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AMINOALKOXYSILANES
I. AMINO DERIVATIVES OF ALKOXY- AND ALKYLALKOXYSILANES

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SUMMARY

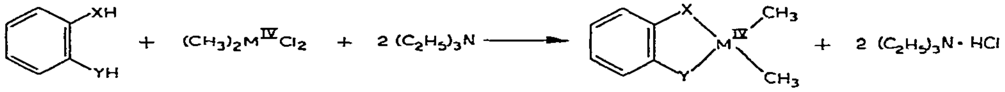
(Aminoalkoxy)silanes have been prepared by alcoholysis of tetraethoxy- methyltriethoxy- and dimethyldiethoxysilane with aminoalcohols in the presence of the corresponding sodium alcoholates. PMR and IR studies show that the compounds are tetrahedral.

INTRODUCTION

Voronkov *et al.*[1] have made a number of (aminoalkoxy)silanes by treating alkylchlorosilanes with aminoalcohols in the presence of a proton acceptor:

$$R_{4-n}SiCl_n + n\,R'R''NCH_2CH_2OH \xrightarrow[Et_2O]{Et_3N} R_{4-n}Si[OCH_2CH_2NR'R'']_n$$
$$(R' = R'' = H, \text{Me or Et})$$

Corresponding heterocyclic silicon and germanium ring compounds have been prepared by Wieber and Schmidt[2]:



Lukevics and coworkers[3] obtained aminoalkoxides by treating silazanes with aminoalcohols and also by transamination[4]:

$$(Me_3Si)_2NH + 2\,HOCH_2CH_2NR_2 \rightarrow 2\,Me_3SiOCH_2CH_2NR_2 + NH_3\uparrow$$
$$Me_{4-n}Si(NEt_2)_n + n\,HOCH_2CH_2NH_2 \rightarrow Me_{4-n}Si[OCH_2CH_2NH_2]_n + n\,Et_2NH$$

In the transaminations, silylation of the NH_2 group was also observed on increasing the temperature or taking a larger proportion of the silicon component:

$$\begin{tikzcd}
Me_3SiNEt_2 + HOCH_2CH_2NH_2 \arrow[r, "-Et_2NH"'] & Me_3SiOCH_2CH_2NH_2 \arrow[d, "+Me_3SiNEt_2"] \\
2\,Me_3SiNEt_2 + HOCH_2CH_2NH_2 \arrow[r, "-2Et_2NH"'] & Me_3SiOCH_2CH_2NHSiMe_3\ \text{(II)} \arrow[d, "+Me_3SiNEt_2 \atop +(NH_4)_2SO_4"] \\
3\,Me_3SiNEt_2 + HOCH_2CH_2NH_2 \arrow[r, "-3Et_2NH"'] & Me_3SiOCH_2CH_2N(SiMe_3)_2\ \text{(III)}
\end{tikzcd}$$

Larsson[5] also reported the reactions of dimethyldiethoxysilane with 2-aminoethanol and 2-(dialkylamino)ethanol in the presence of metallic sodium:

$$Me_2Si(OEt)_2 + 2\ NH_2CH_2CH_2OH \xrightarrow{NaOCH_2CH_2NH_2} Me_2Si(OCH_2CH_2NH_2)_2 + 2\ EtOH$$

Reactions of alkoxides of various elements *viz.*, B[6], Al[7], Ti[8], Zr[9], Ge[10,11], Sn[12] with aminoalcohols have been reported from our laboratories. Except for the derivatives of Ge and Sn, the alkoxides of these elements react only with the hydroxyl group of the aminoalkanol. This differing behaviour of the alkoxides of the Group IVB elements (*i.e.*, Si, Ge and Sn) towards 2-aminoethanols prompted us to investigate in detail the reactions of alkoxysilanes with various aminoalcohols.

