¹⁹F-NMR SPECTRA OF (FLUOROALKYL)-SUBSTITUTED SILANES*

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¹⁹F-NMR spectra of a series of (fluoroalkyl)-substituted silanes of the type $R_3Si(CH_2)_nF$ (R = Cl, CH_3, C_2H_5, OC_2H_5; $n = 1, 2, 3, 5$) and of some carbon analogues have been measured and interpreted.

In conjunction with extensive study of the spectral properties and behaviour of α-functional derivatives of the type R_3MCH_2X (M = Group IV.b elements, X = Group V, VI and VII elements) in various reaction systems, the compounds containing fluorine as group X could be of special interest. Compounds of the type R_3MCH_2X exhibit frequently anomalous properties when series of compounds with varying distance between the functional group X and atom M in $R_3M(CH_2)_nX$ are compared, which has led to the term α-effect[1,2].

Thus with the amines $R_3Si(CH_2)_nNH_2$ the anomalous low basicity of the nitrogen for $n = 1$ does not correspond[3-5] to the inductive effect of the R_3SiCH_2-group. In the case of oxygen-containing compounds the nature of the α-effect has been studied by NMR and IR spectroscopy with trimethylsilylalkyl ethers[6] and by measuring relative rate constants of base-catalysed methanolysis of trimethylsiloxyalkanes[7]. The most studied were however compounds with X = Cl, Br, and I. Thus, for example, dipole moments of H_3SiCH_2X (X = Cl, Br, and I) (ref.[8]) and NQR fre-quencies of R_3SiCH_2Cl (ref.[1,9]) were interpreted in terms of the α-effect. CNDO-2 wave functions and Mulliken's population analysis of model compounds H_3SiCH_2X show that the "through space" interaction between the silicon and group X decreases in the order $NH_2 > OH > F$, the fluoro derivatives being assumed to exhibit significant "through bond" interaction[10]. Un-fortunately, none of these works concerned with the properties of (fluoroalkyl)-substituted silanes, whose preparation is accompanied by a number of difficulties.

In connection with our early papers[11,12] (NMR data for R_3SiCH_2Cl), we have attempted to prepare two series of the silanes:

a) $Cl_3Si(CH_2)_nF$ (*n* = 2, 3) and *b*) $(CH_3)_3Si(CH_2)_nF$ (*n* = 1, 3, and 5). In the case of γ-fluoropropylsilanes we compared them with the triethyl and triethoxy derivatives. The ¹⁹F-NMR spectra of all the compounds prepared were measured.

EXPERIMENTAL

(Fluoromethyl)trimethylsilane. (Hydroxymethyl)trimethylsilane was prepared in 23% yield by oxidation of ether solution of trimethylsilylmethylmagnesium chloride with oxygen at $0-10°C$ (ref.[13]). The corresponding tosylate was obtained from the hydroxy derivative (30 g, 0·29 mol) and tosyl chloride (115 g, 0·6 mol; purified by Pelletier method[14] by a light petroleum-chloroform mixture and filtration with activated carbon). The components were placed in a flask cooled to --40 to $-50°C$ and then 200 ml of pyridine were added. The mixture was slowly warmed up to room temperature and then decomposed with 800 ml of ice water. After extraction with two 250 ml portions of the ether, the ether layer was washed successively with 10% sulphuric acid, water, and 10% potassium hydroxide (always with ice). The ether solution was dried with magnesium sulphate and the solvent was removed by vacuum evaporation at room temperature with rotatory evaporator. Threefold crystallization from light petroleum yielded white crystals of the tosylate which melted at $59-60°C$ (34 g, 0·13 mol, 47%). The IR and NMR spectra confirmed the structure. For $C_{11}H_{18}O_3SSi$ (258·4) calculated: 51·13% C, 7·02% H, 10·87% Si; found: 51·07% C, 6·92% H, 10·55% Si. Decomposition of saturated solution of the tosylate (34 g, 0·13 mol) in 70 ml of diethylene glycol with dried potassium fluoride (12 g, 0·16 mol) under vigorous mixing and heating yielded after distillation from the reaction mixture a mixture of lower boiling compounds (fluorination by the method of Bergman[15]). The mixture was distilled through a column packed with silver spirals to give both dimethylethylfluorosilane contaminated with (fluoromethyl)trimethylsilane (1·5 g, 0·014 mol, 11%; by g.l.c.) and (fluoromethyl)trimethylsilane (a total of 5·2 g, 0·049 mol, 38%) with b.p. $60-61°C$, d_4^{25} 0·7946 (reported[16] b.p. 64°C).

