

HETEROGENEOUS CATALYSIS IN THE PRESENCE OF SALTS AND WITHOUT SOLVENT

I. ALCOHOLYSIS OF SILANES

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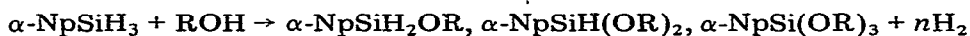
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Summary

Alcoholysis of >Si-H bond is heterogeneously catalysed by salts. The reaction is highly selective and by choice of conditions, it is possible to prepare mono-, di- or tri-alkoxysilanes. A mechanism involving coordination of the salt anions to the silanes is proposed.

Alcoholysis of silanes has been much studied and several catalysts have been used: metal alkoxides [1], amines [2], metal halides [3,4] and transition metals, either in heterogeneous catalysis by copper [5], palladium or nickel [6] or in homogeneous catalysis by a metal complex [7–10]. We recently showed that the reaction can also be satisfactorily carried out in molten dodecylammonium propionate [11] but the miscibility of the products with this salt makes separation difficult. Thus we looked for less lipophilic salts so that the organic phase could be more easily separated.

Alcoholysis of hydrogenosilanes ($\alpha\text{-NpPhSiH}_2$, $\alpha\text{-NpSiH}_3$, Ph_2SiH_2 , $\text{PhCH}_2\text{SiH}_2$, $(n\text{-Pent})_2\text{SiH}_2$) with various types of alcohols or phenols (*m*-cresol, *n*-heptanol, menthol, allyl alcohol and undecynol) was found to give mono- or poly-alkoxy-silanes:



Commercial potassium tartrate, potassium phthalate, SCNK, HCOOK, FK, FCs and CH_3COOCs were used (1 g per g of silane) and the results are shown in Tables 1 to 5. Yields were determined by GLC and confirmed by weighing the products after distillation.

TABLE 1
ALCOHOLYSIS OF α -NAPHTHYLSILANE (yield (%) by GLC)

Exp. number	Salt	Alcohol	Conditions	Products		
				α -NpSH ₂ OR (%)	α -NpSH(OR) ₂ (%)	α -NpSi(OR) ₃ (%)
1	potassium tartrate	cresol (2 eq)	3 min/140°C	0	0	90
2	potassium tartrate	heptanol (3 eq)	90 min/140°C	0	55	0
3	SCNK	cresol (2 eq)	3 min/180°C	0	0	90
4	SCNK	heptanol (3 eq)	5 h/180°C	0	80	0
5	SCNK	menthol (2 eq)	3 h/180°C	30	0	0
6	HCO ₂ K	cresol (3 eq)	5 min/180°C	0	0	100
7	HCO ₂ K	heptanol (3 eq)	1 h/180°C	0	0	100

TABLE 2

ALCOHOLYSIS OF DIPHENYLSILANE (yield (%) by GLC)

Exp. number	Salt	Alcohol	Conditions	Products	
				Ph ₂ SiHOR (%)	Ph ₂ Si(OR) ₂ (%)
1	potassium tartrate	cresol (1 eq)	4 h/140°C	50	0
2	potassium tartrate	cresol (2 eq)	4 h/140°C	40	20
3	SCNK	cresol (2 eq)	7 min/180°C	0	100
4	SCNK	heptanol (2 eq)	30 min/180°C	100	0
5	SCNK	menthol (2 eq)	4 h/180°C	0	0
6	HCO ₂ K	cresol (2 eq)	15 min/180°C	0	100
7	HCO ₂ K	heptanol (2 eq)	15 min/180°C	0	100
8	HCO ₂ K	menthol (1 eq)	5 h/180°C	90	0
9	HCO ₂ K	menthol (2 eq)	5 h/180°C	20	80
10	HCO ₂ K	menthol (3 eq)	5 h/180°C	0	100
11	FK	cresol (2 eq)	4 min/25°C	0	100
12	FK	heptanol (1 eq)	10 min/180°C	0	100
13	FK	menthol (3 eq)	30 min/180°C	0	100
14	FLi	cresol (2 eq)	3 h/180°C	0	0
15	potassium phthalate	cresol (2 eq)	5 min/180°C	0	100
16	potassium phthalate	heptanol (3 eq)	15 min/180°C	0	100
17	potassium phthalate	menthol (1 eq)	30 min/180°C	90	0
18	potassium phthalate	menthol (2 eq)	30 min/180°C	20	80
19	potassium phthalate	menthol (3 eq)	20 min/180°C	0	100

