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Journal of Organometallic Chemistry 521 (1995) 229–234

Journal of Organometallic Chemistry

Oxidation of sterically hindered organosilicon hydrides using potassium permanganate [1]

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Received 1 November 1995

Abstract

The one-pot synthesis of Ph_3SiOH, $^tBu_2Si(OH)_2$, $(Me_3Si)_3CSi(OH)_3$ and $(Me_3Si)_3CSiMe_2OH$ directly from the corresponding bulky silicon hydrides using $KMnO_4$ is described. The size of the substituents, the silane : $KMnO_4$ stoichiometry, the solvent and the application of ultrasound were all shown to influence the rate of the reactions.

Keywords: Silanes; Silicon hydrides; Oxidation; Permanganate; Ultrasound

1. Introduction

The synthesis of bulky silanols such as $^tBu_2Si(OH)_2$, $TsiSi(OH)_3$ [Tsi = $(Me_3Si)_3C$], $TsiSiMe_2OH$ or $TsiSiPh_2OH$ requires either long reaction times in aqueous solutions or multiple stage reactions [1]. The most common precursors to the majority of silanols are the chlorosilanes [2]. The smaller chlorosilanes, e.g. Me_3SiCl, are readily hydrolysed, but this is not the case for sterically hindered chlorosilanes in which attack at the reactive centre is inhibited by bulky substituents. Although $KMnO_4$ has been shown to be a good oxidising agent in organic chemistry, the direct synthesis of silanols from the corresponding silicon hydrides using this reagent (Eq. (1)) has received relatively little attention, the only previously reported examples being those of the oxidation of $TsiSiEt_2H$ to $TsiSiEt_2OH$ and of $(Me_3Si)_2C(SiMe_2H)(SiMe_2CH{=}CH_2)$ to $(Me_3Si)_2C(SiMe_2OH)(SiMe_2CH{=}CH_2)$ [3,4]. It was therefore decided to investigate the potential of $KMnO_4$ and to look at the influence of the solvent (THF or methanol), the size of the substituents, and the silane : salt stoichiometry in the synthesis of silanols.

$$R_xSiH_{4-x} + KMnO_4 \rightarrow R_xSi(OH)_{4-x} + MnO_2 \qquad (1)$$

$x = 1, 2$ or 3

The solubilization of $KMnO_4$ in organic solvents can be achieved by crown-ethers [5,6] or by phase-transfer agents, such as quaternary ammonium salts that form quaternary permanganates soluble in solvents immiscible with water [7] (e.g. purple benzene) [8]. Ultrasonic power is increasingly being used in a variety of heterogeneous systems [9], where it can increase reaction rates and allow the use of phase-transfer agents (which may contaminate products) to be avoided. Ando and Kimura [8] have studied the influence of ultrasound on the oxidation of various organic substrates by $KMnO_4$ in hydrocarbon solvents, and found the reactions to be generally accelerated by ultrasound. Such increases in the rates of reaction were thought to be due to ultrasonic destruction of the crystal lattice of the $KMnO_4$, which both increases the surface area and the number of active sites on it. This paper describes the successful synthesis of Ph_3SiOH, $^tBu_2Si(OH)_2$, $TsiSi(OH)_3$ and $TsiSiMe_2(OH)$ using $KMnO_4$, together with the attempted synthesis of $TsiSiPh_2OH$ and $[(HO)Me_2Si]_4Si$. The results are summarised in Table 1.

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[1] Dedicated to Professor R.J.P. Corriu in recognition of his outstanding contributions to organosilicon chemistry.

