

REACTIONS OF THE AMBIDENTATE SUBSTRATE CHLOROMETHYLDIMETHYLCHLOROSILANE WITH AMINES AND AMIDES

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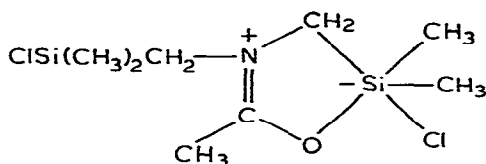
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Summary

Chloromethyldimethylchlorosilane (CMDS) reacts with diethylamine and aniline at the SiCl group to form the corresponding chloromethyldimethylsilyl-amines. With amides, however, substitution on CMDS occurs at the C—Cl bond to form compounds with a 5-membered ring containing a 5-coordinate silicon. Reaction of trimethylsilyl amides with CMDS provides the most convenient route to this ring system but with bis(trimethylsilyl) amides, $RCON[Si(CH_3)_3]_2$, it proceeds only when R is small. Reaction of bis(trimethylsilyl)acetamide and *N*-methyltrimethylsilylacetamide with a variety of substrates of the type $X(CH_2)_nSi(CH_3)_2Y$ occurs when $X = Cl$ or Br and $Y = Cl, Br$ or $N(C_2H_5)_2$ and $n = 2$ but not when $n = 3$ or $Y = OC_2H_5, CH_3, CH=CH_2$, or C_6H_5 .

The product of the reaction of bis(trimethylsilyl)acetamide with chloromethyldimethylchlorosilane (CMDS), initially formulated as *N,N*-bis(chloromethyldimethylsilyl)acetamide [1], was recently found to have the structure



with a 5-coordinate silicon in a planar 5-membered ring [2]. Compounds containing this same ring system are also formed in the reaction of CMDS with *N*-methylformamide, substituted formanilides, *N*-methyl-*N*-trimethylsilylacetamide and trimethylsilylacetanilide [3]. That is, the ring system can be produced either by amination of CMDS with amides in the presence of triethylamine or by "transsilylation" of trimethylsilyl amides.

The objectives of the present work were to: a) determine the structure of the

products formed in the reaction of CMDS with amines, and b) to determine the structural requirements for the formation of the 5-coordinate silicon-containing ring in the reaction of CMDS with amides.

Experimental

All operations were performed under a nitrogen atmosphere using oven-dried glassware and dry reagents. Organosilicon starting materials were obtained from Petrarch Chemical Co., or prepared by literature procedures.

Amination reactions were carried out by adding CMDS dropwise and with stirring to a mixture of the appropriate amine or amide and triethylamine (equimolar ratios) in hexane. The exothermic addition was followed by several hours of stirring at room temperature, filtration of the precipitated triethylamine hydrochloride, removal of solvent at atmospheric pressure, and (for liquid products) fractional distillation of the residue. Solid products were purified by sublimation.

Reactions of trimethylsilyl amides with CMDS or other halomethyl substrates were carried out by rapid dropwise addition (with shaking) of the substrate to the trimethylsilyl derivatives in hexane (ca. 1 to 4 volume ratio of trimethylsilyl derivative to hexane). In most cases precipitation began within two hours. The mixture was allowed to sit overnight and the precipitate was then filtered and washed with either hexane or ether. Attempts to further purify the products by recrystallization, extraction, or sublimation were invariably unsuccessful. In those cases where precipitation did not occur, the absence of product was verified by the superimposability of the NMR spectra of the reactants on the spectrum of the reaction mixture.

Yields, melting or boiling points, analytical data and NMR chemical shifts for the compounds are given in Table 1.

Infrared spectra were recorded on a Perkin-Elmer 621 spectrometer and NMR spectra were obtained on a Perkin-Elmer R-32 (90 MHz) spectrometer.

