

SYNTHESES OF  $\gamma$ -FLUOROPROPYL-SUBSTITUTED SILANES\*V.B.PUCHNAREVIČ<sup>a</sup>, J.VČELÁK<sup>b</sup>, M.G.VORONKOV<sup>a</sup> and V.CHVALOVSKÝ<sup>b</sup><sup>a</sup> Irkutsk Institute of Organic Chemistry,  
Academy of Sciences of the U.S.S.R., Irkutsk, U.S.S.R.,<sup>b</sup> Institute of Chemical Process Fundamentals,  
Czechoslovak Academy of Sciences, 165 02 Prague - Suchbát

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Organosilicon compounds of the type  $F(CH_2)_3SiR_3$  ( $R = Cl, F, CH_3, C_2H_5,$  and  $OC_2H_5$ ) were synthesized. Preparative utility of the following three methods was compared: the addition of silicon hydrides to allyl fluoride, halogen exchange reaction of  $\gamma$ -chloropropylsubstituted silanes with metal fluorides and of  $\gamma$ -hydroxypropylsilanes with the Yarovenko reagent. Some of the above procedures are complicated by  $\gamma$ -elimination reactions which lead to decomposition of  $\gamma$ -substituted silanes.

Within the framework of a broader study of the preparation and properties of fluoroalkyl-substituted silanes in the present work we examined the applicability of several methods for preparing  $\gamma$ -fluoropropylsilanes of the type  $F(CH_2)_3SiR_3$  ( $R = Cl, F, CH_3, C_2H_5$  and  $OC_2H_5$ ).

We attempted first to utilize hydrosilylation of allyl fluoride. Similar reactions were already realised in the presence of radical initiators, *e.g.* with  $CF_3CH=CH_2$  (ref.<sup>1</sup>) and with allyl chloride<sup>2</sup>. Another method tested makes use of comparatively easily available  $\gamma$ -chloropropylsilanes, which could be expected to undergo chlorine-fluorine exchange in the aliphatic chain on the action of commonly used fluorinating agents ( $KF, SbF_3$ ) in a suitable solvent, as reported for halogenoalkanes *e.g.* by Hoffmann<sup>3,4</sup>. With chlorosilyl-substituted derivatives preferential exchange of chlorine atoms bonded to silicon<sup>5</sup> could occur in this case. Resulting from the work by Laane<sup>6</sup> as well as from our experience with other types of silicon compounds<sup>7</sup>, some difficulties are undoubtedly to be expected on employing the reaction of this type. As another type of exchange reactions, fluorination of silyl alcohols by the reagent which has not yet been used in the chemistry of organometalloid compounds, the Yarovenko reagent  $[FCIHCCF_2N(C_2H_5)_2]$  (ref.<sup>8</sup>) was subjected to a study. This reagent was found to exchange the hydroxyl group of aliphatic alcohols directly for fluorine atom under relatively mild conditions<sup>9</sup>.

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Hydrosilylation of allyl fluoride catalysed by hexachloroplatinic acid proved very useful in the case of trichlorosilane addition (93% yield of ( $\gamma$ -fluoropropyl)trichlorosilane). With triethylsilane, only low yield of the corresponding adduct was obtained (23%). The addition of trialkylsilicon hydrides would have undoubtedly been more efficiently catalysed by a rhodium complex, *e.g.* by Wilkinson catalyst,  $\text{RhCl} \cdot [\text{P}(\text{C}_6\text{H}_5)_3]_3$  (ref.<sup>10</sup>).

The exchange of chlorine atoms bonded to silicon for fluorine was realised by using all the exchange reagents tested,  $\text{KF}$ ,  $\text{KHF}_2$ , and  $\text{SbF}_3$ , both in an appropriate solvent, and without solvent. The reaction is complicated, however, by concurrent  $\gamma$ -elimination leading to cyclopropane and  $\text{SiF}_4$ . This reaction was least important with  $\text{KHF}_2$ .

The exchange of the chlorine attached to the aliphatic chain in the  $\gamma$ -position to silicon is more difficult to realise. The reaction is again accompanied by  $\gamma$ -elimination the rate of which depends on other substituents on silicon. This reaction proceeds at a faster rate in the case of ( $\gamma$ -chloropropyl)trichlorosilane (it is comparable to the rate of the exchange of halogens attached to silicon), where nucleophilic species ( $\text{F}^-$ ) attacks the more electron-deficient silicon<sup>11</sup> more easily than in the case of ( $\gamma$ -chloropropyl)trimethylsilane, where  $\gamma$ -elimination does not proceed at all. Reactions of all chloropropyl-substituted silanes with both fluorinating agents ( $\text{KF}$  and  $\text{SbF}_3$ ) under pressure and at a temperature of from 120 to 180°C gave only the products of decomposition of the organosilicon compounds.

