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The Structures of Some Amides Obtained from
Chloromethyldimethylchlorosilane

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Summary

A series of amides of the type $\text{RCONR}'[\text{CH}_2\text{Si}(\text{CH}_3)_2\text{Cl}]$ were prepared by the reaction of chloromethyldimethylchlorosilane with a series of N-alkyl, N-aryl, and trimethylsilyl amides. The structure of the compound obtained from reaction with bis(trimethylsilyl)acetamide was previously determined by x-ray analysis and is used to rationalize the NMR and IR spectra of its ^{14}N and ^{15}N isotopomers. The spectroscopic features of the N-alkyl and N-aryl derivatives are discussed; the derivatives with $\text{R}=\text{CH}_3$ appear to have the oxygen strongly coordinated to silicon within a 5-membered ring.

The structures and dynamics of trimethylsilyl amides have been extensively investigated [1-6]. Recently, several series of amides with other substituents at silicon have been reported. Kowalski and Lasocki have assigned the imidate structure to a series of bis(trialkylsilyl)- and bis(aryldimethylsilyl)acetamides [7] and the amide structure to bis(halomethyldimethylsilyl)acetamides [8]. The objective of the present work was to determine the structure of a series of mono and bis derivatives formed by the reaction of amides with chloromethyldimethylchlorosilane.

Experimental

All operations were performed under a nitrogen atmosphere using oven-dried glassware and dry reagents.

Bis(chlorodimethylsilylmethyl)acetamide(I) was prepared by the addition of 2 ml chloromethyldimethylchlorosilane to a mixture of 1 ml bis(trimethylsilyl)acetamide and 4 ml hexane. The mixture was stirred overnight and the white precipitate was then filtered, washed with ether and dried *in vacuo*; m.p. 113-115°C (Lit. [8] m.p. 128-131°C). (Found: C, 34.80; H, 7.03. $C_8H_{19}ONSi_2Cl_2$ calcd.: C, 35.28; H, 7.03.) The ^{15}N isotopomer was prepared in analogous fashion from ^{15}N bis(trimethylsilyl)acetamide [9].

Chlorodimethylsilylmethylacetanilide(II) was prepared by reaction of trimethylsilylacetanilide [3] with chloromethyldimethylchlorosilane in hexane. The white crystals that formed after refluxing overnight were washed with hexane and dried *in vacuo*; m.p. 97-99°C. (Found: C, 54.68; H, 6.41. $C_{11}H_{16}NOSiCl$ calcd.: C, 54.63, H, 6.68.)

Chlorodimethylsilylmethyl-N-methylacetamide(III) was prepared by the reaction of N-methyl-N-trimethylsilylacetamide with chloromethyldimethylchlorosilane in hexane. The white precipitate was purified by sublimation; m.p. 64-66°C. (Found: C, 39.59; H, 7.92. $C_6H_{14}NOSiCl$ calcd.: C, 40.09; H, 7.85.)

Chlorodimethylsilylmethyl-N-methylformamide(IV) was prepared by amination of chloromethyldimethylchlorosilane in benzene with N-methylformamide in the presence of triethylamine. The precipitated hydrochloride was removed by filtration and solvent removed from the filtrate under vacuum. The white crystals that formed when the volume of filtrate had been reduced by two-thirds were collected and washed with a small amount of hexane and then distilled at reduced pressure: m.p. 67-68°C; b.p. 76-78°C/0.16 mm Hg. (Found: C, 36.98; H, 7.68. $C_5H_{12}NOSiCl$ calcd.: C, 36.23; H, 7.31.)

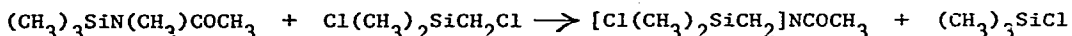
The chlorodimethylsilylmethylformanilide derivatives were prepared by amination of the appropriate formanilide in benzene in the presence of triethylamine using a procedure similar to that employed for the N-methyl-

formamide derivative. Chlorodimethylsilylmethylformanilide(V) was obtained by distillation of the solid remaining after removal of the solvent: b.p. 110°C/0.05 mm Hg. (Found: C, 52.78; H, 6.49. $C_{10}H_{14}NOSiCl$ calcd.: C, 52.72; H, 6.21.) The ^{15}N -isotopomer was prepared by the same method from ^{15}N -formanilide (obtained from ^{15}N -aniline and formic acid). The *p*-CH₃ and *p*-OCH₃ derivatives were obtained after reduction of the filtrate to one-third volume: *p*-CH₃ (VI) washed with hexane, dried in vacuo, m.p. 104-105°C. (Found: C, 54.43; H, 6.81. $C_{11}H_{12}NOSiCl$ calcd.: C, 54.63; H, 6.68.) *p*-OCH₃ (VII) washed with benzene, dried in vacuo, m.p. 113-114°C. (Found: C, 51.22; H, 6.27. $C_{11}H_{12}NO_2SiCl$ calcd.: C, 51.24, H, 6.27.)