Results and discussion

Substitution on $\text{ClCH}_2\text{Si}(\text{CH}_3)_2\text{Cl}$ is possible at either the $\text{Cl}-\text{C}$ or $\text{Cl}-\text{Si}$ sites. If average bond energies ($\text{C}-\text{Cl}$, 81; $\text{C}-\text{N}$, 73; $\text{Si}-\text{Cl}$, 97; $\text{Si}-\text{N}$, 76–87 kcal/mol [4]) are used as a gauge of ΔG° for the substitution reactions, substitution at the $\text{Cl}-\text{C}$ site would appear to be thermodynamically slightly more favorable. Moreover, when the nitrogen nucleophile is an amide rather than an amine, substitution at the $\text{Cl}-\text{C}$ site should be even more favorable because of the lower π -character (and thus lower energy) of the $\text{Si}-\text{NCO}$ bond, relative to the $\text{Si}-\text{NC}$ bond, due to competition between Si and CO for the nitrogen lone pair of electrons. However, substitution at silicon is generally believed to be kinetically more favorable [4].

That substitution of amines at the $\text{Cl}-\text{C}$ site is unfavorable is evident from the fact that reflux of a 1 : 2 molar ratio of $(\text{CH}_3)_3\text{SiCH}_2\text{Cl}$ and diethylamine in hexane produced only a very small amount of precipitated diethylamine hydrochloride even after 72 hours. Moreover, the reaction of CMDS with diethyl-

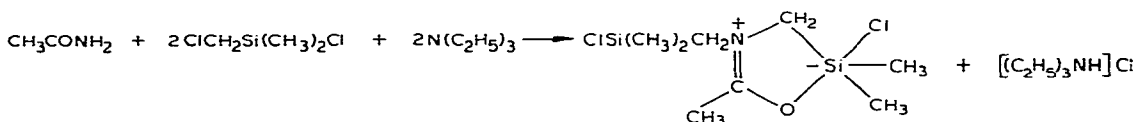
amine in hexane produced the Si—N product



The structure of this product was confirmed by the presence of a peak at 925 cm^{-1} , within the $900\text{--}1000 \text{ cm}^{-1}$ region assigned to the Si—N stretching vibration [5], and the absence of even medium intensity absorptions in the $420\text{--}620 \text{ cm}^{-1}$ region assigned to the Si—Cl stretching vibration in chlorosilanes [6].

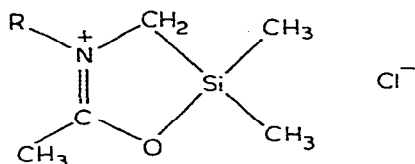
The analogous Si—N structure was also confirmed for the product of the reaction of CMDS with aniline. The NMR spectrum (30% in CDCl_3) of the ^{15}N -isotopomer of this compound, prepared by amination of CMDS with aniline- ^{15}N contained a doublet ($J = 1.0 \text{ Hz}$) for the $\text{Si}(\text{CH}_3)_2$ protons, a singlet for the SiCH_2 protons, and a doublet ($J = 76 \text{ Hz}$) for the NH protons. If substitution had occurred at the Cl—C site to produce the structure $\text{C}_6\text{H}_5\text{NHCH}_2\text{Si}(\text{CH}_3)_2\text{Cl}$, splitting of the SiCH_2 resonance rather than the $\text{Si}(\text{CH}_3)_2$ resonance would likely occur because of the greater magnitude of $^2J(^{15}\text{N}\text{—}^1\text{H})$ than $^4J(^{15}\text{N}\text{—}^1\text{H})$. Because the coupling to the $\text{Si}(\text{CH}_3)_2$ protons is greater than that to the SiCH_2 group the structure is almost surely $\text{C}_6\text{H}_5\text{NHSi}(\text{CH}_3)_2\text{CH}_2\text{Cl}$.

Amination of CMDS with acetamide in a 2 to 1 mole ratio produced a compound whose physical and spectral characteristics were identical to those of the compound previously prepared by transsilylation of bis(trimethylsilyl)acetamide with CMDS [2] *.



This compound and others containing the same 5-membered ring with the 5-coordinate silicon may be obtained more conveniently by transsilylation because of the higher yield and simplicity of isolation. All compounds known to contain this ring system are solids, and all but one (vide infra) are insoluble in hexane.

