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TRIMETHYLSILYL AND HALODIMETHYLSILYLMETHYL DERIVATIVES OF SOME DIAMINES

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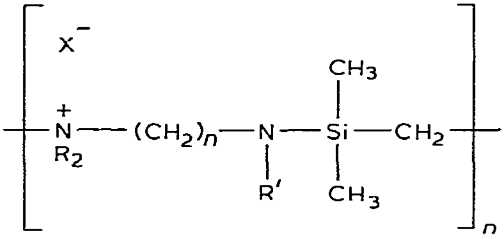
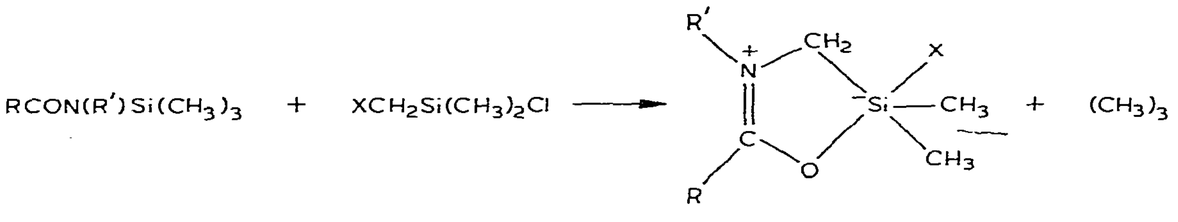
Summary

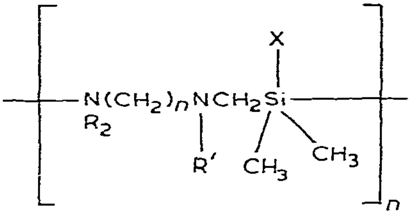
The reaction of chloro- and bromomethyldimethylchlorosilane with a variety of *N,N,N'*-trialkyldiamines resulted in solids which, on the basis of proton, ^{29}Si, and ^{37}Cl chemical shift and molecular weight data, are assumed to have a dimeric or trimeric structure (in solution) that contains a 4-coordinate silicon:



The discovery that the reaction of amines with chloro- and bromomethyldimethylchlorosilane results in displacement of the chlorine at the Si—Cl site, whereas reaction with amides produces displacement at the halomethyl site [1] suggested that a coordinating site in the nucleophile might be sufficient, if not necessary, for attack at the C—Cl bond. Consequently we have now prepared a series of trimethylsilyl amines with a second, tertiary nitrogen site capable of forming a dative N → Si bond, and have reacted these compounds with chloro- or bromomethyldimethylchlorosilane. If the "transsilylation" occurs analogously to the reaction of the amides [2,3] the product would contain a 5-coordinate silicon resulting from a dative N—Si linkage.

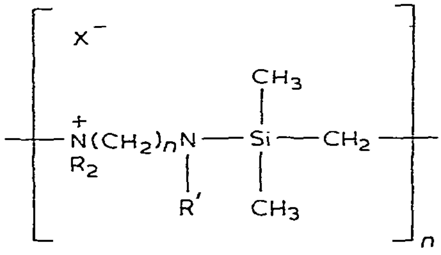


(A)



(B)

However, the reaction could also result in a quaternary ammonium salt containing a four coordinate silicon



(C)

These two possible products differ in a) the coordination number of silicon, b) the displacement of halogen at silicon in C but not B, and c) the presence of a chloride ion in C, whereas B contains a covalently bonded chlorine.

The diamines were prepared in yields of 60—80% by amination of trimethylchlorosilane with *N,N,N'*-trialkylethylenediamines (and *N,N,N'*-trimethylpropylenediamine) in the presence of triethylamine.

$$R_2N(CH_2)_nNHR' + (CH_3)_3SiCl \xrightarrow{(C_2H_5)_3N} R_2N(CH_2)_nNR'Si(CH_3)_3$$

The physical and spectral properties of the diamines (I—III) are presented in Table 1. The NMR spectra (CH_2Cl_2) are easily rationalized by first order effects except for the bridge methylene proton multiplets which in all cases are distorted triplets. The resonance of the protons of the N—CH_3 group attached to silicon appears at lower fields than the $N(CH_3)_2$ protons.

