

## (AMINOALKOXY)SILANES II. SYNTHESIS OF VINYL- AND PHENYL(AMINOALKOXY)SILANES

R. C. MEHROTRA AND P. BAJAJ

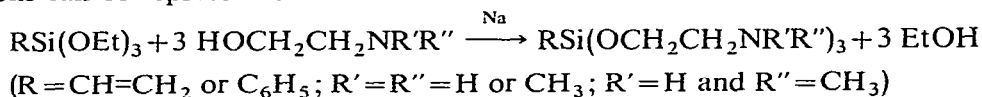
*The Chemical Laboratories, University of Rajasthan, Jaipur-4 (India)*

(Received July 6th, 1970)

### SUMMARY

A number of vinyl- and phenyl(aminoalkoxy)silanes have been synthesised by silylation of OH group of alkanolamines with vinyl- and phenyltriethoxysilanes in the presence of metallic sodium. Some physical and chemical properties including IR spectra are being reported.

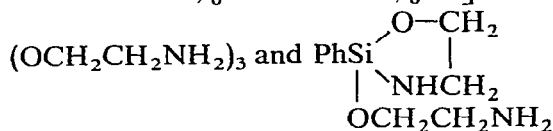
We recently investigated the reactions of tetraethoxysilane and methyltriethoxy- and dimethyldiethoxysilane with alkanolamines<sup>1</sup> and we now describe the reactions of vinyl- and phenyltriethoxysilanes with ethanolamine, 3-aminopropanol, 2-aminobutanol, 2-methyl-2-aminopropanol, 1-(dimethylamino)-2-propanol, 3-(diethylamino)-1-propanol, (methylamino)ethanol and (dimethylamino)ethanol. These reactions can be represented as follows:



Phenylaminoalkoxysilanes have been made previously from phenyltrichlorosilane and amino alcohols in presence of triethylamine<sup>2</sup>.

Alkoxysilanes were mixed with the amino alcohols in 1/3 molar ratio and refluxed in benzene in the presence of a small amount of sodium until the ethanol liberated was completely fractionated off. The reactions were faster than those with alkylalkoxysilanes, and were complete in 2–4 h.

Of the large number of derivatives investigated (see Tables 1 and 2) only PhSi(OCH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>)<sub>3</sub> tends to decompose, with partial polymerisation, on attempted distillation under reduced pressure. The molar ratio of Si/N in the distilled product (b.p. 155–158°/1 mm) remains 1/3, but the actual percentages of silicon and nitrogen are higher than required for PhSi(OCH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>)<sub>3</sub>. [*E.g.*, 10.4% Si; 15.56% N as against 9.84% Si and 14.72% N. The infusible residue (35%) left in the distilling flask contained 19.2% Si and 12.19% N.] The distilled liquid may be a mixture of PhSi-



All the aminoalkoxides obtained are monomeric in boiling benzene and appear to be more susceptible to hydrolysis than alkyl(aminoalkoxy)silanes.

(Continued p. 364)

