rightarrow (C_2H_5)_2SiF + C_2H_5(C_2H_5)_2SiF$$

$X = Cl, I$

The reaction of KF with trimethyl(iodomethyl) silane proceeds in a similar manner, but here the products, besides trimethylfluorosilane and dimethylidemethylfluorosilane, are three disiloxanes.

$$\frac{(CH_3)_3SiCH_2I_{DMFA}}{DMFA} \rightarrow (CH_3)_2SiF + CH_3H(CH_3)_2SiF + [(CH_3)_3Si]_2O$$

The use of DMSO as the solvent does not change the direction of the reaction, but here the yield of the disiloxanes increases substantially. The same as in the previous case, the formation of the disiloxanes is probably associated with the structure of the transition state, in which fluorine ions, solvated by the oxygen-containing solvent, take part [5].

Trimethylfluorosilane and ethylidemethylfluorosilane are the main products of the reaction if it is carried out in hexamethyldiphosphorus triamide (HMPA) medium, and potassium bifluoride and the fluoride are
the fluorinating agents. The starting (CH₃)₂SiCH₂I is recovered unchanged if acetonitrile, ethylene glycol, or its dimethyl ether is used as the solvent.

As a result, only elimination and rearrangement products are formed when trialkyl(halomethyl)silanes are treated with KF in aprotic ionizing solvents (DMFA, DMSO, HMPA). Analogous processes were observed when trialkyl-(α-chloroalkyl)silanes, containing a chlorine atom in a secondary or tertiary alkyl radical, are reacted with SbF₅ and BF₃ [6, 7]. Together with this, (CH₃)₂SiCH₂Cl does not react with SbF₅ [7].

When (CH₃)₃SiCH₂I is heated in DMFA medium for 24 h at 120 °C it fails to undergo noticeable change (based on the GLC data). This indicates that the formed trialkylfluorosilanes are not the fluorination products of the corresponding trialkyliodosilanes, which would be formed if the starting (CH₃)₃SiCH₂I rearranged. The (CH₃)₃SiF and C₂H₅(CH₃)₂SiF isolated by us are also not the transformation products of (CH₃)₂SiCH₂F, since the latter is not inclined toward thermal rearrangement [2]. It may be assumed that the intramolecular rearrangement of the trialkyl(halomethyl)silanes and the elimination process are associated with the nucleophilic action of the fluorine ions on the silicon atom, since it is known that F⁻ in aprotic solvents is a strong base [5]. The small size of the fluorine ion facilitates its nucleophilic attack on the silicon atom, in contrast to bromide and iodide ions, which enter into exchange reactions with the chloromethyl group [1].

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\begin{align*}
\text{F}^- & \rightarrow \text{CH}_2\text{I}^- \\
& \rightarrow \text{F}^- \text{Si} \rightarrow \text{CH}_2 \text{R} + \text{I}^-
\end{align*}
\]

**EXPERIMENTAL METHOD**

The composition of the reaction mixtures was studied by GLC using a Chrom-3 instrument equipped with a detector based on the heat conductivity, and a 4.6-m column packed with 20% polyphenyl ether deposited on Chromatone N-AW-HMDS (0.25-0.5 mm). The products were separated at 80 °C for the trimethylsilyl derivatives, and at 110 °C for the triethylsilyl derivatives, using the same instrument equipped with a preparative attachment. The carrier gas was helium. (CH₃)₃SiF and (C₂H₅)₃SiF were identified by GLC using the method of internal standards, which were obtained by reacting the appropriate trialkylchlorosilanes with 48% HF.

The structure of the other reaction products was established by the ¹H NMR and ¹⁹F NMR methods. The spectra were obtained on a Tesla BS-487C spectrometer (80 MHz). The compounds were investigated as 10-20% solutions in CCl₄, using either cyclohexane or benzotrifluoride as the internal standard. The chemical shifts of the protons are given on the τ scale (τC₆H₁₂ 8.56 ppm), while for ¹⁹F the shifts were recalculated relative to CCl₃F (τCCl₃CF = 63.75 ppm).

All of the solvents were purified and dried well as described in [8]. The KF was dried by ignition at 200 °C for 24 h.

Fluorination of (Chloromethyl)chlorosilanes. With vigorous stirring, the appropriate (chloromethyl)chlorosilane was added to a mixture of KF and nitrobenzene. The Cl₃-n (CH₃)n SiCH₂Cl : KF : nitrobenzene ratio = 1 : 1.4 : 3. The mixture was refluxed for 3-5 h. The products boiling below 190 °C were distilled and condensed in a trap, which was cooled to −70 °C. By fractional distillation through an adiabatic column equipped with a 60-100-cm-long silver spiral we isolated CICH₂(CH₃)₂SiF [9] (50% yield, bp 84 °C and CICH₂SiF₃ [10] (74% yield, bp 25 °C).

Reaction of KF with Triethyl(chloromethyl)silane. A mixture of 8.2 g of (C₂H₅)₃SiCH₂Cl, 5.8 g of KF, and 15 ml of DMFA was heated in a sealed ampul at 160 °C for 24 h. Distillation gave 0.52 g of a fraction with bp 106-135 °C, which contained 61.7% of triethylfluorosilane and 38.4% of diethyl-n-propylfluorosilane (identified by GLC using the internal standard method). The yield was, respectively 5.0 and 2.6%.

Reaction of KF with Triethyl(iodomethyl)silane. A mixture of 6.4 g of (C₂H₅)₃SiCH₂I, 5.8 g of KF, and 10 ml of DMFA was heated at 160 °C for 8 h. Distillation gave 2.38 g of a fraction with bp 100-150 °C, which contained 35.3% of (C₂H₅)₃SiF (25% yield), 53.0% of C₃H₇(C₂H₅)₂SiF (34% yield), and 11.7% of DMFA.

The reaction products, which were separated by preparative gas chromatograph (PGC), had the following constants: (C₃H₇)₃SiF [11]: bp 106 °C; nD₂₀ 1.3910; d₄²₀ 0.8365. C₅H₁₁(C₂H₅)₂SiF: bp 130-131.5 °C; nD₂₀ 1.3990; d₄²₀ 0.8407. Found: C 56.63; H 11.26; Si 18.52; F 12.61%; MR 42.66. C₃H₇SiF.