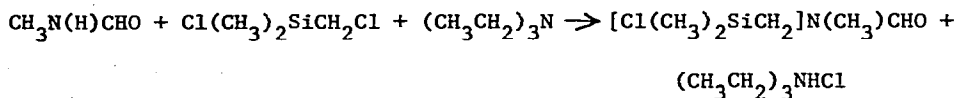
Molecular weights were determined cryoscopically in benzene. Infrared spectra were recorded on a Perkin-Elmer 621 spectrometer and NMR proton spectra were obtained on a Varian A-60D spectrometer equipped with variable temperature accessory V-4341/V-6057. Carbon-13 NMR spectra were obtained with a JEOL FX-60 spectrometer.

Results

Bis(chlorodimethylsilylmethyl)acetamide(I), chlorodimethylsilylmethylacetanilide(II), and *N*-methylacetamide(III) were prepared by reaction of the corresponding trimethylsilyl derivatives with chloromethyldimethylchlorosilane in essentially quantitative yields. Trimethylchlorosilane is produced during the reaction, which for the formation of III can be depicted as



Chlorodimethylsilylmethyl-*N*-methylformamide(IV) and a series of chlorodimethylsilylmethyl-substituted formanilides--V *p*-H, VI *p*-CH₃, VII *p*-OCH₃--were prepared by reaction of the appropriate amide with chloromethyldimethylchlorosilane in the presence of triethylamine. The yields of the amination reactions were lower, generally 30-50%.



The proton chemical shifts of the compounds are summarized in Table I.

Table I Chemical Shifts, δ ppm^a

RCONR' [CH ₂ Si(CH ₃) ₂ Cl]								
	R	R'	SiCH ₃	SiCH ₂	COCH ₃	NCH ₃	COH	Ar-X
I	CH ₃	CH ₂ Si(CH ₃) ₂ Cl	0.08, 0.96	2.45, 2.77	1.41			
II	CH ₃	C ₆ H ₅	0.86	3.07	1.56			
III	CH ₃	CH ₃	0.76	2.57	1.52	2.40		
IV	H	CH ₃	0.70	2.42		2.49		
V	H	C ₆ H ₅	0.78	2.91			7.83	
VI	H	C ₆ H ₄ CH ₃	0.81	2.98			7.94	2.17
VII	H	C ₆ H ₄ OCH ₃	0.76	2.90			7.75	3.47

^aca. 10% in ClC₆H₅, except for I (C₆H₆)

The spectrum of I in C₆H₆ contains two singlets for the Si(CH₃)₂ groups, a singlet (2.45 ppm) and a barely resolved quartet (2.77 ppm, *J* ca. 0.8 Hz) for the SiCH₂ groups, and a barely resolved triplet for the COCH₃ group (1.41 ppm, *J* ca. 0.8 Hz). The spin-spin interaction of the one SiCH₂ group and the COCH₃ group was confirmed by decoupling. The spectrum of the ¹⁵N-isotopomer is identical to that of the ¹⁴N derivative except that the upfield SiCH₂ resonance appears as a doublet (*J* 1.9 Hz) and the COCH₃ resonance is a broad multiplet. The spectra are temperature invariant from -60 to ca. 120°C. Above 120°C (in mesitylene) the Si(CH₃)₂ resonances broaden and by 140°C have coalesced to a very broad peak.

The NMR spectra of both II and III contain a singlet for the Si(CH₃)₂ protons, a barely resolved quartet (*J* ca. 0.8 Hz) for the SiCH₂ protons, and a barely resolved triplet (*J* ca. 0.8 Hz) for the COCH₃ protons. Spin-spin interaction between the SiCH₂ and COCH₃ groups was confirmed by decoupling in both cases. The spectra are unaffected by a decrease in temperature to -60°C.