RESULTS AND DISCUSSION

This paper describes the reactions of tetraethoxy-, methyltriethoxy- and dimethyldiethoxysilane with 2-aminoethanol, 3-aminopropanol, 2-aminobutanol, 2-methyl-2-amino-1-propanol, 1-(dimethylamino)-2-propanol, 3-(diethylamino)-1-propanol, 2-(dimethylamino)ethanol and 2-(methylamino)ethanol. These reactions can be represented as follows:

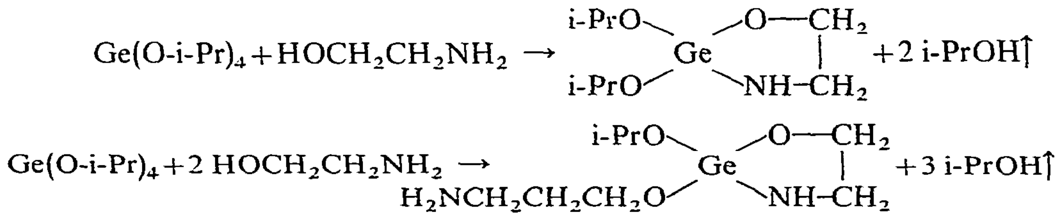
$$R_nSi(OEt)_{4-n} + 4-n\ HOCH_2CH_2NR'R'' \xrightarrow[NaOCH_2CH_2NR'R'']{}$$

$$\rightarrow R_nSi[OCH_2CH_2NR'R'']_{4-n} + 4-n\ EtOH$$

$R' = R'' = H$ or CH_3, $n = 0$, 1 or 2; $R' = H$ and $R'' = CH_3$, $R = CH_3$

The alkoxysilanes were refluxed with the aminoalcohols in stoichiometric ratios in benzene in the presence of a small amount of sodium. The progress of the reaction was checked by estimating the liberated ethanol appearing in the azeotrope. The reactivity of alkoxysilanes towards aminoalcohols is rather low, *e.g.*, only 0.7 mole of ethanol was liberated when methyltriethoxysilane was refluxed for 80 h with 3-amino-1-propanol in 1/1 molar ratio. However, the reactions were faster in the presence of the corresponding sodium alcoholate and were complete within 2–7 h of refluxing.

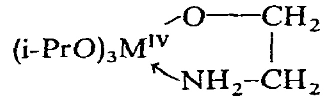
The reactions of Ge[10] and Sn[11] alkoxides with aminoalkanols are very facile and in contrast to alkoxysilanes, both the protons of OH as well as NH_2 get replaced:



$$Sn(O\text{-}i\text{-}Pr)_4 + HOCH_2CH_2NH_2 \rightarrow Sn(O\text{-}i\text{-}Pr)_2(OCH_2CH_2NH) + 2\ i\text{-}PrOH\uparrow$$

In general, the poor reactivity of alkoxysilanes as compared to that of germanium and tin alkoxides could be attributed to the strong $(p\rightarrow d)\pi$ bond interaction in Si–O bond which appears to be reduced substantially in Ge and Sn due to their 4*d* and 5*d* radial nodes respectively[13]. This is further revealed by the M–O bond energies of these elements: Si–O ~ 112 (SiO_2)[14], 106.3 [$(Me_3Si)_2O$][15]; Ge–O ~ 85 (GeO_2)[16]; Sn–O 82 kcal·mole^{-1}.

In the case of tin and germanium, further reactivity of the amino group in a derivative of the type



would probably involve a 5 coordination sp^3d transition state, as depicted above. This sort of hybridisation does not appear to be favoured in case of silicon, unless the *d* orbitals are contracted by the presence of electronegative substituents in the silicon atom[17].

Reactions of methyltriethoxysilane with 2-aminoethanol, 3-aminopropanol and 2-(dimethylamino)ethanol in 1/1 molar ratio tend to give bis products instead of forming mono(aminoalkoxy)diethoxysilanes:

$$2\ MeSi(OEt)_3 + 2\ HO(CH_2)_nNR_2 \xrightarrow{Na} MeSi(OEt)[O(CH_2)_nNR_2]_2 + MeSi(OEt)_3$$

$R = H$ or CH_3, $n = 2$ or 3

Similar behaviour is found in the reaction of dimethyldiethoxysilane with 2-(dimethylamino)ethanol in 1/1 molar ratio.

All the aminoalkoxides obtained are volatile liquids except $Si[OCH_2CH_2NH_2]_4$, which tends to decompose at about 200° on attempted distillation at 0.2 mm pressure. Analysis of the brownish residue revealed that the nitrogen and silicon were present in 2/1 molar ratio instead of the 4/1 ratio found in the liquid taken for distillation. The N/Si ratio becomes even smaller on heating the residue for a longer period. However, $Si[OCH_2CH_2CH_2NH_2]_4$ could be distilled under reduced pressure in good yields.