The results show that the extent of alcoholysis of silanes in the presence of salts is dependent upon several factors, including the nature of the reagents (silane and alcohol or phenol), the nature of the salt, the temperature, and the magnitude of the ratio [silane]/[alcohol]. Thus a reactivity sequence of α -NpSiH₃, Ph₂SiH₂ > PhMeSiH₂ > α -NpPhSiH₂ > (Pent)₂SiH₂ may be deduced from the following observations.

In the presence of SCNK, menthol gives 30% of monoalkoxysilane with α -NpSiH₃ (Table 1, exp. 5) whereas it does not react with Ph₂SiH₂ (Table 2,

TABLE 3

ALCOHOLYSIS OF PHENYLMETHYLSILANE (yield (%) by GLC)

Exp. number	Salt	Alcohol	Conditions	Products	
				PhMeSiHOR (%)	PhMeSi(OR) ₂ (%)
1	potassium tartrate	cresol (2 eq)	2.5 h/140°C	45	0
2	SCNK	cresol (2 eq)	2 h/180°C	5	95
3	SCNK	heptanol (1 eq)	18 h/180°C	0	60
4	HCO ₂ K	cresol (1 eq)	15 min/170°C	0	60
5	HCO ₂ K	heptanol (2 eq)	15 min/180°C	0	90
6	HCO ₂ K	menthol (2 eq)	6 h/180°C	40	60
7	FK	menthol (2 eq)	1 h/180°C	15	85
8	potassium phthalate	menthol (1 eq)	1 h/160°C	80	0

TABLE 4

ALCOHOLYSIS OF α -NAPHTHYLPHENYLSILANE (yield (%) by GLC)

Exp. number	Salt	Alcohol	Conditions	Products	
				α -NpPhSi-(H)OR (%)	α -NpPhSi-(OR) ₂ (%)
1	potassium tartrate	cresol (1 eq)	24 h/140°C	0	0
2	potassium tartrate	menthol (1 eq)	24 h/140°C	0	0
3	SCNK	cresol (1 eq)	3 h/180°C	95	0
4	SCNK	heptanol (2 eq)	4 h/180°C	95	0
5	SCNK	menthol (1 eq)	4 h/180°C	0	0
6	HCOOK	cresol (2 eq)	15 min/180°C	0	95
7	HCOOK	heptanol (2 eq)	2 h/180°C	10	90
8	HCOOK	menthol (1 eq)	4 h/180°C	90	0
9	FK	cresol (2 eq)	5 min/100°C	0	100
10	FK	heptanol (2 eq)	15 min/180°C	10	90
11	FK	menthol (1 eq)	1 h/25°C	0	0
12	FK	menthol (3 eq)	30 min/130°C	10	90
13	potassium phthalate	cresol (2 eq)	20 min/180°C	0	100
14	potassium phthalate	heptanol (2 eq)	15 min/180°C	10	90
15	potassium phthalate	menthol (1 eq)	4 h/120°C	90	0
16	potassium phthalate	menthol (3 eq)	90 min/180°C	55	45
17	FCs	menthol (1 eq)	1 h/25°C	100	0
18	FCs	menthol (1 eq)	1 h/80°C	30	70
19	FCs	menthol (1 eq)	1 h/180°C	0	100
20	CH ₃ COOLi	heptanol (2 eq)	90 min/180°C	55	8
21	CH ₃ COOK	heptanol (2 eq)	90 min/180°C	50	43
22	CH ₃ COOK	heptanol (2 eq)	15 min/180°C	35	0
23	CH ₃ COOCs	heptanol (2 eq)	15 min/180°C	57	8