TABLE 1

## REACTIONS OF VINYLTRIMETHOXY-SILANE WITH AMINOALCOHOLS

$\text{CH}_2=\text{CHSi}(\text{OEt})_3$ (g)	Aminoalcohol (g)	Product formed; b.p. ( $^{\circ}\text{C}/\text{mm}$ ); (yield) (%)	Ethanol content (g) liberated (calcd.)	Analysis found (calcd.) (%)	Molecular weight found (calcd.)	Characteristic IR absorption bands	
				Si	N		
2.44	$\text{CH}_2\text{OH}$   $\text{CH}_2\text{CH}_2\text{NH}_2$ (2.89)	$\text{CH}_2=\text{CHSi}(\text{OCH}_2\text{CH}_2\text{CH}_2\text{NH}_2)_3$ 128-130/0.6 (80)	1.65 (1.77)	10.42 (10.13)	15.10 (15.14)	274 (277)	1.4605 500 vw, 555 m, 660-670 w, 755 s, 830 s, 865 w, 980 m, 1015 (sh), 1065 (sh), 1090 vs, 1105 vs, 1245 w, 1285 w, 1305 w, 1360 (sh), 1395 s, 1410 s, 1430 (sh), 1482 m, 1602 s, 2885 s, 2945 s, 3065 w, 3285 m, 3375 m
2.61	$(\text{CH}_3)_2\text{CCH}_2\text{OH}$   $\text{NH}_2$ (3.72)	$\text{CH}_2=\text{CHSi}[\text{OCH}_2\text{C}(\text{CH}_3)_2]_3$   $\text{NH}_2$ 110/0.7 (91)	1.69 (1.89)	9.01 (8.78)	13.14 (13.14)	309 (319)	1.4392 460 m, 510 vw, 565 m, 685 m, 770 s, 810 s, 865 vs, 950 w, 978 m, 1015 s, 1085 vs, 1105 vs, 1215 m, 1250 w, 1288 m, 1375 s, 1398 m, 1412 m, 1480 s, 1602 s, 2880 s, 2980 s, 3065 w, 3280 m, 3365 m
3.61	$\text{C}_2\text{H}_5\text{CHCH}_2\text{OH}$   $\text{NH}_2$ (5.08)	$\text{CH}_2=\text{CHSi}(\text{OCH}_2\text{CHC}_2\text{H}_5)_3$   $\text{NH}_2$ 123-125/1.5 (90)	2.45 (2.62)	8.84 (8.78)	13.30 (13.14)	305 (319)	1.4472 475 w, 555 m, 670-75 m (b), 795 (sh), 860 s, 990 m, 1015 m, 1085 vs, 1105 vs, 1263 w, 1285 m, 1310 w, 1375 m, 1388 m, 1410 m, 1475 s, 1602 s, 2885 s, 2975 s, 3070 w, 3285 m, 3378 m
3.87	$\text{CH}_2\text{OH}$   $\text{CH}_2\text{NH}_2$ (3.75)	$\text{CH}_2=\text{CHSi}(\text{OCH}_2\text{CH}_2\text{NH}_2)_3$ 130/0.8 (80)	2.77 (2.81)	12.09 (11.93)	18.10 (17.84)	238 (235)	1.4635 510 w, 555 m, 660 w, 775 s, 860 s, 925 s, 980 (sh), 1020 (sh), 1065 (sh), 1090 vs, 1105 vs, 1205 w, 1285 m, 1315 w, 1365 (sh), 1380 w, 1410 s, 1478 m, 1605 s, 2882 s, 2945 s, 3065 w, 3285 m, 3378 m.

5.08	$\begin{array}{c} \text{CH}_2\text{OH} \\   \\ \text{CH}_2\text{NH}(\text{CH}_3) \\ (6.04) \end{array}$	$\begin{array}{c} \text{CH}_2=\text{CHSi}[\text{OCH}_2\text{CH}_2\text{NHCH}_3]_3 \\ 112-115/1.2 \\ (78) \end{array}$	3.40 (3.66)	10.40 (10.13)	15.06 (15.14)	278 (277)	1.4435	440 w, 558 m, 660 w, 775 s, 802 s, 878 m, 975 s, 1018 s, 1035 (sh), 1085 vs, 1105 vs, 1125 (sh), 1250 m, 1280 w, 1290 w, 1325 w, 1370 m, 1398 w, 1410 m, 1455 m, 1485 s, 1605 w, 2800 s, 2850 m, 2890 s, 2948 m, 3065 w, 3290-3310 m (b)
2.56	$\begin{array}{c} \text{CH}_2\text{OH} \\   \\ \text{CH}_2\text{N}(\text{CH}_3)_2 \\ (3.64) \end{array}$	$\begin{array}{c} \text{CH}_2=\text{CHSi}[\text{OCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2]_3 \\ 122-123/2.5 \\ (80) \end{array}$	1.74 (1.85)	8.93 (8.78)	13.11 (13.14)	310 (319)	1.4325	478 w, 555 m, 655 m, 775 s, 788 s, 830 s, 885 m, 975 s, 1015 s, 1065 vs, 1100-1110 vs, 1205 m, 1278 s, 1292 (sh), 1375 m, 1410 m, 1475 s, 1605 w, 2785 s, 2820 m, 2890 m, 2955 s, 3065 w
2.13	$\begin{array}{c} \text{CH}_3\text{CHCH}_2\text{N}(\text{CH}_3)_2 \\   \\ \text{OH} \\ (3.52) \end{array}$	$\begin{array}{c} \text{CH}_2=\text{CHSi}[\text{OCHCH}_2\text{N}(\text{CH}_3)_2]_3 \\   \\ \text{CH}_3 \\ 98-102/0.8 \\ (75) \end{array}$	1.35 (1.54)	7.73 (7.77)	11.51 (11.62)	368 (361)	1.4258	465 w, 525 w, 558 m, 660 m, 770 s, 798 (sh), 835 m, 855 (sh), 892 m, 920 w, 975 m, 1018 s, 1045 (sh), 1088 vs, 1105 vs, 1145 s, 1208 w, 1278 s, 1380 s, 1410 m, 1475 s, 1602 w, 2782 s, 2820 m, 2870 w, 2955 s, 3065 w
1.78	$\begin{array}{c} \text{CH}_2\text{OH} \\   \\ \text{CH}_2\text{CH}_2\text{N}(\text{C}_2\text{H}_5)_2 \\ (3.72) \end{array}$	$\begin{array}{c} \text{CH}_2=\text{CHSi}[\text{O}(\text{CH}_2)_3\text{N}(\text{C}_2\text{H}_5)_2]_3 \\ 186/1.5 \\ (89) \end{array}$	1.26 (1.29)	6.38 (6.30)	9.32 (9.43)	438 (445)	1.4400	

