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RESEARCH NOTE

NMR spectra of some fluorosilyl amines

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Abstract—The ^1H and ^{19}F nuclear magnetic resonance spectra of a number of F_3Si— and —SiF_2— amines are reported and discussed.

INTRODUCTION

THE PROTON magnetic resonance spectra of H_3Si— derivatives have been employed extensively for diagnostic purposes, and proved especially useful in identifying the products of the reactions of CO_2, OCS and CS_2 with silylamines [1, 2].

RESULTS AND DISCUSSION

The NMR parameters of some analogous fluorosilyl amines are given in Table 1. The observation of the couplings $^4J(F \ldots H)$ in several of the spectra indicates that F_3Si— (and —SiF_2—) group exchange is slow on an NMR time scale. There is no evidence from the spectra that the α-methylene protons in F_3SiNEt_2 are magnetically non-equivalent, consistent with the planar heavy-atom skeleton found [3] for F_3SiNMe_2 by electron diffraction. The ^{29}Si—F coupling constant is significantly greater in the —SiF_2— than in the F_3Si— derivatives; a similar difference has been reported [4] for other SiF compounds. The NMR parameters for F_3SiNMe_2 are in agreement with those reported [5] previously for a solution in CCl_3F (ϕ = 156·5 ppm, τ = 7·42 ppm, $^1J(^{29}Si—F)$ = 201·4 Hz, $^4J(F \ldots H)$ not reported).

Samples containing F_3SiNMe_2 and CO_2, OCS or CS_2, in the approximate mole ratio 1:2, exhibited only the trifluorosilyl dimethylamine ^1H and ^{19}F NMR spectra. This is in contrast to the rapid insertion reactions [1] of these compounds with H_3SiNMe_2 to give $H_3SiOC(O)NMe_2$ etc.

EXPERIMENTAL

Trifluorosilyl-piperidine[6], -t-butylamine[6], -dimethylamine[3] and $F_2Si(NMe_2)_2$ [7] were prepared and purified as described previously. Trifluorosilyl diethylamine was obtained by heating SiF_4 (7·7 m-mole) and Me_3SiNEt_2 (2·5 m-mole) to 150° for 45 min in a sealed tube, and was purified by repeated fractional condensation *in vacuo*. A tensiometrically pure sample (v.p. = 11 mm at −23·5°C) having M = 155 (calc. 157·1) was taken as F_3SiNEt_2. The analogous reaction of SiF_4 with Me_3SiNMe_2 has been reported [5] to yield F_3SiNMe_2. The vapour phase reaction between methylamine (9·1 m-mole) and trifluorosilyl bromide (6·4 m-mole) yielded a white involatile solid and $(F_3Si)_2NMe$ (0·7 m-mole); the −45/−96° fraction of the volatiles (M = 208, calc. for $(F_3Si)_2NMe$, 198) was used to obtain the NMR spectra. This compound readily disproportionated to SiF_4, an involatile white solid, and a sublimable crystalline compound. The mass spectrum of the latter exhibited a base peak (intensity 100) corresponding to

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Table 1. NMR parameters

Molecule	ϕ ppm	τ_α ppm	τ_β ppm	$^1J(^{29}Si—F)$ (Hz)	$^4J(F \ldots H)$ (Hz)
F_3SiNMe_2	157·3	7·45		202	1·1
F_3SiNEt_2	154·0	7·08	8·92*	206	1·1
$F_3SiNC_5H_{10}$	156·3	7·04	8·44†	202	<1
F_3SiNH^tBu	147·7		8·77	204	
$(F_3Si)_2NMe$	152·9	7·18		204	0·4‡
$F_2Si(NMe_2)_2$	152·6	7·50		219	1·1
$(F_2SiNMe)_3$	151·3	7·31		218	$<0·3$
e.s.d.	±1·0	±0·02	±0·02	±2	±0·2

* $^3J(H \ldots H) = 7·3$ Hz.

† β plus γ. The H . . . H couplings were not resolved.

‡ not fully resolved.

$Si_3F_6N_3C_3H_8^+$ and a molecular ion (intensity 87) for $Si_3F_6N_3C_3H_9^+$; it was therefore assumed to be the trimer $(F_2SiNMe)_3$. A weak molecular ion (intensity 2) for the tetramer suggested that traces of other oligomers might also be present.

Proton spectra were recorded using a Varian Associates HA 100 spectrometer at 100 MHz, and fluorine spectra using a Perkin–Elmer R 10 spectrometer at 56·46 MHz. Samples were prepared as dilute solutions in CCl_3F ($\phi = 0·0$) containing about 10% Me_4Si ($\tau = 10·00$). Appreciable white precipitates formed on standing in the $(F_3Si)_2NMe$ and F_3SiNMe_2/CO_2 tubes, and traces in most of the others.

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University Chemical Laboratory
Lensfield Road
Cambridge

W. Airey
G. M. Sheldrick

Westfield College
Hampstead, London N.W.3

B. J. Aylett
I. A. Ellis