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Preparation of Some Anilinosilanes

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We wish to report on the preparation of some di- and trianilinosilanes from the reaction of aniline and the corresponding organochlorosilanes by the use of triethylamine as a hydrogen chloride acceptor. Most of the products were crystalline substances and gave the corresponding silanols or siloxanes when hydrolyzed in the presence of an acidic catalyst.

The products were triphenylsiloxytrianilinosilane, bis-triphenylsiloxydianilinosilane, vinyltrianilinosilane, vinylphenyldianilinosilane, vinylbutyldianilinosilane, diphenyldianilinosilane, and phenyltrianilinosilane, the first five being new compounds.

All the products were well-defined and were characterized by their IR spectra. As for the crystalline products, the X-ray powder patterns were determined in order to identify them rapidly.

Experimental

Organochlorosilanes. The triphenylsiloxytrichlorosilane, mp 47°C, and bis-triphenylsiloxydichlorosilane, mp 141°C, were prepared according to a method previously reported.[1] The vinylphenyldichlorosilane, bp 67°C/2 mmHg, and vinylbutyldichlorosilane, bp 65—66°C/20 mmHg, were prepared by the Grignard route.[2] The vinyltrichlorosilane, diphenyldichlorosilane, and phenyltrichlorosilane were obtained from the Shin-etsu Chem. Ind. Co. and were further purified by distillation immediately before use.

Preparation of Anilinosilanes. Typical procedures will be described in detail with the preparation of bis-triphenylsiloxydianilinosilane as an example.

To a stirred mixture of freshly-distilled aniline (19.7 g; 0.21 mol), triethylamine (28.4 g; 0.28 mol), and 200 m*l* of toluene, a toluene solution of bis-triphenylsiloxydichlorosilane (57.2 g; 0.09 mol) was added drop by drop. After the addition was complete, the mixture was further stirred for 10 hr, during which period the temperature was maintained at 100°C. After standing overnight, triethylamine hydrochloride was removed by filtration and the filtrate was evaporated to about 100 m*l*.

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2) T. Takiguchi and M. Abe, *Kogyo Kagaku Zasshi* (*J. Chem. Soc. Japan, Ind. Chem. Sect.*), **66**, 625 (1963).

The concentrate was then combined with 100 ml of warm *n*-hexane and cooled to room temperature to give a white crystalline mass from which 37.8 g (55%) of pure *bis-triphenylsiloxydianilinosilane* as white, acicular crystlas melting at 159—160°C, was obtained by recrystallization from boiling *n*-hexane.

Found: C, 75.06; H, 5.80; N, 3.41; Si, 11.05%; mol wt, 755 (determined cryoscopically in 1,4-dioxane). Calcd for $C_{48}H_{42}N_2O_2Si_3$: C, 75.55; H, 5.56; N, 3.67; Si, 11.04%; mol wt, 763.

The hydrolysis of the anilinosilane in the presence of sulfuric acid gave quantitatively a mixture of hexaphenyltrisiloxane-3,3-diol[1] and its condensation product.

Similar procedures were applied to other chlorosilanes to give the following anilinosilanes, the mean yield being 57%: triphenylsiloxytrianilinosilane, mp 201—202°C, vinyltrianilinosilane, mp 86—87°C, vinylphenyldianilinosilane, mp 87—88°C, vinylbutyldianilinosilane, a low melting solid, bp 149—150°C/1.5 mmHg, diphenyldianilinosilane, mp 161—162°C (lit. mp 153°C,[3] 166—167°C[4]), and phenyltrianilinosilane, mp 138°C (lit. mp 134—135°C[5]). All the anilinosilanes thus obtained were readily soluble in chloroform, acetone, a dioxane, were soluble in benzene and toluene, and were barely soluble in methanol and *n*-hexane.

Triphenylsiloxytrianilinosilane. Found: C, 74.87; H, 5.83; N, 7.57; Si, 9.72%; mol wt, 576. Calcd for $C_{36}H_{23}N_3OSi_2$: C, 74.57; H, 5.74; N, 7.24; Si, 9.69%; mol wt, 580.

Vinyltrianilinosilane. Found: C, 71.33; H, 6.40; N, 12.15; Si, 8.60%; mol wt, 338. Calcd for $C_{20}H_{21}N_3Si$: C, 72.47; H, 6.39; N, 12.68; Si, 8.47%; mol wt, 332.

Vinylphenyldianilinosilane. Found: C, 75.66; H, 6.60; N, 8.57; Si, 8.90%; mol wt, 322. Calcd for $C_{20}H_{20}N_2Si$: C, 75.90; H, 6.37; N, 8.85; Si, 8.87%; mol wt, 317.

Vinylbutyldianilinosilane. Found: C, 71.77; H, 8.20; N, 9.48; Si, 9.53%; mol wt, 289. Calcd for $C_{18}H_{24}N_2Si$: C, 72.92; H, 8.16; N, 9.45; Si, 9.47%; mol wt, 297.

Diphenyldianilinosilane. Found: C, 78.82; H, 5.87; N, 7.70; Si, 7.74%; mol wt, 370. Calcd for $C_{24}H_{22}N_2Si$: C, 78.64; H, 6.05; N, 7.64; Si, 7.66%; mol wt, 367.

Phenyltrianilinosilane. Found: C, 76.33; H, 6.17; N, 10.86; Si, 7.46%; mol wt, 395. Calcd for $C_{24}H_{23}N_3Si$: C, 75.55; H, 6.08; N, 11.01; Si, 7.36%; mol wt, 382.