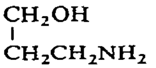
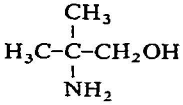
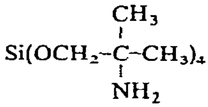
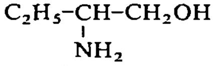
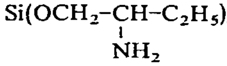
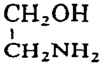
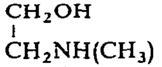
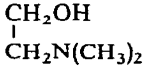
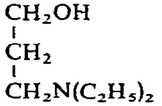
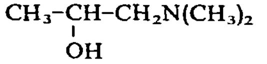
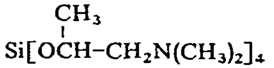
The aminoalkoxides of silicon are monomeric in boiling benzene, whereas those of germanium and tin are polymeric. This may be mainly due to the smaller radius of silicon atom, which hinders intermolecular association through oxygen and/or nitrogen.

IR ABSORPTION SPECTRA

A comparative study of the characteristic absorption bands of alkoxysilanes, and substituted and unsubstituted (aminoethoxy)silanes has been made with a view to finding out if intramolecular coordination (Si ← N) takes place in such compounds, as it does in silatranes[18,19]. Such interaction between the silicon and nitrogen atoms would be repeated to cause some change in the position and intensity of the ν(Si–C), ν(Si–O) and ν(C–N) absorption bands. The ν(Si–C) frequency is known[20] to increase with the electronegativity of the hydrocarbon group attached to silicon atom. In the case of methyltriethoxysilane a band at 645 cm^{-1} is assigned to ν_s(Si–C) whereas in silatranes this frequency is lowered to 609–620 cm^{-1}. This lowering is attributed to the intramolecular (Si ← N) coordination which increases the electron

TABLE 1

REACTIONS OF TETRAETHOXYSILANE WITH AMINOALCOHOLS

$Si(OEt)_4$ (mmoles)	Aminoalcohol (mmoles)	Product formed B.p. (°C/mm) (% yield)	Ethanol liberated found (calcd.) (mmole)
9.85	 $\begin{array}{l} CH_2OH \\ \vert \\ CH_2CH_2NH_2 \end{array}$ (39.41)	$Si(OCH_2CH_2CH_2NH_2)_4$ 126–128/0.3 (78)	35.43 (39.14)
11.71	 $\begin{array}{c} CH_3 \\ \vert \\ H_3C\text{-}C\text{-}CH_2OH \\ \vert \\ NH_2 \end{array}$ (48.03)	Semi-solid  $\begin{array}{c} CH_3 \\ \vert \\ Si(OCH_2\text{-}C\text{-}CH_3)_4 \\ \vert \\ NH_2 \end{array}$ 132/0.1 (88)	44.34 (45.64)
13.73	 $\begin{array}{c} C_2H_5\text{-}CH\text{-}CH_2OH \\ \vert \\ NH_2 \end{array}$ (55.85)	 $\begin{array}{c} Si(OCH_2\text{-}CH\text{-}C_2H_5)_4 \\ \vert \\ NH_2 \end{array}$ 146–148/0.4 (80)	51.51 (53.68)
11.04	 $\begin{array}{l} CH_2OH \\ \vert \\ CH_2NH_2 \end{array}$ (47.48)	$Si(OCH_2CH_2NH_2)_4$ Turned into infusible brownish mass at 200°C bath temp. at 0.2 mm.	42.38 (44.57)
15.03	 $\begin{array}{l} CH_2OH \\ \vert \\ CH_2NH(CH_3) \end{array}$ (62.18)	$Si[OCH_2CH_2NH(CH_3)]_4$ 118–120/0.1 (79)	57.18 (59.99)
15.17	 $\begin{array}{l} CH_2OH \\ \vert \\ CH_2N(CH_3)_2 \end{array}$ (62.82)	$Si[OCH_2CH_2N(CH_3)_2]_4$ 138–140/0.8 (89)	55.43 (59.34)
11.28	 $\begin{array}{l} CH_2OH \\ \vert \\ CH_2 \\ \vert \\ CH_2N(C_2H_5)_2 \end{array}$ (46.30)	$Si[OCH_2CH_2CH_2N(C_2H_5)_2]_4$ 195–198/1 (85)	41.09 (45.22)
11.42	 $\begin{array}{c} CH_3\text{-}CH\text{-}CH_2N(CH_3)_2 \\ \vert \\ OH \end{array}$ (47.52)	 $\begin{array}{l} \quad CH_3 \\ \quad \vert \\ Si[OCH\text{-}CH_2N(CH_3)_2]_4 \end{array}$ 103–105/0.2 (82)	42.38 (45.77)

