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The Structure of Silylated Amides: N-Methyl-N-Trimethylsilyltrifluoroacetamide, a Reassignment of Structure.

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Summary

The ^{29}Si and ^{14}N nmr spectra of some bissilylamides and monosilylamides are reported. The results are compared with those for model silylesters, amines and imines. The compound of formula $CF_3CONCH_3Si(CH_3)_3$ (MSTFA) is shown to exist as a tautomeric mixture of a silylamide and a silylimidate. This assignment is confirmed by ^{13}C nmr. A rationale is proposed for the structure directing effect of substituents on the amide carbon atom.

Introduction

The structure of silylated amides continues to be of interest (1-9). For trimethylsilyl derivatives the rotameric amido forms (I and II) and a tautomeric imidato form (III) have all been observed. No evidence for *syn*-*anti* isomerism has been obtained.

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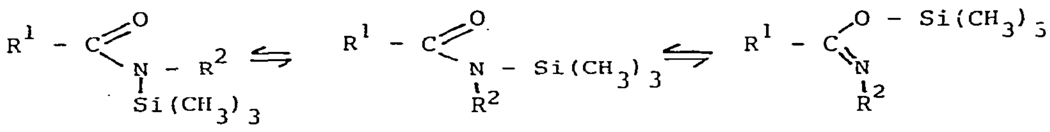


I II III

The position of the equilibrium is strongly dependent on the nature of R^1 and R^2. For monosilylated amides, the proportion of III increases as R^2 becomes more electron withdrawing (1-4,9).

The effect of varying R^2 can be successfully rationalized in terms of the π-character of the amide C-N bond. Substituents, R^2, that increase the electron density on nitrogen, increase the π-character of the C-N bond, thereby stabilizing I and II relative to III. The driving force for formation of III is assumed to be the formation of the strong Si-O bond.

The effect on the equilibrium of varying R^1 is not straightforward. For bissilylated amides ($R^2=Si(CH_3)_3$) the imidate form is preferred for all R^1 except for $R^1=H$; when $R^1=H$ the amide form is observed exclusively (4). A convenient explanation for this would be that the C-N bond in formamide has greater π-character than in other amides. This is indeed so (10), but the correlation of structure with the electronic effect of R^1 is confused by the reported amido forms (I and II) for N-methyl-N-trimethylsilyltrifluoroacetamide (MSTFA) (11). The strongly electron withdrawing trifluoromethyl group should decrease the C-N π-electron density and favour the imidate form (4).

The assignment of the amido structure of MSTFA relied on

^{1}H nmr and is open to reinterpretation. The aims of this study were to reexamine the structure of MSTFA and some bissilylamides, using ^{29}Si, ^{14}N and ^{13}C nmr spectroscopy. Spectra of model compounds were obtained for comparison.

Rühlmann et al (1) have established that in the ^{29}Si nmr spectra of silylated amides, N-trimethylsilylamido resonances appear at ca δ,10ppm and O-silyl resonances of the imidato form resonate in the region of δ,19ppm.

For complete assignment of the structure of silylated amides it is necessary to establish the position of the $>C=N-Si(CH_3)_3$ resonance in bissilylimidates.

Results and Discussion

^{29}Si nmr spectra

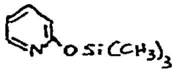
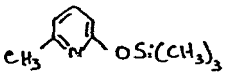
Bis(trimethylsilyl)acetamide (BSA) and bis(trimethylsilyl)-trifluoroacetamide (BSTFA) both show two resonances in their

Table 1. ^{29}Si nmr chemical shifts of $R^1CONR^2Si(CH_3)_3$[a]

R^1	R^2	δ/ppm	
CF_3	CH_3	26.2, 17.0 (peak widths 1.2 and 3.2 Hz respectively)	
CF_3	$Si(CH_3)_3$	24.9, -2.52	
CH_3	$Si(CH_3)_3$	16.2, -5.9 (Lit(1) 16.41, + 5.74)	
H	$Si(CH_3)_3$	8.2	
CH_3	H	4.0	(Lit(1) 5.56, 17.55 minor)
CH_3	CH_3	8.75	(Lit(1) 8.18)

a. approx. 30% solutions in $(CD_3)_2CO$, int. TMS; ca 30 ° pulse angle; 15s. repitition; 100-1000 transients.