TABLE 2

## REACTIONS OF PHENYLTRIMETHOXYSIANE WITH AMINOALCOHOLS

PhSi(OEt) <sub>3</sub> (g)	Amino alcohol (g)	Product formed; b.p. (°C/mm); (yield) (%)	Ethanol content (g) liberated (calcd.)	Analysis found (calcd.) (%)		Molecular weight found (calcd.)	Characteristic IR absorption bands
				Si	N		
2.78	CH <sub>3</sub> OH   CH <sub>2</sub> CH <sub>2</sub> NH <sub>2</sub> (2.70)	PhSi(OCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> NH <sub>2</sub> ) <sub>3</sub> 142-144/0.4 (69)	1.52 (1.59)	8.71 (8.57)	13.10 (12.83)	342 (327)	1.4925 475 m, 535 w (b), 705 s, 740 vs, 825 s, 860 s, 970 m, 990 m, 1095 s, 1105 vs, 1125 (sh), 1218 w, 1240 w, 1392 m, 1425 m, 1485 m, 1598 m, 2878 s, 2945 m, 3070 w, 3285 m, 3375 m
3.75	(CH <sub>3</sub> ) <sub>2</sub> CCH <sub>2</sub> OH   NH <sub>2</sub> (4.31)	PhSi[OCH <sub>2</sub> C(CH <sub>3</sub> ) <sub>2</sub> ] <sub>3</sub>   NH <sub>2</sub> 146-149/2 (83)	2.03 (2.15)	7.82 (7.60)	11.40 (11.37)	362 (369)	1.4732 475 m, 530-540 s (b), 705 s, 740 vs, 770 w, 800 s, 872 vs, 950 w, 988 w, 1015 w, 1085-1095 vs, 1130 vs, 1210 m, 1240 w, 1290 m, 1375 s, 1382 (sh), 1392 m, 1425 m, 1485 m, 1600 s, 2878 s, 2935 m, 3075 w, 3285 w, 3365 m
3.98	C <sub>2</sub> H <sub>5</sub> CHCH <sub>2</sub> OH   NH <sub>2</sub> (4.54)	PhSi(OCH <sub>2</sub> CHC <sub>2</sub> H <sub>5</sub> ) <sub>3</sub>   NH <sub>2</sub> 166/0.3 (75)	2.03 (2.28)	7.57 (7.60)	11.01 (11.37)	355 (369)	1.4795 485 s, 520 m, 590 w, 620 w, 705 s, 742 vs, 782 m, 845 s, 885 s, 925 m, 990 w, 1005 vw, 1015 w, 1085 vs, 1130 vs, 1265 m, 1285 m, 1310 w, 1375 m, 1388 m, 1410 vw, 1430 m, 1480 s, 1600 s, 2885 s, 2935 s, 3075 w, 3290 m, 3380 m