density at the silicon atom. However, in the aminoalkoxides described in the present communication the ν_s(Si–C) band appears to be at 640–695 cm^{-1}. This seems to rule out sp^3d or sp^3d^2 hybridisation of the silicon atom. In spite of increasing the electron density at the nitrogen atom, even in *N*-alkyl and *N,N*-dialkyl substituted aminoalkoxides, $Me_{4-n}Si[OCH_2CH_2NH(CH_3)]_n$ and $Me_{4-n}Si[OCH_2CH_2CH_2N(C_2H_5)_2]_n$, the nitrogen atom does not seem to participate in intramolecular coordination. Further, (*i*) the position of ν_s(Si–O) band between 715–765 cm^{-1} and that of ν_{as}(Si–O) at 780–820 cm^{-1} agree with these in alkylalkoxysilane[21,22]; (*ii*) the ν(C–N) frequency

Analysis found (calcd.) (%) Si	N	Mol.wt. found (calcd.)	n_D^{30}	Characteristic IR absorption bands
8.67 (8.66)	17.24 (17.28)	332 (324)	1.4605	535 m, 755 m, 825 s, 980 m, 995 (sh), 1070 (sh), 1085 vs, 1110 vs, 1250 m, 1265 (sh), 1305 w, 1395 m, 1430 m, 1485 m, 1605 s, 2880 s, 2945 s, 3280 m, 3378 m
7.50 (7.37)	14.60 (14.74)	387 (380)	1.4465	460 m, 535 w, 500 m, 765 w, 880 vs, 945 (sh), 1020 w, 1085 s, 1110 vs, 1205 w, 1292 m, 1375 m, 1398 w, 1480 s, 1600 s, 2882 s, 2940 s, 2985 s, 3180, 3280 m, 3350 m
7.50 (7.37)	14.67 (14.74)	378 (380)	1.4500	
Crude 10.6 (10.46)	20.9 (20.86)	294 (268)		520 m, 785 m, 815 vs, 878 m, 1040 s, 1090 vs, 1165 (sh), 1280 m, 1380 m, 1475 m, 1605 s, 2885 s, 2945 s, 3188 m b, 3285 m, 3375 m
Brownish residue 16.5	19.3			
8.63 (8.65)	17.20 (17.26)	325 (324)	1.4429	535 m, 802 s, 848 s, 892 m, 960 s, 1050 (sh), 1075 vs, 1120 vs, 1180 w, 1205 m, 1280 vs, 1345 m, 1380 m, 1478 vs, 2785 vs, 2830 m, 2900 m, 2975 vs
7.41 (7.37)	14.67 (14.74)	378 (380)		540 m, 805 s, 840 s, 890 m, 965 s, 1065 vs, 1080 (sh), 1110 vs, 1205 m, 1278 s, 1378 m, 1475 s, 2785 vs, 2830 s, 2900 m, 2975 s
5.25 (5.12)	9.95 (10.21)	535 (548)	1.4408	540 w, 805 m, 855 s, 890 (sh), 985 s, 1005 s, 1090 vs, 1105 s, 1175 m, 1205 s, 1275 s, 1300 s, 1390 s, 1480 s, 2800 m, 2882 s, 2945 m, 2980 m
6.50 (6.43)	12.73 (12.83)	430 (436)	1.4240	

at 850–895 cm^{-1}, similar to those in the respective aminoalcohols also indicates the absence of any coordination.