* A referee has suggested that the long Si—Cl bond length (2.38 Å) found for this compound might be better explained by a 4-coordinate ionic structure



(A)

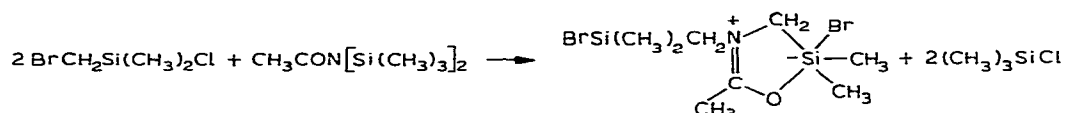
While it is true that the value is larger than the Si—Cl bond length in species such as $(\text{CH}_3)_3\text{SiCl}$ (2.09 Å) and larger than the Si—Cl bond (2.050 Å) at the 4-coordinate silicon in this compound, the 5-coordinate axial Si—Cl bond with a *trans* oxygen would be expected to be longer. The 5-coordinate Si—Cl bond in 1-chlorosilatrane is 2.15 Å [7] and when silicon is attached to 3 equatorial carbons the Si—Cl bond should be even longer. Moreover, the Si—Cl bond is much shorter than the sum of the Si and Cl Van der Waals radii (3.8 Å) which should approximate the Si—Cl distance in structure A.

TABLE 1
YIELDS, MP(BP) AND ANALYTICAL DATA

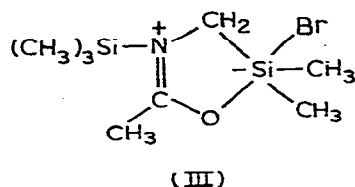
		Prep method	Yield (%)	mp(bp) (°C)	Found (calcd.) (%)		δ (ppm)			
					C	H	Si(CH ₃) ₂	SiCH ₃	Other	
I	$\text{ClCH}_2\text{Si}(\text{CH}_3)_2\text{N}(\text{C}_2\text{H}_5)_2$	a	75	(66/12 mm)	46.70 (46.77)	9.98 (10.01)	0.16 ^c	2.56	0.87 (t), 2.76 (q)	
II	$\text{ClCH}_2\text{Si}(\text{CH}_3)_2\text{NHC}_6\text{H}_5$	a	40	(147/23 mm)	54.28 (54.09)	7.44 (7.06)	0.58 ^c	3.08	3.76 (NH)	
III	$(\text{CH}_3)_3\text{SiNC}(\text{CH}_3)_2\text{O}[\text{CH}_2\text{Si}(\text{CH}_3)_2\text{Br}]$	b	70	104–107	34.05 (34.66)	7.09 (7.22)	0.48, ^d 0.78	2.87	2.13 (CH ₃)	
IV	$(\text{C}_2\text{H}_5)_2\text{NSi}(\text{CH}_3)_2\text{CH}_2\text{N}(\text{CH}_3)\text{CO}[\text{CH}_2\text{Si}(\text{CH}_3)_2\text{Cl}]$	a, b	40	60–65	45.05 (46.54)	9.59 (9.46)	–0.08, ^f 0.94	2.31, 2.82	0.82 (t), 2.53 (q), 1.47 (CCH ₃)	
V	$\text{CH}_3\text{NC}(\text{CH}_3)_2\text{O}[\text{CH}_2\text{Si}(\text{CH}_3)_2\text{Br}]$	b	53	133–139	30.71 (32.15)	7.53 (6.30)	0.40 ^d	2.93	3.26 (NCH ₃) 2.27 (CCH ₃)	
VI	$\text{CH}_3\text{NC}(\text{CH}_3)_2\text{O}[\text{CH}_2\text{Si}(\text{CH}_3)_2\text{Cl}]$	b	41	62–67	31.30 (30.01)	6.50 (5.54)	0.39 ^e	2.97	3.27 (NCH ₃) 2.48 (CCH ₃)	
VII	$\text{CH}_3\text{NC}(\text{CH}_3)_2\text{O}[\text{CH}_2\text{Si}(\text{CH}_3)_2\text{Cl}]$	b	56	64–66	39.59 (40.10)	7.92 (7.85)	0.48 ^d	2.77	3.07 (NCH ₃) 2.11 (CCH ₃)	

a amination, b "transilylation", c neat, d 10% CH₂Cl₂, e 10% CHCl₃, f 10% C₆H₆.