β-(Fluoroethyl)trichlorosilane was prepared by a radical addition of trichlorosilane (32 g, 0·24 mol) to vinyl fluoride (6 g, 0·13 mol) (a modified Haszeldine procedure[17]) initiated by 0·2 g of azobis-isobutyronitrile in a c. 75 ml glass sealed tube. The reaction was carried out at 80 to 90°C (5 h) such that the tube was placed in an autoclave and pressure changes in the tube were compensated by nitrogen counterpressure in the autoclave (maximum counterpressure 80 atp.). After cooling, the tube was unsealed and the unreacted vinyl fluoride (in average 2·5 g, 0·054 mol) was removed by heating the mixture to 20°C. The residual mixture collected from three runs was rectified on an adiabatic column packed with silver spirals at maximum temperature in the flask of 40°C and under vacuum (the rectification under normal pressure has led to decomposition). After distilling off the excess trichlorosilane, the rectification gave 14·1 g (0·078 mol, 34% with respect to the vinyl fluoride reacted) of (β-fluoroethyl)trichlorosilane, b.p. 24°C/28 Torr (recorded[17] b.p. 118°C). For $C_2H_4Cl_3FSi$ (181·5) calculated: 58·60% Cl, 10·47% F; found: 57·37% Cl, 10·05% F.

(ε-Fluoropentyl)trimethylsilane was obtained by fluorination of 6·6 g (0·041 mol) of (ε-hydroxypentyl)trimethylsilane[18] with 20% excess of the Yarovenko reagent $CFClHCF_2N(C_2H_5)_2$, the synthesis of this reagent was reported in the work[19]) in 100 ml of the ether. The mixture was kept under reflux for 6 h, then the ether was distilled off and the residue was vacuum distilled. By separation from the excess Yarovenko reagent and formed N,N-diethyl fluorochloroacetamide, a total of 5·2 g (0·032 mol, 78%) of (ε-fluoropentyl)trimethylsilane were obtained; b.p. 90°C/83 Torr, n_D^{20} 1·4073. For $C_8H_{19}FSi$ (162·3) calculated: 59·19% C, 11·80% H, 11·70% F; found: 58·41% C, 11·66% H, 11·67% F.

Neopentyl fluoride. Exchange reaction between neopentyl bromide and potassium fluoride both in diethylene glycol and in hexamethylphosphorus triamide gave only trace amounts of the required product. The direct fluorination with Yarovenko reagent has produced a mixture of the elimination product, 2-methyl-2-butene, and neopentyl fluoride (12%). Decomposition of neopentyl tosylate with potassium fluoride in diethylene glycol yields a mixture of products

which contains 54% of neopentyl fluoride (21% yield with respect to the starting tosylate), but is essentially unseparable to individual components by rectification.

Only the synthesis of neopentyl fluoride according to Anderson[20], the reaction of neopentyl tosylate (53 g, 0·223 mol) with tetramethylammonium fluoride (26 g, 0·28 mol) in 130 ml of hexamethylphosphorus triamide yielded the product which was contaminated with small amounts of impurities. Neopentyl tosylate was obtained by mixing neopentanol with twofold excess of tosyl chloride in the presence of pyridine at −50°C. The usual work-up and crystallization from diethyl ether afforded neopentyl tosylate in 97% yield (m.p. 49−50°C). Tetramethylammonium fluoride was prepared by neutralization of aqueous solution of tetramethylamonium hydroxide with hydrofluoric acid followed by vacuum evaporation to dryness. Prior to using, the traces of water were removed by dissolving sticky crystals in acetonitrile and drying in vacuo.

A solution of neopentyl tosylate in hexamethylphosphorus triamide was added to tetramethylammonium fluoride and the mixture was stirred and refluxed at about 100°C for 30 h (the reflux condenser was cooled with dry ice–ethanol). By increasing the temperature of the reaction mixture to 150°C, 11 g of neopentyl fluoride (b.p. about 40°C, lit.[20] about 40°C) were obtained. The product contained 8% of 2-methyl-2-butene.