The Yarovenko reagent makes it possible to use corresponding hydroxy derivatives for preparing  $\gamma$ -fluoropropylsilanes. In this case, too, the exchange of the hydroxy group for fluorine is complicated by  $\gamma$ -elimination reaction leading to cyclopropane and trimethylfluorosilane. This elimination can be partially controlled by the choice of reaction conditions. On the use of a low boiling solvent, which prevents the reaction temperature from substantially increasing, the  $\gamma$ -substituted silane undergoes decomposition to a lesser extent than in the absence of solvent. The action of the Yarovenko reagent on silyl-substituted alcohols is the subject of a further study.

The chlorine atoms attached to silicon can be exchanged for ethoxy groups without cleavage the  $\gamma$ -fluoropropyl group.

## EXPERIMENTAL

### Addition of Silicon Hydrides to Olefins

( $\gamma$ -Chloropropyl)trichlorosilane<sup>12</sup> was prepared by addition of trichlorosilane (135 g, 1 mol) to allyl chloride (76.5 g, 1 mol) in the presence of 1 ml of 0.1M tetrahydrofuran solution of hexachloroplatinic acid under reflux of the reaction mixture whose temperature gradually increased to 110°C. Fractional distillation gave 91.2 g (43%) of ( $\gamma$ -chloropropyl)trichlorosilane as a fraction boiling at 176–178°C (ref.<sup>12</sup> 178°C/750 Torr).

*Allyl fluoride.* To a mixture of 58 g (1 mol) of anhydrous KF and 100 ml of diethylene glycol, 60.5 g (0.5 mol) of allyl bromide<sup>13</sup> were added dropwise with stirring at 140°C. Gaseous products were condensed at a dry-ice bath temperature to give 25 ml of allyl fluoride. This substance was also prepared from allyl alcohol (0.7 mol) and the Yarovenko reagent (0.7 mol) which, together with 100 ml of diethyl ether, was placed in a flask and then allyl alcohol was added. The reaction yielded 31 g (0.52 mol, 74%) of allyl fluoride.

( $\gamma$ -Fluoropropyl)trichlorosilane. Allyl fluoride was introduced to a boiling solution of trichlorosilane (27 g, 0.2 mol) and hexachloroplatinic acid (1 ml of 0.1M tetrahydrofuran solution of the acid) at the end of the reaction the mixture was heated at 140°C for another 3 h. Unreacted allyl fluoride in the outlet was condensed and recycled. The catalyst was intermittently (thrice) added, in dependence on the amount of the allyl fluoride reacted. Distillation gave 36.4 g (93%, based on trichlorosilane) of ( $\gamma$ -fluoropropyl)trichlorosilane, b.p. 42°C/12 Torr,  $n_D^{20}$  1.4330,  $d_4^{20}$  1.3113. For C<sub>6</sub>H<sub>6</sub>Cl<sub>3</sub>FSi (195.5) calculated: 18.43% C, 3.09% H, 14.37% Si, 9.71% F, 54.40% Cl; found: 19.11% C, 3.12% H, 14.10% Si, 9.58% F, 53.44% Cl. Its structure was confirmed by <sup>1</sup>H NMR and <sup>19</sup>F NMR spectroscopy.

( $\gamma$ -Fluoropropyl)triethylsilane was prepared by addition of triethylsilane (10 g, 0.17 mol) to allyl fluoride catalysed by 3 × 0.4 ml of 0.1M tetrahydrofuran solution of hexachloroplatinic acid. The temperature of the refluxing reaction mixture increased in 20 h from 106 to 130°C. Vacuum distillation gave a fraction boiling at 45–47°C/7 Torr which was subjected to preparative gas chromatography, yielding 6.9 g of the pure ( $\gamma$ -fluoropropyl)triethylsilane (23%, based on triethylsilane), b.p. 47°C/7 Torr,  $n_D^{20}$  1.4305,  $d_4^{20}$  0.8867. For C<sub>9</sub>H<sub>21</sub>F<sub>1</sub>Si<sub>1</sub> (176.4) calculated: 61.27% C, 12.00% H, 15.93% Si, 10.77% F; found: 61.05% C, 12.06% H, 15.92% Si, 10.34% F. Its structure was confirmed by <sup>1</sup>H NMR and <sup>19</sup>F-NMR spectroscopy.