Absorption bands at 1090–1110 cm^{-1} with two or three split band groups characteristic of ν_{as}(Si–O–C) and ν(C–O) frequencies and δ(NH) band at 1590–1605 cm^{-1} in primary aminoalkoxy derivatives are also observed. Absorption bands at 1465–1480 cm^{-1} and 2780–2810 cm^{-1} characteristic of $\delta(CH_3\text{–}N)$ and $\nu(CH_3\text{–}N)$ respectively[23] are present in the spectra of substituted aminoalkoxides as well as in the corresponding aminoalcohols.

TABLE 2

REACTIONS OF METHYLTRIETHOXYSILANE WITH AMINOALCOHOLS

$MeSi(OEt)_3$ (mmoles)	Aminoalcohol (mmoles)	Product formed B.p. (°C/mm) (% yield)	Ethanol liberated found (calcd.) (mmole)
12.34	$\begin{array}{l}CH_2OH\\ \vert\\ CH_2CH_2NH_2\end{array}$ (37.41)	$MeSi\left[\begin{array}{l}O\text{-}CH_2\\ \quad\ \vert\\ \quad\ CH_2\\ \quad\ \vert\\ \quad\ CH_2NH_2\end{array}\right]_3$ 132/2 (82)	34.77 (36.95)
14.64	$H_3C\text{-}\overset{\displaystyle CH_3}{\underset{\displaystyle NH_2}{C}}\text{-}CH_2OH$ (45.00)	$MeSi[OCH_2\text{-}\overset{\displaystyle CH_3}{\underset{\displaystyle NH_2}{C}}\text{-}CH_3]_3$ 132–133/7 (91)	39.34 (43.04)
18.91	$C_2H_5\text{-}\underset{\displaystyle NH_2}{CH}\text{-}CH_2OH$ (58.22)	$MeSi[OCH_2\text{-}\underset{\displaystyle NH_2}{CH}\text{-}C_2H_5]_3$ 128/0.8 (91)	53.69 (55.43)
14.87	$\begin{array}{l}CH_2OH\\ \vert\\ CH_2\\ \vert\\ CH_2N(C_2H_5)_2\end{array}$ (45.26)	$MeSi[OCH_2CH_2CH_2\cdot N(C_2H_5)_2]_3$ 158/0.5 (89)	42.83 (44.56)
15.54	$\begin{array}{l}CH_2OH\\ \vert\\ CH_2NH_2\end{array}$ (49.28)	$MeSi[OCH_2CH_2NH_2]_3$ 127–128/0.8 (88)	46.61 (46.66)
18.79	$\begin{array}{l}CH_2OH\\ \vert\\ CH_2NH(CH_3)\end{array}$ (58.19)	$MeSi[OCH_2CH_2NH(CH_3)]_3$ 89/0.1 (91)	51.95 (56.30)
17.40	$\begin{array}{l}CH_2OH\\ \vert\\ CH_2N(CH_3)_2\end{array}$ (53.71)	$MeSi[OCH_2CH_2N(CH_3)_2]_3$ 132/1 (93)	47.18 (52.17)
18.74	$\overset{\displaystyle CH_3}{\underset{\displaystyle OH}{HC}}\text{-}CH_2N(CH_3)_2$ (57.51)	$MeSi[O\overset{\displaystyle CH_3}{CH}\text{-}CH_2N(CH_3)_2]_3$ 92–94/0.3 (90)	49.99 (56.08)
23.06	$\begin{array}{l}CH_2OH\\ \vert\\ CH_2N(CH_3)_2\end{array}$ (46.22)	$Me\overset{\displaystyle OEt}{Si}[OCH_2CH_2N(CH_3)_2]_2$ 96–102/5 (80)	40.64 (46.08)
18.12	$\begin{array}{l}CH_2OH\\ \vert\\ CH_2N(CH_3)_2\end{array}$ (18.95)	$Me\overset{\displaystyle OEt}{Si}[OCH_2CH_2N(CH_3)_2]_2$ 95–99/4.5 (60)	18.91 (19.32)
30.63	$\begin{array}{l}CH_2OH\\ \vert\\ CH_2CH_2NH_2\end{array}$ (30.76) (without catalyst)	$Me\overset{\displaystyle OEt}{Si}[OCH_2CH_2CH_2NH_2]_2$ 105–110/1.5 (52)	20.64 (30.62)