Table 2. ^{29}Si nmr chemical shifts for model and miscellaneous compounds.

Compound	δ/ppm
$(C_6H_5)_2C{=}NSi(CH_3)_3$	-1.5
$(\underline{p}CH_3C_6H_4)_2C{=}NSi(CH_3)_3$	-2.1
	19.44
	18.91
$((CH_3)_3Si)_2NH$	2.21 (lit. (13) 2.2)
$(CH_3)_3SiN(C_2H_5)_2$	3.7 (lit. (14) 3.74)
$(CH_3)_3SiN(CH_3)_2$	6.62 (lit. (14) 6.5)
$CF_3COOSi(CH_3)_3$	33.11 (lit. (15) 33.2)
$CH_3COOSi(CH_3)_3$	22.0 (lit. (15) 22.3)

a. See Table 1 for conditions.

^{29}Si nmr spectra (Table 1). The resonances at δ-5.9 and -2.52 ppm respectively, are assigned to the $>C{=}N{-}Si(CH_3)_3$ silicon atoms. The study of $(C_6H_5)_2C{=}NSi(CH_3)_3$ and $(\underline{p}C_6H_4)_2C{=}NSi(CH_3)_3$ as model compounds confirms this assignment. In these examples the iminotrimethylsilyl resonance appears at δ,-1.5 and -2.1 ppm (Table 2).

The high frequency resonances at δ,16.2 and 24.9 ppm in BSA and BSTFA are assigned to the $\underset{\sim}{O}$-silicon atoms. These are in the region established by Rühlmann (1) and are both ca 6-8 ppm to low frequency of the respective carboxylic acid esters, $CH_3COOSi(CH_3)_3$ and $CF_3COOSi(CH_3)_3$ (Table 2).

Yoder (16) showed, by infrared spectroscopy of the ^{15}N labelled compound, that BSA has the imidate structure.

Our ^{29}Si nmr results are in accord with this structure. Ruhlmann (1) apparently observed a bis(trimethylsilyl) amido form for BSA with [imidate] / [amide] = 1.38. This is not consistent with the known structure of BSA and possibly arises from an incorrect assignment of the *N*-silyl resonance. A value of -5.74 ppm for the *N*-silyl resonance would be in line with our results (-5.9 ppm). The greater peak height for the *O*-silyl resonance is understandable as we have observed that *O*-silyl peaks generally have line widths of *ca* 1-3Hz whereas *N*-silyl resonances are frequently 3-10Hz wide.

BSTFA has been assumed to have the imidate structure but the evidence has been circumstantial. The ^{29}Si nmr spectrum leaves no doubt as to the correctness of the imidate structure for this compound.

Yoder (4) established the amide structure for bis(trimethylsilyl)formamide by infrared and ^{15}N labelling. The ^{29}Si resonance at δ,8.2 ppm is consistent with this. The signal is a singlet at the normal operating temperature (37 °C) but broadens and eventually splits into a doublet at low temperatures. No quantitative measurements were made on the rotational barrier in this compound. No signals assignable to the imidate tautomer are observed.

The spectrum of MSTFA has two peaks, at δ,26.2 and 17.0 ppm. The separation of the signals alone probably rules out an equilibrium between two rotameric forms (I and II). The similarity in chemical shifts between the high frequency resonance (26.2ppm) and the *O*-silyl resonance in BSTFA (24.9 ppm) strongly supports the presence of an imidate structure.