exp. 5). In the presence of HCO₂K, Ph₂SiH₂ reacts with menthol to give a greater amount of dialkoxysilane than does PhCH₃SiH₂ (Table 2, exp. 9 and Table 3, exp. 6). PhCH₃SiH₂ and α -NpPhSiH₂ undergo disubstitution by heptanol in the presence of HCO₂K. However, with the former the reaction is complete in 15 min (Table 3, exp. 5) whereas with the latter it takes 2 h (Table 4, exp. 7). With *m*-cresol on the other hand, in the presence of HCO₂K or potassium phthalate, α -NpPhSiH₂ reacts completely in 15 and 20 min, respectively (Table 4, exp. 6 and 13) whereas (Pent)₂SiH₂ takes 1 h to react in both cases (Table 5, exp. 1 and 2).

The reactivities of the hydroxy compounds, fall in the order: *m*-cresol >

TABLE 5

ALCOHOLYSIS OF DIPENTYLSILANE (yield (%) by GLC)

Exp. number	Salt	Alcohol	Conditions	(Pent) ₂ SiHOR (%)	(Pent) ₂ Si-(OR) ₂ (%)
1	HCO ₂ K	cresol (2 eq)	1 h/180°C	0	90
2	potassium phthalate	cresol (2 eq)	1 h/180°C	0	80
3	potassium phthalate	heptanol (2 eq)	1 h/180°C	0	80
4	potassium phthalate	menthol (2 eq)	7 h/180°C	70	0

n-heptanol > menthol. With Ph_2SiH_2 , for example, in the presence of SCNK at 180°C disubstitution by *m*-cresol is complete within 7 min, whereas monosubstitution by heptanol takes 30 min and menthol does not react at all (Table 2, exp. 3, 4, 5). The high reactivity of *m*-cresol is unusual for in homogeneous catalysis, phenols react only very slowly in the presence of rhodium catalysts [10] and not at all in the presence of dicobaltoctacarbonyl [8].

In our salt media the reactivity of menthol and *m*-cresol is inverted; on the basis of the observed order of reactivity, it would appear that the ease of reaction of these compounds is primarily determined by steric effects.

Both, the rate and the nature of the products depend markedly on the salt used as catalyst. Thus with potassium tartrate reaction of cresol with $\alpha\text{-NpSiH}_3$, Ph_2SiH_2 and $\text{PhCH}_3\text{SiH}_2$ occurs, but with $\alpha\text{-NpPhSiH}_2$ no reaction is observed (Tables 1, 2, 3, 4 exp. 1). SCNK is more effective; it not only brings about monosubstitution of $\alpha\text{-NpPhSiH}_2$ (Table 4, exp. 3) but disubstitution of Ph_2SiH_2 (Table 2, exp. 3) and $\text{PhCH}_3\text{SiH}_2$ (Table 3, exp. 2) and even trisubstitution of $\alpha\text{-NpSiH}_3$ (Table 1, exp. 3). With heptanol, disubstitution of dihydrosilanes requires the use of HCO_2K (Table 2, exp. 7, Table 3, exp. 5, Table 4, exp. 7). Disubstitution by menthol (the least reactive alcohol in our study) occurs only partially (45%) with potassium phthalate, but extensively (90%) with FK (Tables 4, exp. 12, 16). FCs is the most efficient salt; indeed monosubstitution of $\alpha\text{-NpPhSiH}_2$ by menthol at room temperature (25°C) can be brought about only with this salt (Table 4, exp. 17). The relative efficiency of the salts, according to our studies is: potassium tartrate < SCNK < HCO_2K < potassium phthalate < FK < FCs. Temperature also can influence the extent of reaction; thus $\alpha\text{-NpPhSiH}_2$ in the presence of FCs undergoes monosubstitution exclusively at 25°C , disubstitution at 180°C and a mixture of the two at 80°C (Table 4, exp. 17, 18, 19).