In order to determine which structural features at silicon are necessary for the formation of this ring system bis(trimethylsilyl)acetamide (BSA) and *N*-methyl-*N*-trimethylsilylacetamide (MSA) were reacted with a variety of substrates of the type $X(\text{CH}_2)_n\text{Si}(\text{CH}_3)_m\text{Y}_{3-m}$. All the solid products formed had the spectral characteristics (e.g., $\nu(\text{C}=\text{O}) = 1600\text{--}1625\text{ cm}^{-1}$) previously associated with the 5-membered ring [3]. Reaction of $\text{BrCH}_2\text{Si}(\text{CH}_3)_2\text{Cl}$ with BSA in a 2 to 1 mole ratio produced the compound previously described as

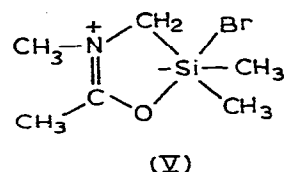


N,N-bis(bromomethyldimethylsilyl)acetamide [1]. The reaction of $\text{BrCH}_2\text{Si}(\text{CH}_3)_2\text{Cl}$ with BSA in a 1 to 1 mole ratio resulted in the displacement of only one $\text{Si}(\text{CH}_3)_3$ group to give compound III.

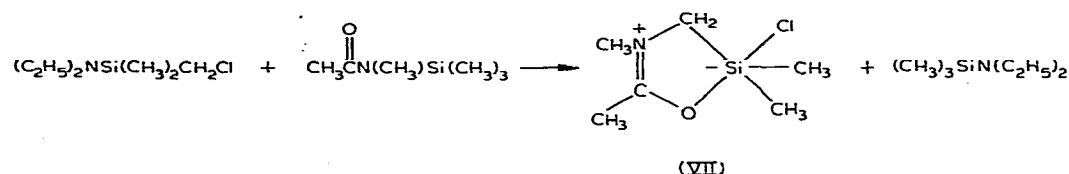


The disubstituted compound was generated from III by addition of $\text{BrCH}_2\text{Si}(\text{CH}_3)_2\text{Cl}$ in a 1 to 1 ratio. Hence, the displacement of $\text{Si}(\text{CH}_3)_3$ groups takes place stepwise with ring formation occurring in the first step.

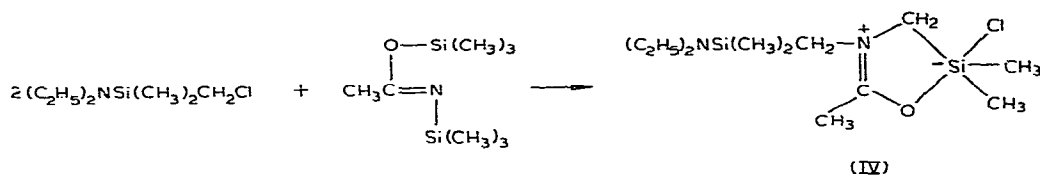
Reaction of $\text{BrCH}_2\text{Si}(\text{CH}_3)_2\text{Cl}$ with MSA also resulted in the 5-membered ring V. It is important to note that in all of the reactions of $\text{BrCH}_2\text{Si}(\text{CH}_3)_2\text{Cl}$,



the bromine, displaced at the methylene, in turn displaces the chlorine attached to silicon. In order to determine whether the group attached to methylene always migrates to silicon, the reaction of MSA with $\text{ClCH}_2\text{Si}(\text{CH}_3)_2\text{Br}$ was carried out. In this case, however, compound V was formed. Thus, it appears that displacement of Cl by Br is favored at silicon and that migration occurs only for certain groups. Migration from the methylene group to the ring silicon also occurred in the reaction of I with MSA. In this case compound VII, containing



chlorine at silicon, was formed. When compound I was mixed with BSA, displacement of both trimethylsilyl groups took place but migration of chlorine occurred only for the ring silicon.