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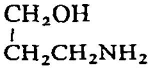
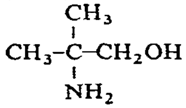
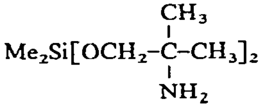
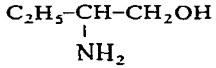
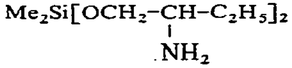
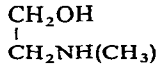
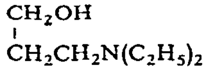
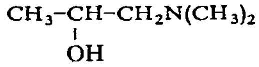
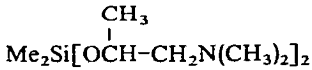
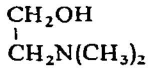
[a] Calcd. for $MeSi(OEt)[OCH_2CH_2N(CH_3)_2]_2$. [b] Calcd. for $MeSi(OEt)_2OCH_2CH_2N(CH_3)_2$.

s calcd.) (%)		Mol.wt. found (calcd.)	n_D^{30}	Characteristic IR absorption bands
	N			
	15.70 (15.85)	312 (265)	1.4545	525 w, 690 w, 720 w, 780 w, 810 m, 855 s, 978 m, 1065 m, 1095 vs, 1105 vs, 1278 vs, 1395 m, 1430 m, 1485 m, 1608 s, 2880 s, 2945 s, 3185 w, 3285 m, 3378 m
	13.58 (13.66)	302 (307)	1.4350	405 m, 448 w, 535 w, 695 m, 782 w, 815 m, 880 vs, 905 w, 948 w, 990 m, 1000 w, 1020 w, 1085 s, 1105 vs, 1215 m, 1280 s, 1375 s, 1398 w, 1480 s, 1600 s, 2880 s, 2940 m, 2985 s, 3170 m, 3275 m, 3355 m
	13.62 (13.66)	305 (307)	1.4435	
	9.60 (9.69)	459 (433)	1.4395	540 w, 720 w, 790 m, 805 m, 870 s, 890 w, 920 w, 985 s, 1010 s, 1085 (sh), 1100 vs, 1300 m, 1360 w, 1392 s, 1465 w, 1480 s, 2810 s, 2885 m, 2960 m, 2990 m
	18.7 (18.8)	256 (223)		
	15.81 (15.85)	264 (265)	1.4358	415 m, 535 w, 695 w, 795 vs, 815 vs, 882 w, 970 s, 1015 w, 1045 w, 1085 vs, 1105 vs, 1120 w, 1190 w, 1260 w, 1272 s, 1296 w, 1365 m, 1395 m, 1455 s, 1482 s, 2700 w, 2745 s, 2845 m, 2885 m, 2935, 3285–3295 m
)	13.58 (13.66)	310 (307)		530 w, 665 w, 795 s, 838 s, 890 m, 970 s, 1068 vs, 1110 vs, 1205 m, 1280 s, 1292 w, 1378 m, 1475 s, 2785 vs, 2830 s, 2900 m, 2975 m
)	11.84 (12.02)	351 (349)		
)	10.70 (10.59)	254 (264)	1.4225	
5 3)[a])[b]	10.78 (10.59)[a] (6.32)[b]	275 (264)[a] (221)[b]		
	11.54 (11.86)	215 (236)	1.4375	
5)	(6.75)			