Interestingly the state of the salt (molten or solid) has no specific effect on the rate of reaction: when $\alpha\text{-NpPhSiH}_2$ and menthol were heated together for a constant period (3 h) over a wide range of temperature above and below the

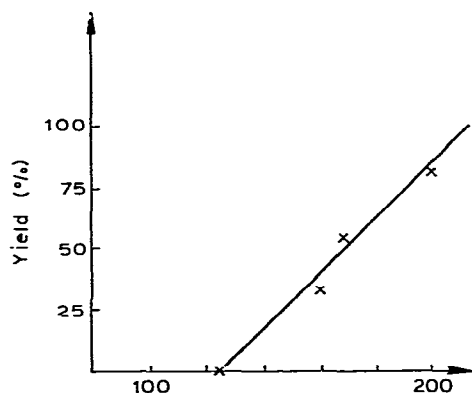


Fig. 1. $\alpha\text{-NpPhSiH}_2$ + menthol/ HCO_2K (m.p. 167°C) 3 h at different temperatures. Product: α -naphthyl-phenylmenthoxyasilane.

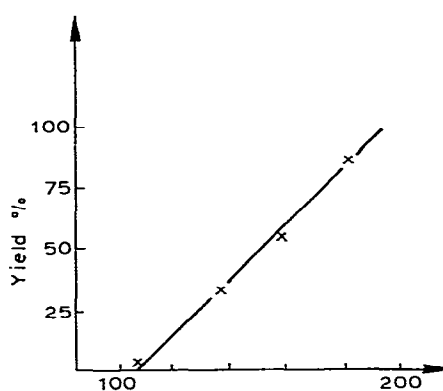


Fig. 2. Ph_2SiH_2 + menthol/ HCO_2K + SCNK (m.p. 100°C) 5 h at different temperatures. Product: diphenyl-menthoxyasilane.

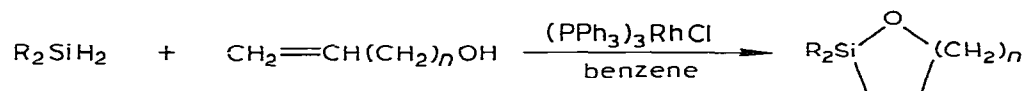
melting point of the added salt (HCO_2K , m.p. 167°C) the yield of α -naphthyl-phenylmethoxysilane was found to vary linearly with temperature (Fig. 1). Likewise when Ph_2SiH_2 was similarly treated, the rate was seen to depend only on the reaction temperature (Fig. 2) and not at all on the state of the added salt.

Selectivity

For synthetic purposes, this new method appears to be at least as selective as homogeneous catalysis [7,10] and more selective than heterogeneous catalysis [5]. It seems invariably possible to establish experimental conditions to obtain either mono- or di-alkoxysilanes exclusively from any alcohol and silane, by changing (a) the salt or (b) the temperature and/or [silane]/[alcohol] ratio.

For example, by changing the ratio $[\text{Ph}_2\text{SiH}_2]/[\text{menthol}]$ mono- or di-substitution can be obtained in the presence of either HCO_2K or potassium phthalate (Table 2, exp. 8, 9, 10, 17, 18, 19) Monosubstitution of α -NpPhSiH₂ and Ph_2SiH_2 by heptanol takes place in the presence of SCNK (Tables 2 and 4, exp. 4) and disubstitution in the presence of HCO_2K , FK and potassium phthalate (Table 2, exp. 7, 12, 16; Table 4, exp. 7, 10, 14). With the same salts, α -NpSiH₃ undergoes alternatively di- or tri-substitution by heptanol (Table 1, exp. 4, 7). Monosubstitution of α -NpPhSiH₂ by menthol occurs with HCO_2K at 180°C , with FCs at 25°C (Table 4, exp. 8, 17) and disubstitution with FK and FCs at 180°C (Table 4, exp. 12, 19).

Selectivity is even more significant in the reactions of ethylenic alcohols with silanes, for under our conditions alkoxy-silanes are formed without affecting the double bond (Table 6). This is in marked contrast with the results obtained by homogeneous catalysis [10] where both functional group react.