3.73	$\begin{array}{c} \text{CH}_2\text{OH} \\   \\ \text{CH}_2\text{NH}(\text{CH}_3) \end{array}$ (3.59)	$\begin{array}{c} \text{PhSi}(\text{OCH}_2\text{CH}_2\text{NHCH}_3)_3 \\ 130/0.2 \\ (82) \end{array}$	2.06 (2.14)	8.56 (8.57)	12.79 (12.83)	340 (327)	1.4825	480 m, 545 m, 620 w, 675 w, 705 s, 742 vs, 800 m, 885 w, 978 s, 1005 vw, 1015 w, 1040 (sh), 1085 vs, 1095 vs, 1130 s, 1255 m, 1295 w, 1365 w, 1395 w, 1428 m, 1455 m, 1480 m, 1598 w, 2785 s, 2845 m, 2885 s, 2925 s, 3065 w, 3280~3310 m (b)
2.97	$\begin{array}{c} \text{CH}_2\text{OH} \\   \\ \text{CH}_2\text{N}(\text{CH}_3)_2 \end{array}$ (3.34)	$\begin{array}{c} \text{PhSi}[\text{OCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2]_3 \\ 133-134/0.1 \\ (76) \end{array}$	1.57 (1.70)	7.74 (7.60)	11.35 (11.37)	365 (369)	1.4725	480 m, 505 s, 545 w, 670 w 705 s, 742 vs, 790 m, 822 m, 885 m, 975 s, 1005 vw, 1070 vs, 1110 vs, 1130 vs, 1202 m, 1280 s, 1292 (sh), 1380 vw, 1430 w, 1475 s, 1598 w, 2775 s, 2812 m, 2885 m, 2948 s, 3055 w
2.92	$\begin{array}{c} \text{CH}_3\text{CHCH}_2\text{N}(\text{CH}_3)_2 \\   \\ \text{OH} \end{array}$ (3.76)	$\begin{array}{c} \text{PhSi}[\text{OCH}(\text{CH}_3)\text{CH}_2\text{N}(\text{CH}_3)_2]_3 \\ 116-118/0.3 \\ (72) \end{array}$	1.42 (1.67)	7.12 (6.82)	9.75 (10.21)	392 (411)	1.4595	475 w, 520 s, 705 s, 730 s, 795 s, 835 m, 865 (sh), 895 m, 920 w, 970 w, 1015 w, 1045 vw, 1085 vs, 1105 vs, 1130 s, 1210 vw, 1280 s, 1325 w, 1385 m, 1410 w, 1430 (sh), 1482 s, 1600 w, 2785 s, 2820 m, 2875 w, 2945 s, 3070 w
4.32	$\begin{array}{c} \text{CH}_2\text{OH} \\   \\ \text{CH}_2\text{NH}_2 \end{array}$ (3.43)	$\begin{array}{c} \text{PhSi}(\text{OCH}_2\text{CH}_2\text{NH}_2)_3 \\ 155-158/1 \\ (43) \\ \text{Residue-insoluble} \\ (35) \end{array}$	2.42 (2.48)	10.40 (9.84)	15.56 (14.72)	319 (285)	1.4975	452 w, 475 w, 525 m, 670 w, 705 s, 740 s, 787 m, 860 m, 1020 vw, 1070 (sh), 1095 vs, 1130 vs, 1192-1205 w (b), 1278 m, 1370 w, 1380 vw, 1430 m, 1475 m, 1600 s, 2880 s, 2950 s, 3065 w, 3285 m, 3390 m
2.79	$\begin{array}{c} \text{CH}_2\text{OH} \\   \\ \text{CH}_2\text{CH}_2\text{N}(\text{C}_2\text{H}_5)_2 \end{array}$ (4.61)	$\begin{array}{c} \text{PhSi}[\text{OCH}_2\text{CH}_2\text{CH}_2\text{N}(\text{C}_2\text{H}_5)_2]_3 \\ 165-170/0.5 \\ (75) \end{array}$	1.47 (1.60)	5.72 (5.66)	8.37 (8.47)	491 (495)	1.4640	