The reaction of the trimethylsilyl diamines with chloro- and bromomethyldimethylchlorosilane in hexane produced moisture-sensitive solids which are insoluble in most solvents but slightly soluble in halogenated hydrocarbons such as CH_2Cl_2, CH_2I_2, $CHCl_3$, and $CHBr_3$. Molecular weights of the solids were determined by the Rast method and also cryoscopically in CH_2I_2, $CHBr_3$, and by osmometry in $C_2H_4Cl_2$, pyridine and acetonitrile. The molecular weight obtained in all solvents except pyridine and acetonitrile were higher than the weights calculated for the monomers and were dependent upon the solvent. The molecular weights obtained by osmometry in pyridine and acetonitrile were close to the monomeric weights.

The proton NMR chemical shifts for the compounds dissolved in CH_2Cl_2 are tabulated in Table 1 and reveal a striking difference in the position of the $N-CH_3$ or $N-CH_2$ resonances of the *N,N*-dialkyl group in the halomethyl derivatives relative to those of the trimethylsilyl derivatives. In all cases the resonance for the halomethyl derivatives is at least 1 ppm lower than that of the trimethylsilyl derivatives. The resonances for the *N*-alkyl (R′) group of the other nitrogen, on the other hand, are fairly similar for both derivatives. These trends parallel the chemical shifts found for the chlorodimethylsilylmethyl amides [1,2], where the resonance of the $N-CH_3$ group in the heterocycle A appears considerably downfield of its position in the trimethylsilyl analog, and suggest a similar placement of a formal positive charge on the $R_2\overset{+}{N}CH_2$ group of the diamines.

The ^{29}Si NMR spectrum of compound IV in CH_2Cl_2 contained two peaks at −4.5 and −4.7 ppm relative to TMS. The ^{29}Si spectrum of compound A, (where $R = CH_2Si(CH_3)_2Cl$) in CH_2Cl_2 which contains both five- and four-coordinate silicons, exhibited peaks at 6.3 ppm and −40.5 ppm. Because neat $(CH_3)_2NSi(CH_3)_2CH_2Cl$ and $ClSi(CH_3)_2CH_2Cl$ have ^{29}Si shifts at 3.2 ppm and 23.3 ppm, respectively, it is likely that the high field peak in the spectrum of A can be assigned to the five-coordinate silicon. This assigment is also supported by the greater shielding of silicon in the five coordinate silatranes relative to triethoxy silanes [4]. Thus, the greater similarity of the ^{29}Si shift of compound IV to compounds containing 4-coordinate silicons in similar environments (e.g., $(CH_3)_2NSi(CH_3)_2CH_2Cl$) suggests the presence of four-coordinate silicon in this compound.

Because the two structures B and C contain quite different types of chlorine, the ^{37}Cl NMR spectrum of compound IV should provide a definite structural assignment. Indeed, the ^{37}Cl spectrum of IV in CH_2Cl_2 contains a sharp peak (hhw ≅ 400 Hz), only slightly downfield (10 ppm) of the resonance for tetramethylammonium chloride in water (hhw = 200 Hz). In acetonitrile, the resonance for IV is 25 ppm downfield of tetramethylammonium chloride, with a similar width. This is in sharp contrast to the width of the ^{37}Cl resonance in compounds containing covalently attached chlorine [4]; for example, $(CH_3)_3SiCl$ absorps 50 ppm downfield of tetramethylammonium chloride with a half height width of over 2500 Hz. The "sharp" resonance observed for IV is almost surely indicative of a slow relaxation time resulting from a high symmetry electric field about the chlorine and the chlorine in IV is therefore best represented by structure C.

The reaction of compound IV with D_2O is also supportive of representation C. The proton NMR spectrum of the compound in D_2O even after several hours was almost identical to the spectrum in CH_2Cl_2, indicating a low rate of reaction with water. Although the low rate is surprising for either structure, B