Mechanism

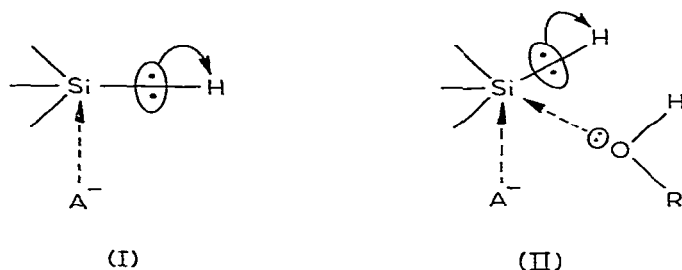
The difference in the catalytic effect of the alkalimetal fluorides is very substantial, for when Ph_2SiH_2 and *m*-cresol are heated together at 180°C for 3 h

TABLE 6
ALCOHOLYSIS OF ETHYLENIC ALCOHOLS (yield (%) by GLC)

Exp. number ^a	Salt	Alcohol	Silane	Conditions	Product	
					SiHOR (%)	Si(OR) ₂ (%)
1	FK	$\text{CH}_2=\text{CH}(\text{CH}_2)_9\text{OH}$	Ph_2SiH_2	3 h/ 100°C	60	0
2	FCs	$\text{CH}_2=\text{CH}(\text{CH}_2)_9\text{OH}$	Ph_2SiH_2	20 min/ 25°C	0	100
3	FCs	$\text{CH}_2=\text{CHCH}_2\text{OH}$	α -NpShSiH ₂	30 min/ 25°C	0	100

^a R = $-(\text{CH}_2)_9\text{CH}=\text{CH}_2$ (exp. 1,2); R = $-\text{CH}_2\text{CH}=\text{CH}_2$ (exp. 3).

in the presence of FLi no reaction is observed. Yet in the presence of FK reaction is instantaneous even at 25°C (Table 2, exp. 11, 14). At the same time, FK fails to bring about reaction between α -NpPhSiH₂ and menthol at room temperature, whereas reaction is quantitative in the presence of FCs under identical conditions (Table 4, exp. 11, 17). The activity of the fluorides thus follows the order: FLi $\ll$ FK $\ll$ FCs, i.e. it increases with increasing ionic character. We believe, that the role of the salt in these reactions is to activate the silicon atom by anionic coordination to form a pentacoordinated silicon atom (I). Coordination of this anion causes delocalisation of the Si—H electron pair and the reaction then takes place by nucleophilic attack of the alcohol molecule at the silicon atom (II). Such extension of coordination of a silicon atom is well



known [12,13,14] and a similar mechanism was proposed for alcoholysis in the presence of rhodium catalysts [10].

Experimental

The NMR spectra were recorded on Varian A60 and T60 spectrometers. The chemical shifts are given in ppm relative to TMS. After the δ , the number of protons (nH) and the nature of the signals (s, singlet; d, doublet; t, triplet; q, quadruplet; m, multiplet) are indicated. The IR spectra were recorded on a Perkin—Elmer 257 spectrophotometer. Analytical gas chromatography (GLC) was carried out on a Girdel 75FH2 using a column packed with 5 or 10% SE 30.

Material

Hydrosilanes were prepared by standard methods. Salts and alcohols were obtained from commercial sources.

General technique

All the alcoholysis reactions were carried out under nitrogen. The following is given as an example: 2.76 g of Ph₂SiH₂ (0.015 mol) 3.56 g of *m*-cresol (0.030 mol) were added together with 3 g of SCNK to the reaction flask under nitrogen. The temperature was maintained at 180°C by use of an oil bath. The mixture was stirred until the evolution of gas stopped (7 min). The salt was filtered off from the organic layer, and the latter was analysed by gas chromatography. Ph₂Si(OCr)₂ (m.p. 81°C) was recrystallized from pentane and identified by its NMR and IR spectra, and by elemental analysis.