The spectrum of each of the compounds IV-VII contains only single peaks for the $\text{Si}(\text{CH}_3)_2$ and SiCH_2 protons (the SiCH_2 resonance in V is a barely resolved doublet). The spectrum of the ^{15}N isotopomer of V contains a doublet (J 12 Hz) for the formyl proton and a barely resolved triplet for the SiCH_2 protons. The spectra of compounds IV-VII are unaffected by a decrease in temperature to -60°C . The ^{13}C spectrum of the ^{15}N -isotopomer of V in CoCl_3 exhibits a singlet at 6.1 ppm for the $\text{Si}(\text{CH}_3)_2$ carbons, a doublet (J 7.8 Hz) for the SiCH_2 carbon at 39.5 ppm, a doublet (J 15.6 Hz) for the carbonyl carbon at 162.8 ppm, and a doublet (J 14.7 Hz) at 139.8 ppm for the ^{15}N -C aromatic carbon.

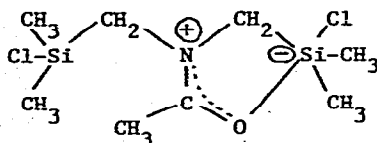
The infrared spectrum of I in CCl_4 contains an intense absorption at 1589 cm^{-1} that shifts to 1580 cm^{-1} in the ^{15}N isotopomer. Four other, weaker absorptions also differ by more than 5 cm^{-1} in the spectra of the isotopomers: $^{14}\text{N}(^{15}\text{N})$, cm^{-1} —1514(1500)m, 1229(1219)m, 1168(1153)w, and 1050(1042)w. The spectra of the mono derivatives contain peaks in the region from 1580 cm^{-1} to 1700 cm^{-1} at: II (CCl_4), 1587s, 1606m; III (CCl_4), 1598s; IV (CHCl_3) 1651s; V (CHCl_3), 1636s, 1656sh; VI (CHCl_3), 1609sh, 1634s; VII (CHCl_3), 1586w, 1644s. The spectrum of the ^{15}N -isotopomer of V contained several peaks that differed by more than 5 cm^{-1} from their ^{14}N counterparts: $^{14}\text{N}(^{15}\text{N})$, cm^{-1} : 1636(1628)s, 1349(1339)m. The ir spectra of IV-VII contain no absorptions in the region 880 – 1010 cm^{-1} ; the spectrum of II contained several weak absorptions in the 980 – 1010 cm^{-1} region, while the spectrum of III contained a weak absorption at 980 cm^{-1} .

Molecular weights for compounds II-VII determined cryoscopically in benzene corresponded to the monomer in solution with little variation with concentration. For compound I, however, the experimental molecular weights increased with concentration: calcd. 272, found 0.01 m 233; at 0.1 m 369.

Discussion

Both the conformational stability and the apparent coupling of ^{15}N to only one methylene group in the NMR spectrum of I are inconsistent with the N,N-bis(chloromethyldimethylsilyl)amide structure, $\text{CH}_3\text{CON}[\text{Si}(\text{CH}_3)_2\text{CH}_2\text{Cl}]_2$,

proposed by Kowalski and Lasocki [8]. (The coalescence temperature for the $\text{Si}(\text{CH}_3)_3$ resonances in the NMR spectrum of N,N -bis(trimethylsilyl)formamide is -46° [2]. The larger size of the $\text{Si}(\text{CH}_3)_2\text{CH}_2\text{Cl}$ group and the generally lower barrier for acetamides would probably produce an even lower rotational barrier for N,N -bis(chloromethyldimethylsilyl)acetamide.) Moreover, the absorption at 1589 cm^{-1} in the infrared spectrum of I is very low for a disilyl amide and the spectrum contains no absorption in the $900\text{--}1000\text{ cm}^{-1}$ region (generally assigned to the Si-N-Si group) that is sensitive to substitution of ^{15}N . (For N,N -bis(trimethylsilylsilyl)formamide the carbonyl absorption appears at 1659 cm^{-1} and an absorption at 983 cm^{-1} shifts to 961 cm^{-1} in the ^{15}N isotopomer.) The recent x-ray structure determination [10] of I reveals that the compound has the N,N -bis(chlorodimethylsilylmethyl) structure with the carbonyl coordinated to one silicon in a planar 5-membered ring.



The C-O and C-N bond lengths are indicative of π -character in both bonds as indicated in the structural formula rather than the $\text{N}=\text{C}=\text{O}$ or $\text{N}-\text{C}=\text{O}$ extremes.