## INFRARED ABSORPTION SPECTRA

A comparison of the characteristic absorption bands of vinyl- and phenyl-(aminoalkoxy)silanes with those of the corresponding triethoxysilanes reveals:

(i). Bands of variable intensity in  $635\text{--}685\text{ cm}^{-1}$  are attributable to  $\nu(\text{Si-C})$  in vinyl compounds; bands at  $755\text{--}775\text{ cm}^{-1}$  due to  $\nu_s(\text{Si-O})$  and  $788\text{--}830\text{ cm}^{-1}$   $\nu_{as}(\text{Si-O})$  are also observed. A band at  $440\text{--}530\text{ cm}^{-1}$  is probably due to  $\delta_{as}(\text{Si-OC})$ , Si-O bending or Si-O-C torsion, as mentioned by Smith<sup>3</sup> for ethoxysilanes in CsBr region.

(ii). Characteristic frequencies of CH=CH<sub>2</sub> group are present at  $975\text{--}990\text{ cm}^{-1}$ , a doublet at  $1015\text{--}1020\text{ cm}^{-1}$  may be due to out-of-plane CH bending and the band at  $1395\text{--}1410\text{ cm}^{-1}$  to the strong CH in-plane bending frequency. (C=C frequencies are also observed in all the vinylalkoxy compounds at  $1602\text{--}1608\text{ cm}^{-1}$ ) (cf. refs 4-8).

(iii). Bands characteristic of phenyl ring on silicon are present, with peaks at  $1425\text{--}1430\text{ cm}^{-1}$ ,  $1485\text{--}1495\text{ cm}^{-1}$  and  $1600\text{ cm}^{-1}$  due to CH and C=C vibrations and ring deformations. The band at  $1125\text{--}1130\text{ cm}^{-1}$  may be due to "X-sensitive" planar ring vibrations, and those at  $735\text{--}740\text{ cm}^{-1}$  and  $705\text{ cm}^{-1}$  to out-of-plane hydrogen deformation modes. Similar assignments have been made by Kriegsman<sup>9</sup> and others<sup>10-13</sup>.

(iv). Bands at  $1088\text{--}1110\text{ cm}^{-1}$ , present in all the (aminoalkoxy)silanes, are attributable to  $\nu_{as}(\text{Si-O-C})$  and  $\nu(\text{C-O})$  modes.

(v). The  $\delta(\text{NH}_2)$  band in primary aminoalkoxides at  $1598\text{--}1608\text{ cm}^{-1}$  overlaps the C=C frequencies of the vinyl and phenyl groups, and causes the intensity of absorption in this region to be greater than that shown by vinyl- or phenyltriethoxysilane.

(vi). Characteristic absorption bands of  $\delta(\text{CH}_3\text{-N})$  and  $\nu(\text{CH}_3\text{-N})$  group<sup>14,15</sup> are observed at  $1465\text{--}1480\text{ cm}^{-1}$  and  $2780\text{--}2810\text{ cm}^{-1}$  respectively, in substituted aminoalkoxides as in the corresponding aminoalcohols.

## EXPERIMENTAL

The apparatus and purification methods used have been described<sup>1</sup>. Molecular weights were determined with Gallenkamp Semimicro Ebulliometer using thermistor sensing. Spectra were run on a model UR-10 double beam IR spectrophotometer with KBr and NaCl prisms in neat state.

Silicon was estimated as silica by decomposing samples with a few drops of H<sub>2</sub>SO<sub>4</sub>(AR) and HNO<sub>3</sub>(AR), and nitrogen, by Kjeldahl's method. The ethanol liberated as ethanol/benzene azeotrope was estimated by chromate oxidimetry<sup>16</sup>.