Product analysis

The yield were determined by GLC and were based on the silane taken. Products

were isolated by distillation or recrystallization, and identified by their NMR and IR spectra and by elemental analysis.

Alcoholysis of α -naphthylsilane. α -Naphthylmenthoxyasilane: b.p. 160°C/0.2 mmHg. NMR (δ , ppm): 7.7 (7H, m), 5.3 (2H, s), 3.5 (1H, m), 1.5 (18H, m). IR (cm^{-1}): $\nu(\text{Si-H})$ 2140. Found: C, 75.97; H, 8.99; Si, 8.68. $\text{C}_{20}\text{H}_{28}\text{OSi}$ calcd.: C, 75.86; H, 9.03; Si, 8.99%.

α -Naphthyl-diheptanoxyasilane: b.p. 195°C/0.6 mmHg. NMR (δ , ppm): 7.7 (7H, m), 5.25 (1H, s), 3.8 (4H, t), 1.3 (26H, m). IR (cm^{-1}): $\nu(\text{Si-H})$ 2130. Found: C, 74.81; H, 9.90; Si, 7.63. $\text{C}_{24}\text{H}_{38}\text{O}_2\text{Si}$ calcd.: C, 74.66; H, 9.84; Si, 7.25%.

α -Naphthyl-tricresoxyasilane: m.p. 60°C (pentane). NMR (δ , ppm): 7.6 (19H, m), 2.2 (3H, s), 1.3 (9H, s). Found: C, 78.21; H, 5.80; Si, 6.04. $\text{C}_{31}\text{H}_{28}\text{O}_3\text{Si}$ calcd.: C, 78.15; H, 5.88; Si, 5.88%.

α -Naphthyl-triheptanoxyasilane: b.p. 210°C/0.1 mmHg. NMR (δ , ppm): 7.7 (7H, m), 3.8 (6H, t), 1.4 (39H, m). Found: C, 74.14; H, 10.26; Si, 5.67. $\text{C}_{31}\text{H}_{52}\text{O}_3\text{Si}$ calcd.: C, 74.44; H, 10.40; Si, 5.60%.

Alcoholysis of diphenylsilane. Diphenyl-dicresoxyasilane: m.p. 81°C (pentane). NMR (δ , ppm): 7.3 (10H, m), 6.65 (8H, m), 2.14 (6H, s). Found: C, 78.44; H, 6.18; Si, 7.41. $\text{C}_{26}\text{H}_{24}\text{O}_2\text{Si}$ calcd.: C, 78.78; H, 6.06; Si, 7.07%.

Diphenyl-cresoxyasilane: b.p. 180°C/15 mmHg. NMR (δ , ppm): 7.5 (10H, m), 6.67 (8H, m), 5.65 (1H, s), 2.16 (3H, s). IR (cm^{-1}): $\nu(\text{Si-H})$ 2130. Found: C, 78.49; H, 6.43; Si, 9.85. $\text{C}_{19}\text{H}_{18}\text{OSi}$ calcd.: C, 78.62; H, 6.20; Si, 9.65%.

Diphenyl-heptanoxyasilane: b.p. 190°C/10 mmHg. NMR (δ , ppm): 7.38 (10H, m), 5.35 (1H, s), 3.7 (2H, t), 1.25 (13H, m). IR (cm^{-1}): $\nu(\text{Si-H})$ 2130. Found: C, 76.75; H, 8.79; Si, 9.45. $\text{C}_{19}\text{H}_{26}\text{OSi}$ calcd.: C, 76.50; H, 8.70; Si, 9.40%.

Diphenyl-diheptanoxyasilane: b.p. 207°C/0.7 mmHg. NMR (δ , ppm): 7.4 (10H, m), 3.7 (4H, t), 1.2 (26H, m). Found: C, 75.48; H, 9.95; Si, 6.47. $\text{C}_{26}\text{H}_{36}\text{O}_2\text{Si}$ calcd.: C, 75.80; H, 9.70; Si, 6.80%.