#### Exchange Reactions of Chloropropyl-Substituted Silanes

( $\gamma$ -Fluoropropyl)trimethylsilane. A flask set up with a stirrer, a reflux condenser, and with a gas outlet tube connected to cooled absorption vessels (–20°C) containing CCl<sub>4</sub> was charged with 10 g of anhydrous KF (0.17 mol) and 50 ml of diethylene glycol, and then 9.5 ml (0.055 mol) of ( $\gamma$ -chloropropyl)trimethylsilane, prepared by methylation of ( $\gamma$ -chloropropyl)trichlorosilane with methylmagnesium chloride in excess, were added dropwise. The mixture was stirred and refluxed for 8 h. The initial temperature 143°C decreased at the end of the reaction to 120°C. In the course of the reaction all gaseous products were introduced into the absorption flask. The NMR analysis of the absorption solution showed that no products of decomposition ( $\gamma$ -elimination) are formed during the exchange reaction. By distilling out from the reaction mixture and by purifying 4.5 g (0.034 mol) of the pure ( $\gamma$ -fluoropropyl)trimethylsilane were obtained (61% yield); b.p. 107–109°C,  $n_D^{20}$  1.3936. For C<sub>6</sub>H<sub>15</sub>FSi (134.3) calculated: 53.67% C, 11.26% H, 14.15% F; found: 52.84% C, 11.19% H, 11.71% F. The structure of the product was confirmed by <sup>1</sup>H NMR spectroscopy.

( $\gamma$ -Fluoropropyl)trifluorosilane. a) Exchange of halogens on silicon. A flask was charged with 10 g (0.06 mol) of anhydrous KHF<sub>2</sub> and then 8 g (0.04 mol) of ( $\gamma$ -fluoropropyl)trichlorosilane were dropwise added at a slow rate. A fraction boiling at 62–82°C was distilled out and boiled under a reflux condenser with anhydrous KF (ref.<sup>14</sup>). Distillation yielded 4.3 g (70%) of a compound boiling at 71.5–72°C;  $n_D^{20}$  1.3642. The product obtained was very unstable in air. For C<sub>3</sub>H<sub>6</sub>F<sub>4</sub>Si<sub>1</sub> (146.2) calculated: 24.65% C, 4.14% H, 19.22% Si; found: 24.38% C, 4.04% H, 18.98% Si. The structure of the compound was confirmed by <sup>1</sup>H NMR and <sup>19</sup>F NMR spectra.

b) Complete exchange of halogens. To a flask set up with a stirrer, a thermometer, a dropping funnel, and a reflux condenser fitted with a gas outlet tube connected to cooled absorption vessels

containing tetrachloromethane and to the traps, 65 g (1.12 mol) of dry KF in 150 ml of nitrobenzene was placed and then 30 g (0.14 mol) of ( $\gamma$ -chloropropyl)trichlorosilane were dropwise added. An exotherm occurred during which the temperature of the mixture raised by 16°C. Then the mixture was stirred and refluxed (179°C) for 5 h. In the course of the reaction all gaseous products evolved were absorbed in CCl<sub>4</sub>. The NMR analysis of this solution revealed the presence of cyclopropane, and the trap cooled by liquid nitrogen contained sublimed SiF<sub>4</sub>. Distillation of the reaction mixture gave 13 g of a mixture of two compounds which, according to the chromatographic, elemental, and <sup>1</sup>H NMR analysis, consists of about 80% of ( $\gamma$ -chloropropyl)trifluorosilane and 20% of ( $\gamma$ -fluoropropyl)trifluorosilane (45% yield and 10% yield, respectively). Nearly half an amount of the starting silane underwent thus decomposition due to  $\gamma$ -elimination.

Reaction of ( $\gamma$ -chloropropyl)trichlorosilane with antimony trifluoride in the absence of solvent (7 h at 100°C) did not lead to the exchange of the chlorine on carbon for fluorine. Instead, Cl(CH<sub>2</sub>)<sub>3</sub>SiF<sub>3</sub>, b.p. 97°C (ref.<sup>6</sup> 94–96°C), was formed. The reaction with SbF<sub>3</sub> in the absence of solvent, carried out in a steel autoclave at 180°C for 7 h (c. 10 atm pressure) yielded only a resinous product. The same product was also obtained on reaction of ( $\gamma$ -chloropropyl)trifluorosilane with SbF<sub>3</sub> (180°C in an autoclave; 140°C in a glass ampoule) and with KF (120°C in a glass ampoule). The resinous product was also formed in the reaction of ( $\gamma$ -chloropropyl)trimethylsilane with SbF<sub>3</sub> in a glass pressure ampoule at 140°C.

#### Syntheses with the Yarovenko Reagent

*Preparation of the reagent.* Trifluorochloroethylene (60 g, 0.52 mol) was condensed at -76°C in an ampoule set up with an inlet capillary tube reaching to the bottom of the ampoule. Another ampoule was charged with 48 ml (0.47 mol) of freshly distilled diethylamine, cooled to -76°C, evacuated at 25–30 Torr and connected to the first ampoule. By opening connecting valves trifluorochloroethylene was transferred to the ampoule with diethylamine which was sealed and then allowed to warm to ambient temperature in a dry ice-ethanol bath. After two days the product was distilled to give 70 g (0.37 mol, 79%, based on diethylamine) of the Yarovenko reagent<sup>9</sup>, b.p. 54°C/18 Torr (ref.<sup>8</sup> 50°C/13 Torr).