TABLE 1

PHYSICAL AND NMR SPECTRAL PROPERTIES OF TRIMETHYLSILYL AND HALODIMETHYLSILYLMETHYL DIAMINES

$R_2N(CH_2)_nNR'X$						Analysis (%)						Chemical shifts (δ, ppm)[a]				
	X	*n*	R	R'	b.p. (m.p.) (°C)	calc.			Found			Si-$(CH_3)_2$	$SiCH_2$	R	R'	$N(CH_2)_nN$
						C	H	Mol. wt.	C	H	Mol. wt.					
I	$(CH_3)_3Si$	2	CH_3	CH_3	68/24 mmHg	55,10	12,72	174	55,64	12,69		0,02		2,13		2,24(t), 2,80(t)
II	$(CH_3)_3Si$	2	C_2H_5	C_2H_5	88—90/ 35 mmHg	61,04	13,04	216	60,71	13,19		0,03	—	0,97(t) 2,43(q)	0,97(t) 2,73(q)	[b]
III	$(CH_3)_3Si$	3	CH_3	CH_3	64—65/8 mmHg	57,38	12,84	188	56,86	14,16		0,03	—	2,15	2,40	1,51(m), 2,17(t), 2,70(t)
IV	$Cl(CH_3)_2SiCH_2$	2	CH_3	CH_3	(222—224)	46,01	10,14	209	45,24	9,96	400 (CH_2I_2) 670 ($HCBr_3$) 173 (C_5H_5N) 158 (CH_3CN)	0,26	3,33	3,55	2,50	3,18(t), 3,94(t)
V	$Br(CH_3)_2SiCH_2$	2	CH_3	CH_3	(117—175)	37,93	8,36	253	38,53	8,65	637 ($C_2H_4Cl_2$)	0,28	3,40	3,54	2,51	3,18(t), 3,92(t)
VI	$Cl(CH_3)_2SiCH_2$	2	C_2H_5	C_2H_5	(178—181)	52,66	10,85	251	51,57	11,02	585 ($CHBr_3$) 221 (C_5H_5N)	0,28	3,18	1,35(t) 3,65(q)	1,05(t) 2,80(q)	3,16[b], 3,85(t)
VII	$Br(CH_3)_2SiCH_2$	2	C_2H_5	C_2H_5	(147—152)	44,73	9,22	295	43,57	9,33	773 ($HCBr_3$) 442 ($C_2H_4Cl_2$)	0,30	3,22	1,40(t), 3,64(q)	1,08(t) 2,88(q)	3,21[b], 3,82(t)
VIII	$Br(CH_3)_2SiCH_2$	3	CH_3	CH_3	(116—131)	40,44	8,67	267	37,76	8,20		0,26	3,44	3,49	2,54	2,11(m), 3,07(t), 3,90(t)

[a] Ca. 10% in CH_2Cl_2. [b] Obscured.

or C, it is more reasonable for structure C. After several days, two new peaks (ca. 0.1 ppm upfield of the $N(CH_3)_2$ peak and 0.2 ppm upfield of the $Si(CH_3)_2$ peak) appeared. The fact that the chemical shift of the $N(CH_3)_2$ peak of the hydrolysis product is very similar to the shift of IV suggests that the positive charge is retained on the $N(CH_3)_2$ group. Thus the product is more likely to result from the hydrolysis of structure C rather than structure B where the SiCl bond and SiN dative bond would presumably be very sensitive to hydrolysis.

The "monomeric" molecular weights obtained in pyridine and acetonitrile can probably be ascribed to the higher dielectric constants of these solvents (especially acetonitrile) and their greater solvating ability. Thus, in these solvents the cation-anion dissociation is presumably nearly complete, whereas in solvents such as the halocarbons the ions are more tightly paired. Although *n* in structure C, as well as the extent of dissociation, is solvent dependent, most of the molecular weights suggest that *n* is small, probably in the range of 2—4.

Experimental

All operations were carried out in a nitrogen atmosphere using dry reagents and glassware. Proton NMR spectra were obtained on a 90 MHz Perkin-Elmer R-32 spectrometer. Silicon-29 and chlorine-29 and chlorine-37 spectra were obtained on a Bruker WM-250 spectrometer operating at 49.7 and 24.5 mHz, respectively. Carbon-hydrogen analyses and molecular weights by osmometry were obtained from Schwarzkopf Microanalytical Laboratory (Woodside, NY).

Trimethylsilyl dianines were prepared by amination of trimethylchlorosilane with the appropriate diamine in the presence of triethylamine (1 : 1 : 1 mole ratio) using hexane as a solvent. After filtration of the precipitated triethylamine hydrochloride, solvent was removed and product isolated by fractional distillation. The halodimethylsilylmethyl derivatives were prepared by reaction of a trimethylsilyl diamine with the halomethyldimethylchlorosilane in hexane at room temperature. With the *N,N,N'*-trimethyl derivatives precipitation of the product occurred within several hours, but approximately 12 hours were necessary for complete precipitation of the *N,N*-dimethyl-*N'*-ethyl derivative, while 3 days were required for the triethyl and *N*-phenyl derivatives. The products were isolated by filtration. Attempts at further purification were unsuccessful.

The melting points reported in Table 1 represent the best range obtained for each compound; some samples had melting ranges extending over more than 30 degrees. The molecular weights obtained by the Rast method for compounds IV—VII were all greater than 10^3. Molecular weights in CH_2I_2 and $CHBr_3$ were determined cryoscopically.

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