Synthesis of the silanes $(CH_3)_3Si(CH_2)_3F$, $Cl_3Si(CH_2)_3F$, $(C_2H_5)_3Si(CH_2)_3F$, and $(C_2H_5O)_3$. $.Si(CH_2)_3F$ and their properties were reported earlier[19], as well as the synthesis and properties of 1-fluoroheptane[21].

^{19}F-NMR Spectra

The spectra were measured with Varian XL-100 spectrometer (94·1 MHz) using solutions of the compounds in $CDCl_3$ and C_6F_6 as internal standard. Also "spin decoupling" technique was employed by which the splitting of fluorine signals by nuclei of geminal protons was avoided. Chemical shift of $FCH_2Si(CH_3)_3$ could not be measured in the usual way with the use of internal standard, since it was out of the measurable frequencies. This spectrum was measured by NMR technique which employes superstabilizator. Some of the values presented in Table I were obtained with Tesla BS 847 spectrometer using 15% solutions in CCl_4 and the same internal standard as in the above mentioned case. As it is seen from Table I, the values of chemical shifts are comparable. From measured positions of the signals the shifts of fluorine atoms with respect to $CFCl_3$ were calculated and are given in p.p.m. In conversion of the shift of a signal determined with respect to C_6F_6 to the shift with respect to $CFCl_3$ we used the value of shift of C_6F_6 with respect to $CFCl_3$ of −162·28 p.p.m.

DISCUSSION

As follows from Table I, chemical shifts of fluorine of all the silanes studied except neopentyl fluoride, (fluoromethyl)trimethylsilane, and (fluoroethyl)trichlorosilane lie in the 215−220 p.p.m. interval. In this interval there is also the shift of fluorine of monofluoroheptane. The chemical shift of (fluoroethyl)trichlorosilane which is by 5 p.p.m. out of this interval toward lower shielding indicates the possibility of the Si...F interaction which would lead to the lowering of electron density on the fluorine. As there are also other possibilities which would account for this shift, the data so far reported do not allow to discuss this problem in detail. The chemical shift of fluorine in (fluoromethyl)trimethylsilane is however quite extraordinary. It is

Table I

^{19}F-NMR Chemical Shifts and Coupling Constants of Fluorine Signals of (Fluoroalkyl)-substituted Silanes

Compound	C_6F_6 p.p.m.	$CFCl_3$ p.p.m.	$^2J_{H-F}$ Hz	$^3J_{H-F}$ Hz
$(CH_3)_3SiCH_2F$	—108·09	—270·37	47·0	—
$(CH_3)_3CCH_2F$	— 59·95	—222·23	48·0	—
$(CH_3)_3Si(CH_2)_3F$	— 52·81	—215·09	48·0	21·5
$(C_2H_5)_3Si(CH_2)_3F$	— 52·79	—215·07	48·0	21·5
		—214·98[a]	47·4[a]	20·7[a]
$(C_2H_5O)_3Si(CH_2)_3F$		—216·91[a]	46·5[a]	21·5[a]
$(CH_3)_3Si(CH_2)_5F$	— 55·78	—218·06	48·0	23·7
$CH_3(CH_2)_6F$	— 55·91	—218·19	47·5	24·0
$Cl_3Si(CH_2)_2F$		—210·51	47·0	20·0
$Cl_3Si(CH_2)_3F$		—219·85	46·5	23·5

[a] Values measured with Tesla spectrometer.

necessary to stress that the chemical shift in this compound is more diamagnetic, *i.e.* in opposite direction than it could be expected on the basis of naive concepts about the mechanism of shielding and α-effect. The prevailing electronic effect in (fluoromethyl)trimethylsilane seems therefore to be the + I effect of the trimethylsilyl group; this effect is without any doubt much greater than the effect of the tert-butyl group in neopentyl fluoride.

More detailed discussion of the ^{19}F-NMR data presented is supposed to be possible after all ^{13}C- and ^{29}Si-NMR data and Del Re calculations of net charges on fluorine atom in (fluoroalkyl) silanes will be obtained. This part of our study is under work.

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