Diphenyl-menthoxyasilane: b.p. 200°C/10 mmHg. NMR (δ , ppm): 7.4 (10H, m), 5.4 (1H, s), 3.5 (1H, m), 0.9 (18H, m). IR (cm^{-1}): $\nu(\text{Si-H})$ 2130. Found: C, 77.60; H, 8.69; Si, 8.82. $\text{C}_{22}\text{H}_{30}\text{OSi}$ calcd.: C, 78.10; H, 8.30; Si, 8.80%.

Diphenyl-dimenthoxyasilane: b.p. 260°C/1 mmHg. NMR (δ , ppm): 7.5 (10H, m), 3.45 (2H, m), 1.3 (38H, m). Found: C, 77.48; H, 9.44; Si, 6.09. $\text{C}_{32}\text{H}_{48}\text{O}_2\text{Si}$ calcd.: C, 77.98; H, 9.82; Si, 5.69%.

Diphenyl-diundecylenoxyasilane: b.p. 190°C/0.5 mmHg. NMR (δ , ppm): 7.33 (10H, m), 5.1 (6H, m), 3.7 (4H, t), 1.42 (32H, m). Found: C, 78.50; H, 9.53; Si, 5.36. $\text{C}_{34}\text{H}_{52}\text{O}_2\text{Si}$ calcd.: C, 78.46; H, 10.00; Si, 5.38%.

Diphenyl-undecylenoxyasilane: b.p. 160°C/1 mmHg. NMR (δ , ppm): 7.4 (10H, m), 5.32 (1H, s), 5 (2H, d), 4.75 (1, m), 3.7 (2H, t), 1.4 (16H, m). IR (cm^{-1}): $\nu(\text{Si-H})$ 2130. Found: C, 80.32; H, 8.18; Si, 7.30. $\text{C}_{23}\text{H}_{32}\text{OSi}$ calcd.: C, 80.41; H, 8.24; Si, 7.21%.

Alcoholysis of phenylmethylsilane. Phenylmethyl-dicresoxyasilane: b.p. 175°C/15 mmHg. NMR (δ , ppm): 7.2 (13H, m), 2.2 (6H, s), 0.5 (3H, s). Found: C, 75.00; H, 6.60; Si, 8.40. $\text{C}_{21}\text{H}_{22}\text{O}_2\text{Si}$ calcd.: C, 74.75; H, 6.54; Si, 8.90%.

Phenylmethyl-diheptanoxyasilane: b.p. 70°C/0.1 mmHg. NMR (δ , ppm): 7.4 (5H, m), 3.6 (4H, t), 1.2 (26H, m), 0.25 (3H, s). Found: C, 71.17; H, 11.17; Si, 8.23. $\text{C}_{21}\text{H}_{38}\text{O}_2\text{Si}$ calcd.: C, 71.02; H, 11.10; Si, 7.74%.

Phenylmethyl-cresoxyasilane: b.p. 130°C/15 mmHg. NMR (δ , ppm): 0.5 (3H, m), 2.3 (3H, s), 7.1 (9H, m). IR (cm^{-1}): $\nu(\text{Si-H})$ 2130. Found: C, 73.63; H, 7.04;

Si, 12.29. $C_{14}H_{16}OSi$ calcd.: C, 73.68; H, 6.60; Si, 12.28%.

Phenylmethyldimethoxysilane: b.p. $160^{\circ}C/15$ mmHg. NMR (δ , ppm): 7.4 (5H, m), 5.1 (1H, s), 3.4 (1H, m), 1.3 (21H, m). IR (cm^{-1}): $\nu(Si-H)$ 2130. Found: C, 74.23; H, 10.37; Si, 10.06. $C_{17}H_{28}OSi$ calcd.: C, 73.9; H, 10.14; Si, 10.14%.

Phenylmethyldimethoxysilane: b.p. $120^{\circ}C/0.1$ mmHg. NMR (δ , ppm): 7.5 (5H, m), 3.5 (2H, m), 1.5 (36H, m), 0.4 (3H). Found: C, 75.02; H, 10.70; Si, 6.74. $C_{27}H_{46}O_2Si$ calcd.: C, 75.34; H, 10.69; Si, 6.50%.