The other resonance at δ, 17.0 ppm can be assigned to the amide tautomer. In general, electron withdrawing groups bonded to $Si(CH_3)_3$ groups result in silicon shifts to high frequency. This resonance is some 8 ppm to high frequency of the corresponding resonance in $CH_3CONCH_3Si(CH_3)_3$ (Table 2). The corresponding difference in chemical shift between $CF_3COOSi(CH_3)_3$ and $CH_3COOSi(CH_3)_3$ is about 11 ppm. Oxygen is known to transmit substituent effects in ^{29}Si nmr to a greater extent than nitrogen (17).

The separation of the two resonances (9.2 ppm) and comparison with the model compounds strongly supports the idea that MSTFA exists as a tautomeric mixture of amide and imidate. This is confirmed by ^{13}C nmr spectroscopy (*vide infra*) With this reassignment of structure of MSTFA it is now possible to suggest that the effect of substituents (R^1) on the amide carbon atom on the equilibrium I, II $\rightleftharpoons$ III is a direct result of changes in C-N π - electron density. Electron withdrawing substituents that lower the C-N π - electron density favour the imidate tautomer. Experiments are in progress to assess the relative importance of the steric and electronic effects of R^1.

^{29}Si nmr chemical shifts of some other, related, compounds were measured. Of particular interest is the finding that the two silylated hydroxypyridines have single narrow peaks in the *O*-silyl region (19.44 and 18.91 ppm). This is consistent with suggestion by Cragg (8) that they have the aromatic, *O*-silyl structures. The chemical shifts of these silylated hydroxypyridines are similar to that of $C_6H_5OSi(CH_3)_3$ (16.4 ppm).

By contrast, bis(trimethylsilyl)urea, $CO(NHSi(CH_3)_3)_2$ has the N-silylated structure as shown by the appearance of one signal at δ 1.5 ppm (cf silylamines and $CH_3CONHSi(CH_3)_3$, δ 4.0 ppm)

^{14}N nmr spectra

^{14}N nmr spectroscopy was investigated as a further aid to the structure determination of silylated amides. The results obtained (Table 3) show that ^{14}N nmr can have significant diagnostic use in this area but is very qualitative. N-silylated amides show a moderately broad signal at about −270 ppm (in a similar range to the parent amides − see for

Table 3. ^{14}N nmr chemical shifts for $R^1CONR^2Si(CH_3)_3$[a]

R^1	R^2	δ/ppm[b]	approx. line width/Hz
CF_3	CH_3	−271	400
CF_3	$Si(CH_3)_3$	−173	1000
CH_3	CH_3	−282	450
CH_3	H	−260	450
H	$Si(CH_3)_3$	−255	400
CH_3	$Si(CH_3)_3$	no signal observed (see text)	
$C_6H_5C{=}NSi(CH_3)_3$			

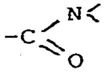
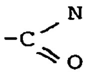
a. neat liquids, ext. $CDCl_3$ lock or concentrated solutions in $CDCl_3$ (solids).

b. average of at least three runs, relative to ext. NO_3^-. Minus sign indicates to low frequency of standard.

example 18). It is known (18) that trigonal nitrogen atoms, such as those in imines and imidates, give rise to broad signals in their ^{14}N nmr spectra. We observe a signal at −173 ppm of line width about 1000 Hz for BSTFA. This resonance is well outside the normal amine range, and together with its width is diagnostic for the imidate structure. None of the other compounds containing trigonal nitrogen gave a ^{14}N spectrum. This is probably due to our inability to observe signals of width greater than 1000 Hz owing to pulse breakthrough.

MSTFA has a ^{14}N spectrum, consisting of a single band at −271 ppm with width *ca* 400 Hz. This is appropriate to the amido tautomer, but no band for the imidate is observed.

^{13}C nmr spectra

Rühlmann *et al* (1) established that, in general, there is a difference of *ca* 15 ppm between the  $-C(=O)N<$ and  $-C(=O)N<$ resonances in the ^{13}C nmr spectra.

