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(AMINOALKOXY)SILANES
III. INTERACTION OF (AMINOALKOXY)SILANES WITH ORGANOHALOSILANES

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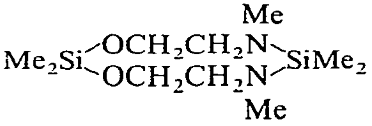
SUMMARY

Silylation of the amino group in (aminoalkoxy)silanes has been carried out by use of organohalosilanes in the presence of triethylamine. A number of new chain and cyclic compounds have been characterised by IR spectra and chemical analysis.

RESULTS AND DISCUSSION

This paper reports the reactions of dimethylbis(aminoalkoxy)silane and methyl-, vinyl- and phenyltris(*N*-methylaminoalkoxy)silanes with organohalosilanes in the presence of a base, Et_3N:

$$Me_2Si(OCH_2CH_2NH_2)_2 + 2\ Me_3SiCl + 2\ Et_3N \longrightarrow$$
$$Me_2Si(OCH_2CH_2NHSiMe_3)_2 + 2\ Et_3N \cdot HCl$$
$$\Big\downarrow {\scriptstyle +2\ Me_3SiCl \atop +2\ Et_3N}$$
$$Me_2Si[OCH_2CH_2N(SiMe_3)_2]_2 + 2\ Et_3N \cdot HCl \quad (1)$$



$$Me_2Si(OCH_2CH_2NHMe)_2 + Me_2SiCl_2 + 2\ Et_3N \longrightarrow Me_2Si\begin{matrix}\diagup OCH_2CH_2\overset{Me}{N}\diagdown \\ \diagdown OCH_2CH_2\underset{Me}{N}\diagup\end{matrix}SiMe_2$$
$$+ 2\ Et_3N \cdot HCl \quad (2)$$

$$RSi(OCH_2CH_2NHMe)_3 + 3\ Me_3SiCl + 3\ Et_3N \longrightarrow RSi[OCH_2CH_2N(SiMe_3)Me]_3$$
$$+ 3\ Et_3N \cdot HCl \quad (3)$$

$(R = Me,\ CH{=}CH_2 \text{ or } C_6H_5)$

The reaction between $Me_2Si(OCH_2CH_2NH_2)_2$ and $(CH_3)_3SiCl$ in 1/4 molar ratio in refluxing ether resulted in the replacement of only one proton per amino group. The product, $Me_2Si(OCH_2CH_2NHSiMe_3)_2$, was found to react with trimethylchlorosilane in refluxing benzene with further replacement of the remaining amino protons to give $Me_2Si[OCH_2CH_2N(SiMe_3)_2]_2$.