Infrared Absorption Spectra and X-Ray Power Diffraction Data. The absorption bands due to Si–R bonding,[2,6-7] and aromatic secondary amine attached to Si[8,9] were distinctly observed throughout all the samples. The X-ray powder patterns were also satisfactorily recorded by using Cu$K\alpha$ radiation filtered by Ni.

IR Data

$(Ph_3SiO)_2Si(NHPh)_2$ 700(S) 715(VS) 750(M) 760 (M) 800(VW) 905(M) 933(S) 1000(M) 1029(M) 1100(VS) 1120(VS) 1292(S) 1394(M) 1430(S) 1504 (M) 1605(M) 3035(W) 3380(W)

$Ph_3SiOSi(NHPh)_3$ 700(M) 710(M) 743(M) 780(W) 920(S) 1000(W) 1028(W) 1100(S) 1115(VS) 1285(S) 1383(M) 1430(W) 1504(M) 1605(M) 3045(VW) 3350(W)

$C_2H_3Si(NHPh)_3$ 695(M) 754(VS) 770(S) 823(W) 892(VS) 906(VS) 968(M) 995(S) 1011(M) 1025(M) 1076(M) 1177(M) 1230(M) 1280(VS) 1322(M) 1380(VS) 1475(VS) 1489(VS) 1598(VS) 2943(VW) 3026 (W) 3326 (M)

C_2H_3·PhSi(NHPh)$_2$ 698(S) 708(S) 738(VS) 754(VS) 770(S) 821(VW) 863(M) 900(VS) 966(S) 995(S) 1010(M) 1028(M) 1078(M) 1113(S)118 1(M) 1230(S) 1281(VS) 1323(M) 1378(VS) 1425(S) 1474(VS) 1491(VS) 1597(VS) 3024(W) 3346(W)

C_2H_3·BuSi(NHPh)$_2$ 692(S) 754(S) 890(S) 903(S) 962(M) 998(M) 1028(M) 1078(M) 1152(VW) 1170 (W) 1228(W) 1283(VS) 1382(S) 1474(S) 1494(S) 1601(S) 2850(W) 2924(M) 3036(W) 3390(M)

$Ph_2Si(NHPh)_2$ 690(S) 740(S) 754(S) 890(S) 906 (VS) 995(M) 1025(VW) 1075(VW) 1110(S) 1178 (VW) 1230(VW) 1283(VS) 1320(VW) 1378(M) 1388(M) 1424(M) 1466(S) 1484(S) 1595(VS) 3014 (VW) 3336 (W)

$PhSi(NHPh)_3$ 695(M) 740(M) 754(S) 780(W) 890(M) 910(VS) 928(S) 995(M) 1028(W) 1078 (W) 1120(M) 1170(W) 1226(W) 1278(VS) 1390(S) 1425(VW) 1478(S) 1490(S) 1599(S) 3026(VW) 3351(M)

X-Ray Data

$(Ph_3SiO)_2Si(NHPh)_2$

d, *kX*:	11.33	11.05	9.61	5.54	5.44	4.46		
I/I_0:	0.40	1.00	0.13	0.13	0.10	0.51		

$Ph_3SiOSi(NHPh)_3$

d, *kX*:	14.26	9.41	8.12	7.03	4.67	4.51	4.11	3.53
I/I_0:	1.00	0.16	0.70	0.13	0.54	0.51	0.13	0.18

C_2H_3·PhSi(NHPh)$_2$

d, *kX*:	9.21	9.12	8.51	8.35	5.61	5.22	4.96	4.93
	4.77	4.70	4.58	4.35	4.29	4.15	4.04	3.92
	3.77	3.38	3.31	3.10	3.05	2.95		
I/I_0:	0.81	0.14	1.00	0.35	0.19	0.24	0.35	0.38
	0.18	0.79	0.48	0.34	0.41	0.79	0.23	0.15
	0.49	0.16	0.31	0.26	0.14	0.15		

$C_2H_3Si(NHPh)_3$

d', *kX*:	10.53	8.35	7.63	7.25	6.28	5.47	5.31	5.07
	4.65	4.46	4.37	4.29	4.15	4.06	3.97	3.63
	3.60	3.52	3.27	3.22	3.09	3.01	2.96	2.87
I/I_0:	0.56	0.23	0.39	0.48	0.39	0.28	0.36	0.21
	1.00	0.80	0.32	0.56	0.31	0.23	0.49	0.53
	0.52	0.26	0.24	0.22	0.39	0.37	0.23	0.19

$Ph_2Si(NHPh)_2$

d, *kX*:	10.05	9.41	9.31	7.38	5.61	5.07	4.96	4.72
	4.67	4.51	4.44	4.27	4.00	3.66	3.38	
I/I_0:	0.12	0.27	0.21	0.23	0.17	0.11	0.11	1.00
	0.34	0.20	0.25	0.46	0.11	0.15	0.33	

$PhSi(NHPh)_3$

d, *kX*:	10.78	10.16	9.72	7.83	7.63	7.20	6.24	5.54
	5.34	5.04	4.82	4.65	4.53	4.40	4.19	4.00
	3.79	3.56	3.41	3.28	3.12	3.07	2.73	

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I/I_0: 0.15 0.14 0.26 0.28 0.21 0.13 0.15 0.19
0.13 0.30 0.30 0.64 0.75 1.00 0.69 0.15
0.43 0.49 0.21 0.15 0.17 0.34 0.22

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