*Reaction between vinyltriethoxysilane and 2-methyl-2-amino-1-propanol (molar ratio 1/3)*

Vinyl triethoxy silane 2.61 g (13.71 mmoles) was mixed with 2-methyl-2-amino-1-propanol 3.72 g (41.73 mmoles) in 40 ml benzene and a small piece of sodium was added. The mixture was refluxed and the ethanol-benzene azeotrope was collected during  $2\frac{1}{2}$  h, in which time the liberation of ethanol was complete. The product was purified by vacuum distillation (b.p.  $110^\circ/0.7\text{ mm}$ , 91% yield). (Found: N, 13.14; Si, 9.01. C<sub>14</sub>H<sub>33</sub>N<sub>3</sub>O<sub>3</sub>Si calcd.: N, 13.14; Si, 8.78%.) The total ethanol liberated was 1.69 g compared with the 1.89 g required for the replacement of three moles.

*Reaction between phenyltriethoxysilane and N-methyl ethanolamine (molar ratio 1/3)*

A small piece of sodium was added to a benzene solution of phenyltriethoxysilane 3.73 g (15.52 mmoles) and *N*-methylethanolamine 3.59 g (47.80 mmoles) and the mixture was refluxed for 3½ h, during which ethanol was fractionated off as the binary azeotrope and estimated. The remaining solvent was stripped off under reduced pressure and the product was distilled at 130°/0.2 mm in 82% yield. (Found: N, 12.79; Si, 8.56. C<sub>15</sub>H<sub>29</sub>N<sub>3</sub>O<sub>3</sub>Si calcd.: N, 12.83; Si, 8.58%.)

The alcohol liberated was 2.06 g, compared with 2.14 g for the replacement of three moles. Details of other reactions are given in Tables 1 and 2.

## ACKNOWLEDGEMENTS

We thank the CSIR, New Delhi for awarding a Senior Research Fellowship to P. Bajaj. The authors are also indebted to Dr. V. B. Chipalkatti and Dr. R. T. Thampy, Sh. Ram Institute, for providing the facilities for recording IR spectra.

## REFERENCES

- 1 R. C. MEHROTRA AND P. BAJAJ, *J. Organometal. Chem.*, 24 (1970) 611.
- 2 M. G. VORONKOV, L. LIBERTS AND E. LUKEVICS, *Zh. Obshch. Khim.*, 37 (1967) 1673; *Chem. Abstr.*, 68 (1968) 29763r.
- 3 A. L. SMITH, *Spectrochim. Acta*, 19 (1963) 849.
- 4 J. W. CURRY, *J. Amer. Chem. Soc.*, 78 (1956) 1686.
- 5 K. C. FRISCH, P. A. GOODWIN AND R. E. SCOTT, *J. Amer. Chem. Soc.*, 74 (1952) 4584.
- 6 M. KANAZASHI, *Bull. Chem. Soc. Jap.*, 26 (1953) 493.
- 7 E. R. SHULL, R. A. THURSACK AND C. M. BIRDSALL, *J. Chem. Phys.*, 24 (1956) 147.
- 8 M. C. HENRY AND J. G. NOLTES, *J. Amer. Chem. Soc.*, 82 (1960) 555.
- 9 H. KRIEGSMANN AND K. H. SCHOWTKA, *Z. Phys. Chem. (Leipzig)*, 209 (1958) 261.
- 10 L. SPIALTER, D. C. PRIEST AND C. W. HARRIS, *J. Amer. Chem. Soc.*, 77 (1955) 6227.
- 11 R. D. KROSS AND V. A. FASSEL, *J. Amer. Chem. Soc.*, 77 (1955) 5858.
- 12 D. H. WHIFFEN, *J. Chem. Soc.*, (1956) 1350.
- 13 S. G. DURGAR'YAN AND YU. P. EGOROV, *Zh. Obshch. Khim.*, 30 (1960) 2600.
- 14 R. D. HILL AND G. D. MEAKINS, *J. Chem. Soc.*, (1958) 760.
- 15 I. A. DEGEN, *Appl. Spectrosc.*, 23 (1969) 239.
- 16 D. C. BRADLEY, F. M. A. HALIM AND W. WARDLAW, *J. Chem. Soc.*, (1950) 3450.