TABLE 1

REACTIONS OF (AMINOALKOXY)SILANES WITH ALKYLHALOSILANES

(Aminoalkoxy)silane (g)	Halosilane (g)	Et_3N (g)	Molar ratio	Reflux period (h)	Product formed, yield (%)	B.p. (°C/mm)	n_D^{35}	Analysis found (calcd.) (%)		Mol.wt. found (calcd.)
								Si	N	
$Me_2Si(OCH_2CH_2NH_2)_2$ 1.82	Me_3SiCl 2.20	2.32	1/2	10	$Me_2Si(OCH_2CH_2NHSiMe_3)_2$ 80	85/0.2	1.4235	25.67 (26.10)	8.41 (8.69)	325 (322)
$Me_2Si(OCH_2CH_2NH_2)_2$ 2.66	Me_3SiCl 6.64	6.63	1/4	40	$Me_2Si(OCH_2CH_2NHSiMe_3)_2$ 72	88–90/0.3		25.90 (26.10)	8.61 (8.69)	320 (322)
$Me_2Si[O(CH_2)_3NH_2]_2$ 1.46	Me_3SiCl 1.60	1.57	1/2	12½	$Me_2Si[O(CH_2)_3NHSiMe_3]_2$ 72	96–98/0.8	1.4280	23.63 (24.03)	8.02 (7.98)	345 (350)
$Me_2Si(OCH_2CMe_2NH_2)_2$ 1.18	Me_3SiCl 1.12	1.30	1/2	15	$Me_2Si(OCH_2CMe_2NHSiMe_3)_2$ 75	86–88/0.7		21.98 (22.25)	7.30 (7.39)	382 (378)
$Me_2Si(OCH_2CHEtNH_2)_2$ 1.35	Me_3SiCl 1.37	1.43	1/2	12	$Me_2Si(OCH_2CHEtNHSiMe_3)_2$ 60	58–60/2.5	1.4210	21.96 (22.25)	7.25 (7.39)	365 (378)
$Me_2Si(OCH_2CH_2NHSiMe_3)_2$ 1.73	Me_3SiCl 1.39	1.25	1/2	10½	$Me_2Si[OCH_2CH_2N(SiMe_3)_2]_2$ 50	75–80/1.5	1.4250	28.95 (30.06)	6.30 (6.01)	452 (466)
$Me_2Si(OCH_2CH_2NHMe)_2$ 3.05	Me_3SiCl 3.32	3.20	1/2	9½	$Me_2Si(OCH_2CH_2NMeSiMe_3)_2$ 75	104–106/0.4	1.4205	23.60 (24.04)	7.95 (7.99)	334 (350)
$Me_2Si(OCH_2CH_2NHMe)_2$ 4.57	Me_2SiCl_2 3.00	4.92	1/1	8	$(-Me_2SiOCH_2CH_2NMe-)_2$ 40	56–60/0.8		20.91 (21.33)	10.79 (10.68)	
$MeSi(OCH_2CH_2NHMe)_3$ 2.35	Me_3SiCl 2.97	3.10	1/3	8½	$MeSi(OCH_2CH_2NMeSiMe_3)_3$ 65	130–132/1.0	1.4329	22.50 (23.33)	9.06 (8.72)	472 (481)
$ViSi(OCH_2CH_2NHMe)_3$ 3.43	Me_3SiCl 4.22	4.14	1/3	4½	$ViSi(OCH_2CH_2NMeSiMe_3)_3$ 40	80–85/0.5	1.4200	22.64 (22.75)	8.39 (8.50)	475 (493)
$PhSi(OCH_2CH_2NHMe)_3$ 3.10	Me_3SiCl 3.59	3.04	1/3	6	$PhSi(OCH_2CH_2NMeSiMe_3)_3$ 30	90–92/0.8	1.4422	20.61 (20.65)	7.59 (7.72)	

All the aminoalkoxides obtained are monomeric and are volatile under reduced pressure, but the yields of the distilled vinyl and phenyl compounds are rather poor, probably because of thermal degradation.

IR absorption spectra

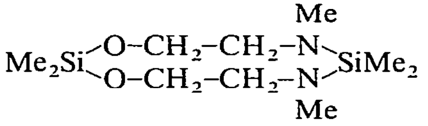
The following observations throw light on the nature of the products:

(*i*). The disappearance of $\delta(NH_2)$band at 1600 cm^{-1} and appearance of only one band in 3390–3400 cm^{-1} region indicates deprotonation of NH_2 group.

(*ii*). The appearance of characteristic absorption bands of three methyls on silicon at 750–765 cm^{-1} and 835–845 cm^{-1}, due to methyl rocking, along with the $\delta_s(CH_3)$band at 1275 cm^{-1} indicates the silylation of aminoalkoxides by trimethylchlorosilane.

(*iii*). Stretching vibrations due to the Si–N bond in aminosilanes, Me_3SiNHR' ($R' = Me$, Et or Ph) appear at about 700 cm^{-1} and are strongly coupled with other vibrations of the molecule[1]. Fessenden[2] has also observed in silazanes strong absorption at 833 cm^{-1}, which could be due to the Si–N grouping, but this band is shifted to lower wavelengths, *i.e.*, 731 cm^{-1} in *N*,*N*-diethyltriethylsilazane because of the added mass of the ethyl group. Consistently, the compounds we have prepared show a strong peak at 745–758 cm^{-1} which could be attributed to the Si–N frequency. However, characteristic peaks of the Me_3Si group[3–5] and of ν(Si–O) also lie in this very region, and the Si–N frequency might overlap with the fundamental vibrations of the methyl group and the Si–O bond.

In the spectra of disilazanes[2], a band at 935 cm^{-1} appears to be characteristic of Si–N–Si group. Aylett and his coworkers[6] have reported bands at 975 cm^{-1} in $(SiH_3)_2NH$ and 996 cm^{-1} in $(SiH_3)_3N$ due to the ν_{as}(Si–N–Si) vibration. Similarly a strong peak at 970 cm^{-1} in $Me_2\,Si[OCH_2CH_2N(SiMe_3)_2]_2$ is probably due to the ν_{as}(Si–N–Si) mode. Although the ν_s(Si–N–Si) mode is IR active, it is expected to give only a weak absorption; the weak bands at 1510 cm^{-1} and 1670 cm^{-1} in the spectra of $Me_2Si[OCH_2CH_2N(SiMe_3)_2]_2$ can be tentatively assigned to a combination of asymmetric and symmetric stretching of (Si–N–Si) modes, as mentioned by Aylett and coworkers[6], or they could be overtones of the fundamental vibration bands observed in the 830–850 cm^{-1} region. A very weak band at 1660–1665 cm^{-1} is also present in the spectra of compounds (I), (II) and (III).



