Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

(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[1] 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:

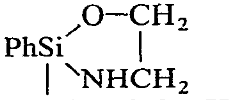
$$\mathrm{RSi(OEt)_3 + 3\ HOCH_2CH_2NR'R''} \xrightarrow{\mathrm{Na}} \mathrm{RSi(OCH_2CH_2NR'R'')_3 + 3\ EtOH}$$

$$(\mathrm{R = CH{=}CH_2 \text{ or } C_6H_5;\ R' = R'' = H \text{ or } CH_3;\ R' = H \text{ and } R'' = CH_3})$$

Phenylaminoalkoxysilanes have been made previously from phenyltrichlorosilane and amino alcohols in presence of triethylamine[2].

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 $\mathrm{PhSi(OCH_2CH_2NH_2)_3}$ 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 $\mathrm{PhSi(OCH_2CH_2NH_2)_3}$. [*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 $\mathrm{PhSi(OCH_2CH_2NH_2)_3}$ and



$$\mathrm{PhSi(OCH_2CH_2NH)(OCH_2CH_2NH_2)}$$

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

(*Continued* p. 364)

TABLE 1

REACTIONS OF VINYLTRIETHOXYSILANE WITH AMINOALCOHOLS

CH_2=CHSi-$(OEt)_3$ (g)	Aminoalcohol (g)	Product formed; b.p. (°C/mm); (yield) (%)	Ethanol content (g) liberated (calcd.)	Analysis found (calcd.) (%)		Molecular weight found (calcd.)	n_D^{35}	Characteristic IR absorption bands
				Si	N			
2.44	CH_2OH | $CH_2CH_2NH_2$ (2.89)	$CH_2{=}CHSi(OCH_2CH_2CH_2NH_2)_3$ 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	$(CH_3)_2\underset{NH_2}{\underset{\mid}{C}}CH_2OH$ (3.72)	$CH_2{=}CHSi[OCH_2\underset{NH_2}{\underset{\mid}{C}}(CH_3)_2]_3$ 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	$C_2H_5\underset{NH_2}{\underset{\mid}{C}}HCH_2OH$ (5.08)	$CH_2{=}CHSi(OCH_2\underset{NH_2}{\underset{\mid}{C}}HC_2H_5)_3$ 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	CH_2OH | CH_2NH_2 (3.75)	$CH_2{=}CHSi(OCH_2CH_2NH_2)_3$ 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	CH_2OH | $CH_2NH(CH_3)$ (6.04)	$CH_2{=}CHSi(OCH_2CH_2NHCH_3)_3$ 112–115/1.2 (78)	3.40 (3.68)	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	CH_2OH | $CH_2N(CH_3)_2$ (3.64)	$CH_2{=}CHSi[OCH_2CH_2N(CH_3)_2]_3$ 122–123/2.5 (80)	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	$CH_3CHCH_2N(CH_3)_2$ | OH (3.52)	$CH_2{=}CHSi[OCHCH_2N(CH_3)_2]_3$ | CH_3 98-102/0.8 (75)	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	CH_2OH | $CH_2CH_2N(C_2H_5)_2$ (3.72)	$CH_2{=}CHSi[O(CH_2)_3N(C_2H_5)_2]_3$ 186/1.5 (89)	1.26 (1.29)	6.38 (6.30)	9.32 (9.43)	438 (445)	1.4400	

TABLE 2

REACTIONS OF PHENYLTRIETHOXYSILANE WITH AMINOALCOHOLS

$PhSi(OEt)_3$ (g)	Amino alcohol (g)	Product formed; b.p. (°C/mm); (yield) (%)	Ethanol content (g) liberated (calcd.)	Analysis found (calcd.) (%)		Molecular weight found (calcd.)	n_D^{35}	Characteristic IR absorption bands
				Si	N			
2.78	CH_2OH | $CH_2CH_2NH_2$ (2.70)	$PhSi(OCH_2CH_2CH_2NH_2)_3$ 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	$(CH_3)_2CCH_2OH$ | NH_2 (4.31)	$PhSi[OCH_2C(CH_3)_2]_3$ | NH_2 146–149/2 (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	$C_2H_5CHCH_2OH$ | NH_2 (4.54)	$PhSi(OCH_2CHC_2H_5)_3$ | NH_2 166/0.3 (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	CH_2OH | $CH_2NH(CH_3)$ (3.59)	$PhSi(OCH_2CH_2NHCH_3)_3$ 130/0.2 (82)	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	CH_2OH | $CH_2N(CH_3)_2$ (3.34)	$PhSi[OCH_2CH_2N(CH_3)_2]_3$ 133–134/0.1 (76)	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	$CH_3CHCH_2N(CH_3)_2$ | OH (3.76)	$PhSi[OCH(CH_3)CH_2N(CH_3)_2]_3$ 116–118/0.3 (72)	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	CH_2OH | CH_2NH_2 (3.43)	$PhSi(OCH_2CH_2NH_2)_3$ 155–158/1 (43) Residue-infusible (35)	2.42 (2.48)	10.40 (9.84) residue 19.12	15.56 (14.72) 12.19	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	CH_2OH | $CH_2CH_2N(C_2H_5)_2$ (4.61)	$PhSi[OCH_2CH_2CH_2N(C_2H_5)_2]_3$ 165–170/0.5 (75)	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 635–685 cm^{-1} are attributable to ν(Si–C) in vinyl compounds; bands at 755–775 cm^{-1} due to ν_s(Si–O) and 788–830 ν_{as}(Si–O) are also observed. A band at 440∼530 cm^{-1} is probably due to δ_{as}(Si–OC), Si–O bending or Si–O–C torsion, as mentioned by Smith[3] for ethoxysilanes in CsBr region.

(*ii*). Characteristic frequencies of CH=CH$_2$ group are present at 975–990 cm^{-1}, a doublet at 1015–1020 cm^{-1} may be due to out-of-plane CH bending and the band at 1395–1410 cm^{-1} to the strong CH in-plane bending frequency. (C=C frequencies are also observed in all the vinylalkoxy compounds at 1602–1608 cm^{-1}) (*cf.* refs 4–8).

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

(*iv*). Bands at 1088–1110 cm^{-1}, present in all the (aminoalkoxy)silanes, are attributable to ν_{as}(Si–O–C) and ν(C–O) modes.

(*v*). The δ(NH$_2$) band in primary aminoalkoxides at 1598–1608 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 δ(CH$_3$–N) and ν(CH$_3$–N) group[14,15] are observed at 1465–1480 cm^{-1} and 2780–2810 cm^{-1} respectively, in substituted aminoalkoxides as in the corresponding aminoalcohols.

EXPERIMENTAL

The apparatus and purification methods used have been described[1]. 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_2SO_4(AR) and HNO_3(AR), and nitrogen, by Kjeldahl's method. The ethanol liberated as ethanol/benzene azeotrope was estimated by chromate oxidimetry[16].

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 2½ h, in which time the liberation of ethanol was complete. The product was purified by vacuum distillation (b.p. 110°/0.7 mm, 91% yield). (Found: N, 13.14; Si, 9.01. $C_{14}H_{33}N_3O_3Si$ 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. $C_{15}H_{29}N_3O_3Si$ 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.