

Studies on Silicon-Nitrogen Compounds: Part V†—Preparation & Characterisation of Some Substituted Organoaminoalkoxysilanes

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Benzylamino/*n*-butylamino/2-chloroanilino/2,4-difluoroanilino/2-fluoroanilino/4-methylanilino-bis(2,2,2-trifluoroethoxy)methyl/bis(2,2,2-trifluoroethoxy)*n*-propoxy/tris(2,2,2-trifluoroethoxy)/tri-*n*-propoxy-silanes as well as bis(2-chloroanilino)/(2-fluoroanilino)/4-methylanilino-di-*n*-butoxy/di-*n*-propoxy-silanes have been isolated under strictly anhydrous conditions and characterised by elemental analyses and IR, PMR and ¹⁹F NMR spectroscopy.

Synthesis, characterisation and reactions of organo-aminoalkoxysilanes have attracted attention during the past few years¹⁻⁹. However, such compounds having fluoro-substituted alkoxy groups are unknown probably due to high reactivity and volatility of these compounds and/or their precursors. In view of the importance of such compounds in synthesis and industry, presently some chloroanilino/fluoroanilino/organoamino-2,2,2-trifluoroethoxy/*n*-propoxy-silanes have been isolated and characterised.

Materials and Methods

All operations were carried out under oxygen-free dry nitrogen atmosphere. Volatile compounds were handled in all-glass vacuum line and the liquid compounds were not exposed to atmosphere. All the reactions were carried out under anhydrous conditions.

Infrared spectra were recorded as neat liquids or in CCl₄ solution using KBr and CsI optics on a Perkin-Elmer (model 621) double beam grating spectrophotometer.

Proton magnetic resonance and ¹⁹F NMR spectra were recorded on a Varian (EM 390) 90 MHz spectrometer in CDCl₃ or CCl₄ using TMS as internal and Freon-11 as external references respectively. 2,2,2-Trifluoroethanol (Fluka AG), *n*-propanol (BDH, pure), 2-fluoroaniline (Fluka AG), 2,4-difluoroaniline (Fluka AG), aniline, benzylamine and *n*-butylamine (all BDH, pure) and methyltrichlorosilane (Fluka AG) were used as obtained.

Bis(2,2,2-trifluoroethoxy)(chloro)methylsilane

To the cold methyltrichlorosilane (22 g, 0.15 mol) was added 2,2,2-trifluoroethanol (33 g, 0.33 mol)

dropwise with stirring under dry N₂ atmosphere. After the addition, the mixture was slowly warmed, evacuated (50 mm) to expel the HCl produced in the reaction and fractionally distilled in slow stream of oxygen-free dry nitrogen through a long column. After repeated distillations the relevant fraction (as evidenced by Cl⁻ estimation and ¹H and ¹⁹F NMR spectra) was collected for use.

2-Fluoroanilino-tris(2,2,2-trifluoroethoxy) silane

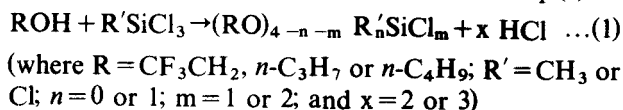
To a solution of chloro-tris(2,2,2-trifluoroethoxy) silane (20 g, 0.06 mol) and triethylamine (5.6 g, 0.05 mol) in *n*-hexane or benzene was added 2-fluoroaniline (6.7 g, 0.06 mol) in the same solvent, as described above. The solid obtained was filtered off and the solvent slowly removed under reduced pressure (It is important that the hydrochloride should be completely removed before distillation) and the residue repeatedly distilled *in vacuo* (wherever possible) to obtain the desired fraction.

The other chloro and aminosilanes reported here have been obtained employing essentially the above method.

Results and Discussion

The relevant analytical data of all the compounds prepared are recorded in Table I.

Chloro-tris(2,2,2-trifluoroethoxy)/bis(2,2,2-trifluoroethoxy)methyl/tri-*n*-propoxy-silanes and dichloro-di-*n*-propoxy- and di-*n*-butoxy-silanes have been obtained by the reactions of silicon tetrachloride or methyltrichlorosilane and corresponding alcohols in stoichiometric ratios in accordance with Eq. (1):



†For Part IV, see ref. 4.