*Reaction in the absence of solvent.* To 55 g (0.42 mol) of ( $\gamma$ -hydroxypropyl)trimethylsilane (obtained by reaction of trimethylsilylmethylmagnesium chloride with ethylene oxide<sup>11</sup>), Yarovenko reagent (88 g, 0.55 mol) was added. This reaction was exothermic and the temperature of the reaction mixture raised to 45°C, which was accompanied by strong evolution of gaseous products. The gases were led to the trap in which trimethylfluorosilane condensed at -10°C (a total of 29 g; 0.32 mol, 76%) and then to an absorption vessel containing CCl<sub>4</sub> which served as an absorbent of the gas which passed through the trap (-20°C). As found by <sup>1</sup>H NMR spectroscopy, the solution contained cyclopropane. Distillation of the reaction mixture yielded a fraction containing a small amount of impure ( $\gamma$ -fluoropropyl)trimethylsilane.

*Reaction in the presence of solvent.* The reaction mixture, containing 20 ml of diethyl ether, 8 g (0.042 mol) of the Yarovenko reagent, and 5 g (0.04 mol) of ( $\gamma$ -hydroxypropyl)trimethylsilane, gave, after removal of trimethylfluorosilane and the ether by distillation, ( $\gamma$ -fluoropropyl)trimethylsilane (1 g, 0.007 mol, 19%), the structure of which was confirmed by <sup>1</sup>H NMR spectroscopy and by comparison of its retention time with that of the ( $\gamma$ -fluoropropyl)trimethylsilane described above.

#### Exchange of Chlorine Atoms on Silicon for Ethoxy Groups in ( $\gamma$ -Fluoropropyl)chlorosilanes

( $\gamma$ -Fluoropropyl)triethoxysilane was prepared by adding dropwise 13 g (0.28 mol) of absolute ethanol to a solution of 16.7 g (0.085 mol) of ( $\gamma$ -fluoropropyl)trichlorosilane in 30 ml of chloro-

form. During the reaction air was bubbled through the mixture, and after the reaction was complete a solution of 15 g of urea in 15 mol of n-heptane was added. Vacuum distillation gave 14.5 g (0.066 mol, 76%) of ( $\gamma$ -fluoropropyl)triethoxysilane, b.p. 82–83°C/7 Torr,  $n_D^{20}$  1.3968,  $d_4^{20}$  0.9248. For  $C_9H_{21}FO_3Si$  (224.1) calculated: 48.18% C, 9.42% H, 12.53% Si, 8.46% F; found: 48.20% C, 9.58% H, 12.69% Si, 8.19% F. The structure of the product was confirmed by  $^1H$  and  $^{19}F$  NMR spectra.

## REFERENCES

1. Bell T. M., Haszeldine R. N., Newlands M. J., Plumb J. B.: *J. Chem. Soc.* 1965, 2107.
2. Ryan J. W., Menzie G. K., Speier J. L.: *J. Am. Chem. Soc.* 82, 3601 (1960).
3. Hoffmann F. W.: *J. Org. Chem.* 14, 105 (1949).
4. Hoffmann F. W.: *J. Am. Chem. Soc.* 70, 2596 (1948).
5. Frost L. W.: *J. Am. Chem. Soc.* 75, 3855 (1956).
6. Laane J.: *J. Am. Chem. Soc.* 89, 1144 (1967).
7. Puchnarevič V. B., Včelák J., Voronkov M. G., Chvalovský V.: Unpublished results.
8. Jarovenko N. N., Rakša M. A.: *Ž. Obšč. Chim.* 29, 2159 (1959).
9. Liška F.: *Chem. listy* 66, 189 (1972).
10. Svoboda P., Čapka M., Hetflejš J., Chvalovský V.: *This Journal* 37, 1585 (1972).
11. Sommer L. H., Van Strien R. E., Whitmore F. C.: *J. Am. Chem. Soc.* 71, 3056 (1949).
12. Mironov V. F., Nepomina V. V.: *Izv. Akad. Nauk SSSR, Otd. Chim. Nauk* 1960, 2140.
13. Moss S. J., Jennings K. R.: *Trans. Faraday Soc.* 65, 415 (1969).
14. Voronkov M. G., Skorik J. I.: *Izv. Akad. Nauk SSSR, Otd. Chim. Nauk* 1964, 1215.

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