Alcoholysis of α -naphthylphenylsilane. α -Naphthylphenylcresoxysilane: b.p. $195^{\circ}C/0.5$ mmHg. NMR (δ , ppm): 7.3 (16H, m), 6.03 (1H, s), 2.14 (3H, s). IR (cm^{-1}): $\nu(Si-H)$ 2130. Found: C, 80.73; H, 5.92; Si, 7.98. $C_{23}H_{20}OSi$ calcd.: C, 81.18; H, 5.89; Si, 8.24%.

α -Naphthylphenylheptanoxysilane: b.p. $180^{\circ}C/0.3$ mmHg. NMR (δ , ppm): 7.66 (12H, m), 5.63 (1H, s), 3.73 (2H, m), 1.25 (13H, m). IR (cm^{-1}): $\nu(Si-H)$ 2130. Found: C, 79.10; H, 7.97; Si, 8.15. $C_{23}H_{28}OSi$ calcd.: C, 79.31; H, 8.04; Si, 8.04%.

α -Naphthylphenyldicresoxysilane: m.p. $77^{\circ}C$ (pentane). NMR (δ , ppm): 7.4 (20H, m), 2.2 (6H, s). Found: C, 80.32; H, 5.88; Si, 6.46. $C_{20}H_{26}O_2Si$ calcd.: C, 80.71; H, 5.83; Si, 6.28%.

α -Naphthylphenyldiheptanoxysilane: b.p. $205^{\circ}C/0.3$ mmHg. NMR (δ , ppm): 1.4 (26H, m), 3.74 (4H, m), 7.72 (12H, m). Found: C, 77.86; H, 9.15; Si, 6.07. $C_{30}H_{26}O_2Si$ calcd.: C, 77.82; H, 8.90; Si, 6.03%.

α -Naphthylphenyldimethoxysilane: b.p. $195^{\circ}C/0.04$ mmHg. NMR (δ , ppm): 7.6 (12H, m), 3.5 (2H, m), 1.5 (36H, m). Found: C, 78.99; H, 9.03; Si, 5.19. $C_{36}H_{50}O_2Si$ calcd.: C, 79.7; H, 9.22; Si, 5.16%.

α -Naphthylphenyldiallyloxysilane: b.p. $193^{\circ}C/2$ mmHg. NMR (δ , ppm): 7.65 (12H, m), 5.8 (2H, m), 5.1 (4H, m), 4.25 (4H, d). Found: C, 76.11; H, 6.17; Si, 8.55. $C_{22}H_{22}O_2Si$ calcd.: C, 76.30; H, 6.35; Si, 8.09%.

Alcoholysis of dipentylsilane. Dipentyldicresoxysilane: b.p. $102^{\circ}C/0.1$ mmHg. NMR (δ , ppm): 7 (8H, m), 2.4 (6H, s), 1.1 (22H, m). Found: C, 75.37; H, 9.64; Si, 7.38. $C_{24}H_{36}O_2Si$ calcd.: C, 75.00; H, 9.37; Si, 7.29%.

Dipentylmethoxysilane: b.p. $70^{\circ}C/0.1$ mmHg. NMR (δ , ppm): 4.58 (1H, s), 3.5 (1H, m), 1.18 (40H, m). IR (cm^{-1}): $\nu(Si-H)$ 2130 cm^{-1} . Found: C, 73.45; H, 12.82; Si, 8.79. $C_{20}H_{42}OSi$ calcd.: C, 73.61; H, 12.88; Si, 8.58%.

Dipentyldiheptanoxysilane: b.p. $90^{\circ}C/0.1$ mmHg. NMR (δ , ppm): 3.6 (4H, m), 1.1 (48H, m). Found: C, 71.52; H, 13.47; Si, 6.80. $C_{24}H_{52}O_2Si$ calcd.: C, 72.00; H, 13.00; Si, 7.00%.

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