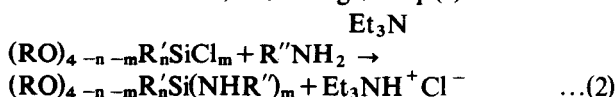
Table 1—Physical and Analytical Data of Chloro/Organoamino Alkoxy Silanes

Sl. No.	Compd*	b.p.† (°C/mm)	Si (%)		Cl/N (%)	
			Found	Reqd	Found	Reqd
1	(CF ₃ CH ₂ O) ₃ SiCl	88.90/740	7.6	7.8	9.9	9.9
2	CH ₃ (CF ₃ CH ₂ O) ₂ SiCl	81.83/745	9.8	10.1	12.7	12.8
3	(CF ₃ CH ₂ O) ₂ (C ₃ H ₇ O)SiCl	110-12/740	8.5	8.7	11.0	11.1
4	(CF ₃ CH ₂ O) ₃ SiNHCH ₂ C ₆ H ₅	123-24/745	6.3	6.5	3.3	3.2
5	CH ₃ (CF ₃ CH ₂ O) ₂ SiNHCH ₂ C ₆ H ₅	115-17/740	7.8	8.0	3.9	4.0
6	(CF ₃ CH ₂ O) ₂ (C ₃ H ₇ O)SiNHCH ₂ C ₆ H ₅	136-38/745	7.0	7.1	3.4	3.6
7	(CF ₃ CH ₂ O) ₃ SiNHC ₆ H ₄ F	105-07/740	6.1	6.4	3.0	3.2
8	(C ₃ H ₇ O) ₃ SiNHC ₆ H ₄ F	130-32/15	8.5	8.8	4.5	4.4
9	(C ₃ H ₇ O) ₃ SiNHC ₆ H ₄ F ₂	135-38/15	8.1	8.4	4.0	4.2
10	(CF ₃ CH ₂ O) ₃ SiNHC ₆ H ₃ F ₂	126-28/740	6.1	6.2	3.0	3.1
11	(CF ₃ CH ₂ O) ₃ SiNHC ₆ H ₅	110-12/740	6.5	6.7	3.1	3.3
12	(CF ₃ CH ₂ O) ₃ SiNHC ₆ H ₉	90-93/740	6.8	7.0	3.4	3.5
13	(C ₃ H ₇ O) ₃ SiNHC ₆ H ₄ Cl	101-03/10	8.1	8.4	4.3	4.2
14	(C ₄ H ₉ O) ₃ SiNHC ₆ H ₄ Cl	108-10/10	7.4	7.5	3.5	3.7
15	(C ₄ H ₉ O) ₂ Si(NHC ₆ H ₄ Cl) ₂	120-22/7	6.3	6.5	6.4	6.5
16	(C ₃ H ₇ O) ₂ Si(NHC ₆ H ₄ Cl) ₂	112-14/7	6.9	7.0	6.8	7.0
17	(C ₄ H ₉ O) ₃ SiNHC ₆ H ₄ CH ₃	116-18/10	7.7	7.9	3.7	3.8
18	(C ₃ H ₇ O) ₂ Si(NHC ₆ H ₄ CH ₃) ₂	125-28/6	7.5	7.8	7.7	7.8
19	(C ₃ H ₇ O) ₂ Si(NHC ₆ H ₄ F) ₂	126-28/12	7.4	7.6	7.5	7.6
20	(C ₃ H ₇ O) ₂ Si(NHC ₆ H ₅) ₂	130-32/15	8.3	8.5	8.4	8.5

*Chlorine was estimated only for compounds at Sl Nos 1-3.

†Boiling points are uncorrected.

