

The structure of bis(organosilyl) amides containing the dimethylsilyl and bis(dimethylsilyl)ethylene groups

Marjorie S. Samples and Claude H. Yoder*

Department of Chemistry, Franklin and Marshall College, Lancaster, PA 17604 (U.S.A.)

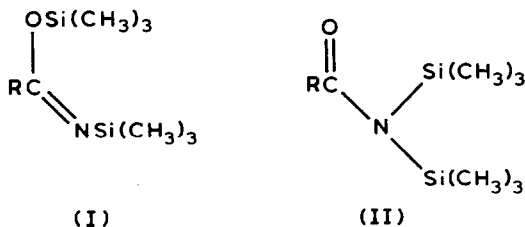
(Received January 29th, 1987)

Abstract

In contrast to the structure of bis(trimethylsilyl) amides, which, except for the formamide, exist in the imidate form and undergo rapid exchange of trimethylsilyl groups, the bis(dimethylsilyl)amides prepared in this study exist in the amide form and undergo rapid rotation around the C–N bond. The reaction of several bis(trimethylsilyl) amides with 1,2-bis(dimethylchlorosilyl)ethane also produced amides containing a 5-membered silazane ring. Structures were determined by ^{13}C , ^{29}Si , ^{14}N , and ^{17}O NMR, and free energies of activation for hindered rotation were determined by variable temperature ^{13}C or ^{29}Si NMR. The difference in structure can be attributed to the spatial requirements of the groups attached to silicon.

Introduction

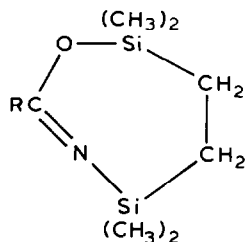
All bis(trimethylsilyl) amides, except bis(trimethylsilyl)formamide (BSF), have been shown to exist in the imidate form I [1,2]. These compounds are generally prepared by silylation of the appropriate amide with trimethylchlorosilane or by



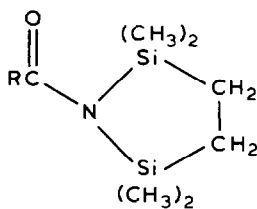
lithioamination of an acid chloride with lithiohexamethyldisilazane. It has also been established that there is exchange between the trimethylsilyl groups in the imidate form and a mechanism involving an intermediate amide has been proposed for this exchange [3]. The barriers (free energies) for the exchange depend on the nature of

the carbonyl substituent and vary from ca. 15 to 22 kcal/mol. The free energy of activation for rotation around the carbonyl–nitrogen bond in the amide is lowered relative to *N,N*-dialkylformamides to about 12 kcal/mol. The roughly 6 kcal/mol lowering has been attributed to a combination of the bulk of the trimethylsilyl group and (*p-d*) π interactions in the transition state [2].

Although a few bis(organosilyl) amides have been prepared with groups other than trimethylsilyl [4,5], there have been no systematic attempts to determine how substituents on silicon affect the structure of these compounds. The present study is an attempt to determine the effect of the size of the organosilyl group on the structure and dynamics of these compounds. To this end several amides containing the dimethylsilyl group were prepared and studied by multinuclear NMR, and the bis(dimethylsilyl)ethylene group was employed to uncover the effects of a ring, which could exist in either the imidate or amide form (III, IV). The spatial



(III)



(IV)

requirements around the silazane portion of the bis(dimethylsilyl)ethylene amide are somewhat less than those in bis(trimethylsilyl) amides because the ethylene bridge “pins back the ears” of the silicons and lowers steric interactions.

Experimental

All preparations were carried out under an argon atmosphere using dry reagents and oven-dried glassware. Bis(trimethylsilyl)formamide was prepared by amination of trimethylchlorosilane with formamide according to literature procedure [2]. Bis(trimethylsilyl)benzimidate and bis(trimethylsilyl)trimethylacetimidate were prepared by lithioamination of the appropriate acid chlorides with lithio hexamethyldisilazane. The boiling points of the products were in good agreement with the literature boiling points [2,3]. Bis(dimethylsilyl)acetamide was obtained from Petrarch Chemical Co.