The carbonyl signal for BSTFA appears at δ 143.4 ppm and no other signal is apparent in the carbonyl region. MSTFA has, as is appropriate for amide/imidate tautomerism, two resonances in the carbonyl region separated by 18 ppm (δ 162.2 and 143.9 ppm).
The ^{13}C nmr spectrum of MSTFA is not markedly temperature dependent down to about −80 °C. By analogy to $CH_3CONHSi(CH_3)_3$ (5) it is possible that MSTFA exists in only one rotameric form (probably II). Table 4 gives complete ^{13}C nmr data, including coupling constants, for BSTFA and MSTFA.

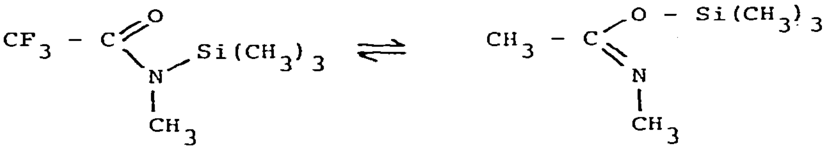
Table 4. ^{13}C nmr chemical shifts and coupling constants for $CF_3CONCH_3Si(CH_3)_3$ and $CF_3CON(Si(CH_3)_3)_2$[a]

	δ/ppm, (J/H_3)			
	C(i)	C(2)	C(3)	C(4)
$CF_3CONCH_3Si(CH_3)_3$	116 ($^1J_{CF}$,290)	162.2 ($^2J_{CF}$,33.7)	−0.48	33.6 (s)
1 2 4 3	117 ($^1J_{CF}$,277)	143.9 ($^2J_{CF}$,37.3)	−1.58	30.0 ($^4J_{CF}$,3.7)
$CF_3CON(Si(CH_3)_3)_2$	116.6($^1J_{CF}$,284)	143.4 ($^2J_{CF}$,40.4)	−0.18	
1 2 3			0.79	

a. 50% in $CDCl_3$

^1H nmr spectra

It has been reported (11) that the ^1H nmr spectrum of MSTFA in CCl_4 consists of a pair of overlapping quartets (J=1.43 Hz) ($N-CH_3$) and a singlet for the trimethylsilyl protons In benzene-d_6 we observe two well separated $N-CH_3$ quartets (δ 3.06 ppm $^5J_{HF}$=1.47 Hz and δ 2.73 ppm $^5J_{HF}$=1.83 Hz) and two $SiCH_3$ singlets (0.35 and 0.32 ppm). The integration of high frequency to low frequency quartets is in the ratio 1.2:1. The quartet with the smaller coupling constant is most likely to be associated with the amide tautomer (less 's' character in the intervening bonds) and gives an equilibrium constant for II $\rightleftharpoons$ III of 1.2. On heating the sample of MSTFA in benzene, the trimethylsilyl resonances broaden and coalesce at ca. 73°C. From this, and the separation in the absence of exchange of 2.2 Hz the free energy of activation for the imidate/amide tautomerism can be estimated as 19.4 Kcal $mole^{-1}$. This compares with $\Delta G^{\ddagger}$ = 22.1 k cal $mole^{-1}$ for the same processes in BSTFA (4). Taken together, the evidence presented here unambiguously assigns the compound MSTFA to a mixture of amide and imidate forms. By comparison with the previous work of Yoder (2-5, 16) the most probable structures for the tautomers are;



The two isomers shown here are the most probable on both steric and electronic grounds and their interconversion is possible without the intervention of C-N rotation in the amide form.

Experimental

Compounds

All compounds used were known, and either commercially available or prepared by the literature methods (eg. hydroxypyridines by the method of Cragg (8)). Compounds were handled and stored under nitrogen.

nmr measurements

Nmr spectra were obtained on a Bruker WP-60 spectrometer equipped with a variable temperature probe and ^{29}Si, ^{13}C, ^{14}N and ^{1}H channels.

Acknowledgements

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