The high conformational stability of compound I is therefore a result of the coordination to silicon; presumably at higher temperatures there is sufficient energy to produce magnetically equivalent $\text{Si}(\text{CH}_3)_2\text{Cl}$ groups through rotational averaging about the C-N bond. Since ^{15}N - ^1H coupling constants are known to be quite stereospecific [11,12], the difference in the two bond couplings of ^{15}N to the protons of the two methylene groups can be at least partially attributed to the rigid orientation of the ring CH_2 protons relative to the *exo* CH_2 protons. The upfield SiCH_2 resonance, which is a doublet in the spectrum of the ^{15}N isotopomer, can be attributed to the uncoordinated SiCH_2 group (*vide infra*). The two-bond ^{15}N - ^1H coupling is similar to other two-bond ^{15}N - ^1H couplings through tetracoordinate carbons [11]. The low field $\text{Si}(\text{CH}_3)_2$ resonance can be assigned to the pentacoordi-

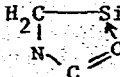
nate silicon because of the similarity of its chemical shift to those of the $\text{Si}(\text{CH}_3)_2$ groups of derivatives II and III which also have intramolecular coordination to silicon (vide infra). It should be noted that this assignment is contrary to the generally observed upfield shift of nuclei in the acceptor portion of Lewis complexes [13]. The SiCH_2 protons of the ring and the COCH_3 protons undergo 5-bond coupling, possibly a result of their trans orientation across the C-N bond.

The 1589 cm^{-1} absorption in the infrared spectrum of I can almost certainly be assigned to the CO group and the shift observed upon substitution of ^{15}N is indicative of coupling to the CN vibration. The low value of the CO vibration is probably a result of coordination to silicon.

The infrared spectra of the formamide, IV, and formanilide derivatives, V-VII, contain strong absorptions in the $1630\text{--}1660 \text{ cm}^{-1}$ region and no absorptions in the $880\text{--}1010 \text{ cm}^{-1}$ region. Since all of the N-trimethylsilyl amides examined previously [9,2], as well as trimethylsilyl amide-imidate mixtures [3], contain absorptions between 930 and 980 cm^{-1} , derivatives IV-VII probably also contain the $\text{N-CH}_2\text{Si}(\text{CH}_3)_2\text{Cl}$ group. This is supported by the $^{15}\text{N-}^{13}\text{C}$ coupling of 7.8 Hz in the ^{15}N isotopomer of V which is typical of one bond ^{15}N couplings to tetracoordinate carbons [11].

There are several possible explanations for the single set of resonances in the NMR spectra of compounds IV-VII: a) rotation about the carbonyl-nitrogen bond rapid even at -60°C , b) coincidentally equivalent resonances for the two rotamers of each derivative, or c) a significantly greater (close to 100%) population of one rotamer. The amide form of trimethylsilylformanilide has a coalescence temperature of 25°C and the most populated (81%) rotamer has the trimethylsilyl group cis to the carbonyl [3]; N-ethylformanilide has a coalescence temperature of 64°C and the most populated rotamer (83%) has the same conformation [14]. It is unlikely that the $\text{CH}_2\text{Si}(\text{CH}_3)_2\text{Cl}$ group would lower the rotational barrier by more than several kilocalories and hence explanation a) appears improbable. In fact, since the carbonyl absorptions for compounds V-VII appear at lower frequencies than those of the trimethyl-

silyl analogs (in which $\nu(\text{CO})$ ca. 1660 cm^{-1}), the $\text{CH}_2\text{Si}(\text{CH}_3)_2\text{Cl}$ derivatives probably exist almost solely as the rotamer with the $\text{CH}_2\text{Si}(\text{CH}_3)_2\text{Cl}$ group cis to the carbonyl. Coordination of the CO group to silicon in this conformation is more favorable than coordination in the $\text{Si}(\text{CH}_3)_3$ analogs because of the sterically favorably 5-membered ring possible in the $\text{H}_2\text{C}-\text{Si}$ moiety



and also because of the increased Lewis acidity of the silicon due to the presence of the chloro group. Therefore, the temperature invariance of the NMR spectra is a result of the nearly 100% population of only one rotational isomer.

The NMR spectra of the acetanilide(II) and N-methylacetamide(III) derivatives show the same temperature invariance and these compounds also exist as only one rotational isomer. However, the CO vibrational frequency for these derivatives is low, 1606 cm^{-1} and 1598 cm^{-1} respectively, and suggestive of strong coordination to silicon of the type present in I. The NMR spectra of these derivatives also contain the SiCH_2 triplet and COCH_3 quartet present in the NMR of I. Since the $\text{Si}(\text{CH}_3)_2$ resonances for these derivatives appear at ca. 0.8 ppm, the low field $\text{Si}(\text{CH}_3)_2$ resonance in I can be assigned to the coordinated silicon, and the low field SiCH_2 resonance (the quartet) in I is therefore also attributable to the coordinated SiCH_2 group.

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