Bis(dimethylsilyl)propionamide was prepared by amination of 0.2 mol dimethylchlorosilane with 0.1 mol propionamide in 0.22 mol triethylamine and 60 ml benzene. After addition of the dimethylchlorosilane at 0°C, the reaction mixture was heated under reflux for 2 h. The solvent was removed by distillation and the product was then obtained (13 cm column packed with glass helices) in 70% yield at 27°C/0.5 Torr. (Found: C, 44.20; H, 10.08. C₇H₁₉NOSi₂ calcd.: C, 44.39; H, 10.11%.)

The bis(dimethylsilylethylene) derivatives (IV) of three amides were prepared by transsilylation. Equal molar amounts (0.05 mol) of bis(trimethylsilyl)acetimidate (BSA) and 1,4-dichloro-1,1,4,4-tetramethyldisilylethylene were heated to reflux for 3

h in a two-necked flask fitted with a thermometer and a 4 inch column fitted with a distillation head. Trimethylchlorosilane was removed at 57–60°C. The residue was then distilled under vacuum through a 13 cm column packed with glass helices. Product was obtained at 106°C/20 Torr in 76% yield. (Found: C, 47.12; H, 9.85. $C_8H_{19}NOSi_2$ calcd.: C, 47.40; H, 9.51%.) The formamide derivative was obtained with the same procedure. Product was obtained in 83% yield at 61–64°C/1 Torr. The compound decomposed slowly and could not be obtained pure. (Found: C, 43.46; H, 9.32. $C_7H_{17}NOSi_2$ calcd.: C, 44.86; H, 9.14%.) The trifluoromethylacetamide derivative was also prepared by transsilylation. However, production of trimethylchlorosilane was slow (no reflux after 4 h at 100°C) and approximately 1 mol% $AlCl_3$ was added. Vigorous refluxing then commenced, trimethylchlorosilane was removed, and product was obtained at 65°C/5 Torr in 70% yield. (Found: C, 37.33; H, 6.70. $C_8H_{16}F_3NOSi_2$ calcd.: C, 37.62; H, 6.31%.)

The ^{13}C , ^{29}Si , ^{14}N , and ^{17}O spectra were obtained on a JEOL FX-90Q spectrometer operating at 22.49, 17.75, 6.41 and 12.11 MHz, respectively. The ^{13}C and ^{29}Si spectra were obtained on 50% solutions in CH_2Cl_2 in 10 mm tubes with an inner tube of acetone- d_6 as lock solvent and TMS as a reference. The ^{14}N and ^{17}O spectra were obtained on neat samples with an inner tube containing a saturated solution of NH_4Cl in D_2O (for ^{14}N) and neat D_2O (for ^{17}O). The ^{14}N shifts were converted to the nitromethane scale by subtracting 352.9 ppm. The pulse sequence PALSE XY was used to reduce roll in the base line for these nuclei.

Results and discussion

Organosilyl amines and amides are generally prepared by amination, lithioamination or transamination. Attempts to utilize transsilylation as a synthetic route were unsuccessful with organosilyl chlorides such as triethylchlorosilane, phenyldimethylchlorosilane, and dichloromethyldimethylchlorosilane, but were successful with $Cl(CH_3)_2SiCH_2CH_2Si(CH_3)_2Cl$. With this halide, the extent, and presumably the rate of the reaction are favored (relative to two moles of a monosilyl halide) by entropy. In the transsilylation of bis(trimethylsilyl)trifluoroacetimidate, the use of $AlCl_3$ was necessary to increase the rate of the reaction. Because no solvent is employed and the liberated trimethylchlorosilane was removed by distillation, yields were generally high and the product needed little purification.

Transsilylation with 1,2-bis(dimethylchlorosilyl)ethane was not successful with bis(trimethylsilyl)benzimidate and bis(trimethylsilyl)trimethylacetimidate. Products were also not obtained by transsilylation of BSA with 1,5-dichlorohexamethyltrisiloxane, 1,7-dichlorooctamethyltetrasiloxane, and 1,6-bis(chlorodimethylsilyl)hexane. In each case the reaction was run first without $AlCl_3$, and when no trimethylchlorosilane was observed, $AlCl_3$ was added. In most cases, starting materials were isolated, but in a few reactions, decomposition of the imidate to the nitrile was detected.