(I)

$Me_2Si[OCH_2CH_2N(SiMe_3)Me]_2$

(II)

$MeSi[OCH_2CH_2N(SiMe_3)Me]_3$

(III)

The absorption band at 970 cm^{-1} in these cyclic derivative parallels that observed for 1,2,2,3-tetramethyl-1,3-diaza-2-silacyclopentane in 926–960 cm^{-1} region, and can be ascribed to the Si–N frequency[7].

(*iv*). The vibrations of the Me_2 group on silicon show characteristic bands at 805 cm^{-1} and 830–855 cm^{-1}, due to ν_s(Si–C) and methyl rocking.

(*v*). A medium to strong intensity band at 675–685 cm^{-1} present in all the open chain compounds may be attributed to ν_s(Si–C), probably overlapped with ν_s(Si–O) modes.

(*vi*). The position of ν_{as}(Si–O–C) + ν(C–O) frequency in 1085–1110 cm^{-1} range remains unaffected on silylation of the NH_2 group of alkyl(aminoalkoxy)silanes, but in the cyclic compound (I) an additional strong peak at 1045 cm^{-1} appears along with the 1090–1110 cm^{-1} bands.

EXPERIMENTAL

Moisture was rigorously excluded. Chlorosilanes were freshly distilled before use and (aminoalkoxy)silanes were synthesised by alcoholysis[8].

Molecular weights, refractive indices and IR spectra of neat liquids, and nitrogen and silicon contents were obtained as previously described[9,10].

Reaction between trimethylchlorosilane and dimethylbis(aminoethoxy)silane in 2/1 molar ratio

Trimethylchlorosilane (2.2 g) was added gradually to a cooled mixture of dimethylbis(aminoethoxy)silane (1.8 g) and triethylamine (2.32 g) in ether (30 ml). The reaction was exothermic, and triethylamine hydrochloride precipitated immediately. The mixture was refluxed for 10 h, triethylamine hydrochloride was filtered off, the solvent was removed under reduced pressure and the residue was distilled to give the compound $Me_2Si(OCH_2CH_2NHSiMe_3)_2$ (n.c.) b.p. 85°/0.2 mm (80% yield). (Found: N, 8.41; Si, 25.67. $C_{12}H_{34}N_2O_2Si_3$ calcd.: N, 8.69; Si, 26.10%.)

Reaction between dimethylbis(aminoethoxy)silane and trimethylchlorosilane in 1/4 molar ratio

Trimethylchlorosilane (5.25 g) was added slowly to the cooled mixture of dimethylbis(aminoethoxy)silane (2.02 g) and triethylamine (5.25 g) in 40 ml ether, and the mixture was refluxed for 39–40 h. After filtering off the $Et_3N \cdot HCl$, excess solvent was stripped off and contents were distilled to give the compound $Me_2Si[OCH_2CH_2N(SiMe_3)_2]_2$ b.p. 95–97°/0.6 mm (76% yield). (Found: N, 8.65; Si, 25.90. $C_{12}H_{34}N_2O_2Si_3$ calcd.: N, 8.69; Si, 26.10;$C_{18}H_{50}N_2O_2Si_5$ calcd.: N, 6.01; Si, 30.06%.)

Reaction between dimethylbis(N-methylaminoethoxy)silane with dimethyldichlorosilane in 1/1 molar ratio

Dropwise addition of dimethyldichlorosilane (3.0 g) to a cooled mixture of dimethylbis(*N*-methylaminoethoxy)silane (4.57 g) and triethylamine (4.92 g) in benzene 30 ml gave triethylamine hydrochloride and a yellowish liquid. Distillation gave a liquid, b.p. at 56–60°/0.8 mm, in 40% yield. On standing at room temp. (34–40°) a few solid particles appeared in the product. (Found: N, 10.79; Si, 20.91. $C_{10}H_{26}N_2O_2Si_2$ calcd.: N, 10.68; Si, 21.33%.)

The details of other reactions are given in Table 1.

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