Tris(2,2,2-trifluoroethoxy)/bis(2,2,2-trifluoroethoxy)methyl/tri-*n*-propoxy-2,4-difluoroanilino/2-fluoroanilino/anilino/benzylamino/*n*-butylamino-silanes and di-*n*-propoxy/di-*n*-butoxy-bis(2-chloroanilino)/(2-fluoroanilino)/(4-methylanilino)-silanes are formed by the reactions of the chlorosilanes and amines in molar ratio 1:1 or 1:2 in the presence of equivalent quantity of triethylamine in *n*-hexane or benzene, according to Eq. (2):



The infrared spectra of aminosilanes as thin films exhibit νNH modes at lower wavenumbers (3470-3360 cm⁻¹) in comparison to those observed (3490-3410 cm⁻¹) in CCl₄ solutions. This may be due to occurrence of hydrogen bonding to variable degree in these aminosilanes. In the case of fluoroanilinosilanes, the degree of hydrogen bonding is the least.

The bands due to νCF₃, ν_{as}Si-O-(C) and δSi-O-(C) are observed in the regions 1280-1260, 1090-1020 (two bands) and 490-470 cm⁻¹ respectively. In addition, the benzene ring absorptions are observed around 750 ± 10 and 700 ± 10 cm⁻¹.

¹H and ¹⁹F spectra

The PMR spectra of the aminosilanes exhibit signals at δ 0.3, 1.0, 1.3-1.8, 3.8-4.3 and 6.9-7.35 for Si-CH₃, CH₃, CH₂, OCH₂ and aromatic ring protons

respectively. These signals do not differ much from those of the corresponding pure alcohols and amines except for the -OCH₂ protons, which appear downfield due to the presence of (*p* → *d*)π-bonding between silicon and oxygen atoms¹⁰. The deshielding of -OCH₂ protons is more pronounced in the case of CF₃CH₂O derivatives as compared to *n*-C₃H₇O ones.

The signals due to NH proton† vary considerably (1.5 to 4.6 ppm) depending upon their environments. In the case of trialkoxyanilinosilanes, this proton is observed at ~3.6 ppm⁷ and for dialkoxy-bis(anilino)silanes at ~3.7 ppm which is in accordance with the observation reported earlier⁵. Though for trialkoxy(2-fluoroanilino)silanes, the NH proton appears essentially around δ 3.6, in dialkoxy bis(2-fluoroanilino)silanes NH proton appears downfield (δ 4.1). In trialkoxy-4-methylanilinosilanes NH signals appear slightly upfield (δ 3.5) as compared to those in the corresponding trialkoxyanilinosilanes, probably due to the (+*I*) effect of the methyl group. However, substitution of second (4-methylanilino) group for an alkoxy group in the molecule renders NH proton to appear slightly downfield. In triisopropoxy(4-chloroanilino)silane in CCl₄ the NH proton has been reported to appear⁶ at δ 3.46. In trialkoxy-(2-chloroanilino)silanes, the NH protons appear in the region δ 4.3-4.4. In dialkoxy bis(2-chloro-

†Values are slightly concentration dependant and can vary in the range ±0.1-0.3 ppm.

anilino)silanes, the NH proton appears at δ 4.6. The reason for such a drastic change in the chemical shift value of NH protons is yet to be understood.

Further it has been observed that replacement of alkoxy groups by 2,2,2-trifluoroethoxy group renders the NH protons to appear downfield. For example, in trialkoxybenzylaminosilanes NH proton appears⁷ at δ 1.1 while in bis(2,2,2-trifluoroethoxy)-propoxybenzylaminosilane the signal is observed at 1.5 and in tris(2,2,2-trifluoroethoxy)- and bis(2,2,2-trifluoroethoxy) methylbenzylaminosilanes at 1.5 and 1.7 respectively. Similarly, in the case of tris(2,2,2-trifluoroethoxy)anilino- and tris(2,2,2-trifluoroethoxy)-*n*-butylamino-silanes these signals appear at 4.1 and 1.3 as against 3.6 and 1.1 in trialkoxyanilino- and *n*-butylaminosilanes respectively. This may be attributed to the higher electronegativity of 2,2,2-trifluoroethoxy group causing greater deshielding of the NH protons.

Fluorine-19 NMR spectra show CF_3 at δ 17 (triplet), $\text{C}_6\text{H}_4\text{F}$ at 135-137 (singlet) and $\text{C}_6\text{H}_3\text{F}_2$ as a doublet at 120-124 ppm.

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