TABLE 3

REACTIONS OF DIMETHYL DIETHOXYSILANE WITH AMINOALCOHOLS

$Me_2Si(OEt)_2$ (mmoles)	Amino alcohol (mmoles)	Product formed B.p. (°C/mm) (% yield)	Ethanol liberated found (calcd.) (mmoles)
17.54	 $\begin{matrix}CH_2OH\\ \vert\\ CH_2CH_2NH_2\end{matrix}$ (35.95)	$Me_2Si[OCH_2CH_2CH_2NH_2]_2$ 105/5 (85)	32.18 (35.00)
17.68	 $CH_3-\underset{NH_2}{\overset{CH_3}{C}}-CH_2OH$ (36.46)	 $Me_2Si[OCH_2-\underset{NH_2}{\overset{CH_3}{C}}-CH_3]_2$ 90–92/6 (93)	32.82 (35.43)
17.41	 $C_2H_5-\underset{NH_2}{CH}-CH_2OH$ (35.89)	 $Me_2Si[OCH_2-\underset{NH_2}{CH}-C_2H_5]_2$ 90/2 (92)	31.52 (34.77)
23.55	 $\begin{matrix}CH_2OH\\ \vert\\ CH_2NH(CH_3)\end{matrix}$ (49.40)	$Me_2Si[OCH_2CH_2NH(CH_3)]_2$ 68/1.5 (93)	43.69 (47.18)
14.44	 $\begin{matrix}CH_2OH\\ \vert\\ CH_2CH_2N(C_2H_5)_2\end{matrix}$ (29.91)	$Me_2Si[OCH_2CH_2CH_2N(C_2H_5)_2]_2$ 115/0.5 (95)	25.65 (28.91)
15.65	 $CH_3-\underset{OH}{CH}-CH_2N(CH_3)_2$ (32.10)	 $Me_2Si[O\overset{CH_3}{CH}-CH_2N(CH_3)_2]_2$ 60/0.5 (88)	26.95 (31.08)
27.39	 $\begin{matrix}CH_2OH\\ \vert\\ CH_2N(CH_3)_2\end{matrix}$ (27.50)	$Me_2Si[OCH_2CH_2N(CH_3)_2]_2$ 95–100/20 (50)	21.40 (21.74)

The PMR spectrum of $Me_2Si[OCH_2CH_2NH(CH_3)]_2$ also confirms the tetrahedral structure of these compounds. A comparison of the chemical shifts of the N–CH_2 protons in the aminoalkoxide with that of the N–CH_2 protons of the corresponding aminoalcohol, *i.e.*, τ 7.3 (in both the cases) reveals that electron density on nitrogen atom in the silicon compound is not changed. The existence of sp^3d hybridization in silatranes and sp^3 hybridization in dialkyl(diaminoalkoxy)silanes can be attributed to the presence of an additional methyl group on silicon in the latter. They might release electrons to silicon through a hyperconjugative interaction with the empty *d* orbitals, thus making the silicon atom less ready to accept electrons from nitrogen. This is consistent with the tetrahedral structure of $Me_2Si(Acac)_2$[24].

EXPERIMENTAL

Precautions were taken to exclude moisture. Alkoxysilanes were fractionated

Analysis found (calcd.) (%)		Mol.wt. found (calcd.)	n_D^{30}	Characteristic IR absorption bands
Si	N			
13.47 (13.62)	13.48 (13.58)	222 (206)	1.4415	525 w, 565 w, 640 m, 715 w, 800 s, 855 s, 880 s, 970 m, 1060 (sh), 1095 vs, 1275 s, 1395 s, 1425 w, 1482 m, 1610 s, 2880 s, 2945 s, 3170 w, 3280 m, 3365 m
11.92 (11.99)	11.90 (11.95)	247 (234)	1.4228	425 w, 450 m, 525 m, 655 m, 770 (sh), 805 s, 855–880 vs, 905 (sh), 948 w, 990 w, 100 m, 1018 w, 1085 s, 1105 vs, 1215 m, 1275 vs, 1375 s, 1398 m, 1485 s, 1600 s, 2880 s, 2940 w, 2982 s, 3278 m, 3355 m(b)
11.74 (11.99)	11.90 (11.95)	242 (234)	1.4335	
13.46 (13.62)	13.58 (13.60)	215 (206)	1.4260	525 w, 645 w, 720 (sh), 805 s, 855 s, 885 (sh), 945 w, 970 s, 1015 (sh), 1045 w, 1085 vs, 1098 vs, 1125 w, 1190 w, 1270 vs, 1298 m, 1360 m, 1398 m, 1470 s, 1485 s, 2810 s, 2865 s, 2890 m, 2965 m
8.78 (8.82)	8.68 (8.80)	321 (318)	1.4315	540 w, 645 w, 712 w, 800 vs, 860 s, 890 w, 920 w, 982 m, 1008 m, 1085 s, 1098 vs, 1178 m, 1205 m, 1275 vs, 1300 m, 1392 s, 1465 (sh), 1480 m, 2810 m, 2885 m, 2955 s, 2988 s
10.70 (10.71)	10.64 (10.67)	255 (262)	1.4175	
12.17 (11.99) (14.69)	11.5 (11.95) (7.32)	230 (234) (191)		

and aminoalkanols were distilled before use. Molecular weights were determined in boiling benzene in a semi-micro Gallenkamp ebulliometer. Spectra were recorded on neat liquids with UR-10 double beam IR spectrophotometer having KBr and NaCl prisms. The PMR spectra of the compounds were recorded on $CDCl_3$ solutions; tetramethylsilane was used as an internal standard.