The NMR chemical shifts are listed in Table 1. The shifts for BSA and BSF are given because their structures are known to be imidate and amide, respectively. In the ^{13}C spectra, the amide carbonyl comes at higher frequency than the imidate carbon. The largest differences, however, appear in the ^{14}N and ^{17}O spectra, where the ^{14}N shift of the amide is more than 100 ppm to lower frequency and the ^{17}O shift of the amide is more than 200 ppm to higher frequency than that of the

Table 1
Chemical shifts and activation parameters

Compound	R	Structure	Chemical shifts (ppm)			Activation parameters ^a			
			$\delta(^{13}\text{C})$	$\delta(^{29}\text{Si})$	$\delta(^{14}\text{N})$	$\delta(^{17}\text{O})$	T_c	$\Delta\nu$	ΔG
RCON[Si(CH ₃) ₃] ₂	H	amide	1.5, 169.6	8.23	-245	403	-37	47.5	11.5
	CH ₃	imide	1.11, 1.33 23.7, 161.1	-5.5, 16.6	-120	170	78	394	15.9
RCON[Si(CH ₃) ₂ H] ₂	CH ₃	amide	-1.30, 24.81 177.56	-6.48	-253	403	-74	24.1	9.9
	CH ₃ CH ₂	amide	-1.19, 9.8 30.7, 182.5	-11.42	-262	403	-65.0	105.6	9.8
RCON[Si(CH ₃) ₂ CH ₂] ₂	CH ₃	amide	-0.76, 7.96 26.0, 178.4	9.4	-247	413	-36	84.8	11.3
	H	amide	-0.92, 7.86 168.1	16.7	-245	393	-23	11.8	12.9
CF ₃		amide	-0.70, 8.7 116.8, 164.5	20.9	-253	394	-44.3	152.6	10.6

^a Determined from ²⁹Si spectra, except for CH₃CON[Si(CH₃)₂H]₂, whose activation parameters were determined from variable temperature ¹³C spectra. T_c in °C, $\Delta\nu$ in Hz, ΔG in kcal/mol.

imidate. These differences can be attributed to a combination of π -character and the $1/\Delta E$ term in the expression for the paramagnetic contribution to the chemical shift.

These differences in chemical shift can be used to determine the structures of the remaining entries in Table 1. Based on the ^{13}C , ^{14}N , and ^{17}O shifts all can be assigned the amide structure. Moreover, all have temperature dependent ^{13}C and ^{29}Si spectra from which free energies of activation can be obtained. The coalescence temperature, T_c , $\Delta\nu$ (the difference in chemical shifts of the SiCH_3 groups extrapolated to T_c from three or four low temperature spectra), and ΔG , the free energy of activation for rotation [2] about the carbonyl–nitrogen bond, are also given in Table 1. The similarity of the free energies of activation to that of BSF (11.7 kcal/mol from the ^{13}C spectrum ($T_c - 44^\circ\text{C}$), 11.5 kcal/mol from the ^{28}Si spectrum ($T_c - 37^\circ\text{C}$) also confirms the amide structure. The previous observation that two silicons attached to an amide nitrogen lower the free energy of activation for rotation about the carbonyl–nitrogen bond [2] is also substantiated by these compounds. Both bis(dimethylsilyl) derivatives have slightly lower barriers, an observation which can not be explained by decreased steric interactions in the ground state.

The existence of the dimethylsilyl and 1,2-bis(dimethylchlorosilyl)ethane derivatives in the amide form can be more easily rationalized by steric than electronic effects. Both the groups have a lower steric requirement around the carbonyl nitrogen, a factor that seems to be important in the case of the formamide derivative as well. That is, in all bis(silyl) "amides" with small groups attached to either the carbonyl or to the nitrogen, the amide form is favored. Conversely, when the group attached to carbonyl is methyl or larger, the bis(trimethylsilyl) derivatives are imidates. Experiments are underway to determine what groups constitute the minimum requirements for the amide form.

Acknowledgement

The authors are indebted to the National Science Foundation, the Petroleum Research Fund, administered by the American Chemical Society, and Franklin and Marshall College for support of this work.

References

- 1 C.H. Yoder and D. Bonelli, *Inorg. Nucl. Chem. Lett.*, 8 (1972) 1027.
- 2 C.H. Yoder, W.C. Copenhafer and B. DuBeshter, *J. Am. Chem. Soc.*, 96 (1974) 4283.
- 3 K. Itoh, M. Katsuda, Y. Ishii, *J. Chem. Soc. B*, (1970) 302.
- 4 J. Kowalski and Z. Lasocki, *J. Organomet. Chem.*, 128 (1977) 37.
- 5 C.L. Hausman and C.H. Yoder, *J. Organomet. Chem.*, 161 (1978) 313.