The same compound (IV) was produced by reacting bis(chlorodimethylsilylmethyl)acetamide with diethylamine (in both a 1 to 2 and 1 to 4 mole ratio).

Solid products were also formed in the reactions of both BSA and MSA with $\text{ClCH}_2\text{SiCH}_3\text{Cl}_2$ and $\text{ClCH}_2\text{SiCl}_3$. However, purification of these proved to be very difficult and only the properties of product VI from the reaction of MSA with $\text{ClCH}_2\text{Si}(\text{CH}_3)_2\text{OC}_2\text{H}_5$, $\text{ClCH}_2\text{Si}(\text{CH}_3)_2\text{CH}=\text{CH}_2$, $\text{ClCH}_2\text{Si}(\text{CH}_3)_3$, $\text{ClCH}_2\text{Si}(\text{CH}_3)_2\text{C}_6\text{H}_5$, $\text{ClCH}_2\text{CH}_2\text{Si}(\text{C}_2\text{H}_5)_2\text{Cl}$, and $\text{ClCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{CH}_3)_2\text{Cl}$. From these observations it can be concluded that groups such as $\text{C}_2\text{H}_5\text{O}$, CH_3 , C_6H_5 , $\text{CH}=\text{CH}_2$ attached to silicon do not promote formation of the 5-membered ring and that 6- and 7-membered rings are not formed in these reactions.

In order to determine what R groups of bis(trimethylsilyl) amides, $\text{RCON}[\text{Si}(\text{CH}_3)_3]_2$, promote the formation of the 5-membered ring, CMDS was mixed with bis(trimethylsilyl) amides with $\text{R} = \text{H}$, C_2H_5 , $\text{C}(\text{CH}_3)_3$, C_6H_5 , and CF_3 . Only when $\text{R} = \text{H}$ and C_2H_5 were solid products formed. The $\text{R} = \text{C}_2\text{H}_5$ product was moderately soluble in hexane and difficult to purify while the $\text{R} = \text{H}$ derivative rapidly became an oil which could not be purified. The other groups have widely different electronic effects but since all are larger than CH_3 and C_2H_5 the lack of reaction of the amides with $\text{R} = \text{C}(\text{CH}_3)_3$, C_6H_5 , and CF_3 can be tentatively attributed to a size effect.

These results indicate therefore that: a) reaction of CMDS with amines involves displacement of chlorine at silicon, whereas with amides displacement of chlorine at carbon occurs; b) the 5-membered ring system containing the 5-coordinate silicon can be obtained through both amination and "transsilylation"; c) "transsilylation" occurs stepwise with the formation of the ring taking place in the first step; d) migration of the X group from the methylene group in $\text{XCH}_2\text{Si}(\text{CH}_3)_2\text{Y}$ to the ring silicon occurs for some X, Y combinations (when $\text{X} = \text{Br}$ and $\text{Y} = \text{Cl}$ but not when $\text{X} = \text{Cl}$ and $\text{Y} = \text{Br}$); e) ring formation only occurs for certain Y groups in the substrate $\text{X}(\text{CH}_2)_n\text{Si}(\text{CH}_3)_2\text{Y}$ (for $\text{Y} = \text{Cl}$, Br , $\text{N}(\text{C}_2\text{H}_5)_2$ but not OC_2H_5 , CH_3 , $\text{CH}=\text{CH}_2$, and C_6H_5), and only when $n = 1$; and f) ring formation does not occur for large R groups in $\text{RCON}[\text{Si}(\text{CH}_3)_3]_2$.

Although the reaction of CMDS with amides results in products in which displacement of chlorine at carbon has occurred, it seems likely that the mechanism involves more conventional attack at silicon. Experiments designed to provide additional mechanistic information are in progress.

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