Silicon was estimated as silica by decomposing the compound as previously described[25]. Nitrogen was estimated by the Kjeldahl method. The ethanol liberated as ethanol/benzene azeotrope was estimated by an oxidimetric method[26].

Reaction between tetraethoxysilane and aminoethanol (molar ratio 1/4)

Tetraethoxysilane (2.30 g, 11.04 mmoles) and aminoethanol (2.90 g, 47.48 mmoles) were added to anhydrous benzene (50 ml). A small piece of metallic sodium was added and reaction mixture was refluxed for about ½ h, The ethanol/benzene azeotrope was then slowly fractionated off at 68° until the temperature reached to

80°. The total ethanol liberated was 1.95 g compared with the 2.05 g expected for the replacement of four ethoxide groups. The reaction was complete in 2 h. Solvent was removed under reduced pressure to leave a colourless liquid. On attempted distillation at 0.2 mm pressure a few drops of aminoethanol distilled at 80–85/0.6 mm and the residue became brown and viscous at a bath temperature of 180° and an infusible mass at a bath temperature of 200°. [Found (in crude liquid): N, 20.9; Si, 10.6. Found (in residue after attempted distillation): N, 19.3; Si, 16.5; Si/N 1/2.34. $C_8H_{24}N_4O_4Si$ calcd.: N, 20.86; Si, 10.46%.]

Reaction between methyltriethoxysilane and 3-aminopropanol

Methyltriethoxysilane (2.20 g, 12.34 mmoles) and 3-aminopropanol (2.81 g, 37.41 mmoles) were added to benzene (50 ml) followed by a small piece of sodium. The ethanol/benzene azeotrope was collected during 3 h of refluxing. When the liberation of ethanol was complete, the product was purified by vacuum distillation (b.p. 132°/2 mm, 82% yield). Found: N, 15.7; Si, 10.54. $C_{10}H_{27}N_3O_3Si$ calcd.: N, 15.85; Si, 10.59%.)

The total ethanol liberated was 1.60 g as against the 1.70 g for replacement of three ethoxide groups.

Reaction between methyltriethoxysilane and 3-aminopropanol in 1/1 molar ratio (without catalyst)

Methyltriethoxysilane (5.45 g, 30.63 mmoles) was mixed with 3-aminopropanol (2.31 g, 30.76 mmoles) in 50 ml benzene. The mixture was refluxed for about 80 h and the ethanol/benzene azeotrope was fractionated off slowly. When the reaction was complete, the excess of the solvent and unreacted material were removed under reduced pressure, and the residue was distilled at 105–110°/1.5 mm in 52% yield. (Found: N, 11.54; Si, 12.10. $C_9H_{24}N_2O_3Si$ calcd.: N, 11.85; Si, 11.90. $C_8H_{21}NO_3Si$ calcd.: N, 6.75; Si, 13.55%.)

The total ethanol liberated was 0.95 g as against the 1.4 g required for the replacement of one ethoxide group.

Reaction between dimethyldiethoxysilane and 2-amino-2-methyl-1-propanol

To a benzene solution of dimethyldiethoxysilane (2.62 g, 17.68 mmoles) was added 2-amino-2-methyl-1-propanol (3.25 g, 36.46 mmoles) and a small piece of sodium, and the mixture was boiled under reflux. The reaction was complete in 3–4 h and the ethanol produced was fractionated off as the binary azeotrope. The remaining solvent was stripped off under reduced pressure at room temperature (25–30°/5 mm). The product was distilled under reduced pressure at 90–92°/6 mm. in 93% yield. (Found: N, 11.90; Si, 11.92. $C_{10}H_{26}N_2O_2Si$ calcd.: N, 11.95; Si, 11.99%.)

The alcohol liberated was 1.51 g as against the 1.63 g required for replacement of two ethoxide groupes. Details of other reactions are given in Tables 1–3.

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