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PII S0022-328X(95)06068-5

2. Results and discussion

2.1. Ph_3SiOH

When a mixture of Ph_3SiH and $KMnO_4$ was stirred at room temperature in THF for 22 h the colour of the reaction mixture went gradually from colourless to pale purple then to brown. After removal of the solids by filtration using silica-gel, and removal of THF from the filtrate under vacuum, a white solid identified as Ph_3SiOH (88%) was isolated. When the cleaning bath or the probe were used to accelerate the oxidation process, the formation of the violet and brown solutions was much more rapid than with stirring. The sonication was terminated after complete disappearance of the Si–H resonance in the ^1H NMR spectrum, giving isolated yields of 66 and 92% respectively in 4 and 1 h for the cleaning bath and the probe. This corresponds to an approximate 22-fold rate of increase when using the probe with respect to the silent reaction. The rate accel-

Table 1
Oxidation of bulky silanes using $KMnO_4$

Starting material	Method [a]	Solvent and reagent ratio	Time (h)	Product	Yield (%)
Ph_3SiH	stirring	THF 1.05 $KMnO_4$	22	Ph_3SiOH	88 [b]
	c.b.	THF 1.05 $KMnO_4$	4	Ph_3SiOH	66 [b]
	probe	THF 1.05 $KMnO_4$	1	Ph_3SiOH	92 [b]
$^tBu_2SiH_2$	stirring	THF 2.12 $KMnO_4$	23	$^tBu_2Si(OH)_2$	51 [c]
				$+^tBu_2Si(OH)H$	3 [c]
	stirring	MeOH 2.12 $KMnO_4$	23	$^tBu_2Si(OH)_2$	40 [c]
				$+^tBu_2Si(OH)H$	6 [c]
	c.b.	THF 2.12 $KMnO_4$	10	$^tBu_2Si(OH)_2$	42 [c]
				$+^tBu_2Si(OH)H$	5 [c]
	probe	THF 2.12 $KMnO_4$	5	$^tBu_2Si(OH)_2$	72 [c]
				$+^tBu_2Si(OH)H$	2 [c]
$TsiSiH_3$	stirring	THF 3.15 $KMnO_4$	1	$TsiSi(OH)_3$	83 [b]
	stirring	MeOH 3.15 $KMnO_4$	0.75	$TsiSi(OH)_3$	90 [c]
				$+TsiSiH_2OH$	10 [c]
		MeOH 3.65 $KMnO_4$	0.75	$TsiSi(OH)_3$	77 [b]
	stirring	MeOH 1.0 $KMnO_4$	0.75	$TsiSiH_3$	27.2 [c]
				$+TsiSiH_2OH$	18 [c]
				+TsiH	44 [c]
				+unknown	11 [c]
	stirring	MeOH 2.0 $KMnO_4$	0.75	$TsiSiH_2OH$	20 [c]
				+TsiH	28 [c]
				+unknown	52 [c]
	stirring	THF 1.0 $KMnO_4$	24	$TsiSiH_2OH$	5 [c]
	probe	THF 1.5 $KMnO_4$	1	$TsiSi(OH)_3$	28 [c]
				$TsiSiH_3$	41
				$TsiSiH_2OH$	31 [c]
		+1.0 $KMnO_4$	1	$TsiSi(OH)_3$	62 [c]
				$+TsiSiH_2OH$	37 [c]
				$+TsiSiH_3$	trace
				+TsiH	trace
		+1.0 $KMnO_4$	5 min	$TsiSi(OH)_3$	86 [c]
				+TsiH	14 [c]
$TsiSiMe_2H$	stirring	THF 1.20 $KMnO_4$	6	$TsiSiMe_2OH$	84 [b]
	stirring	MeOH 1.20 $KMnO_4$	6	$TsiSiMe_2OH$	54 [c]
	c.b.	THF 1.20 $KMnO_4$	1.5	$TsiSiMe_2OH$	82 [b]
	c.b.	MeOH 1.20 $KMnO_4$	1.5	$TsiSiMe_2OH$	63 [c]
	probe	MeOH 1.20 $KMnO_4$	0.5	$TsiSiMe_2OH$	92 [b]
$TsiSiPh_2H$	probe	THF 1.05 $KMnO_4$	2	—	
		MeOH 1.05 $KMnO_4$	4	—	
$(HMe_2Si)_4Si$	probe	THF 4.25 $KMnO_4$	2	siloxanes	

[a] Stirring at room temperature, cleaning bath (c.b.): 20 ± 2°C in the reactor, probe: 20 ± 3°C in the reactor
[b] Isolated yield.
[c] Yield determined by ^1H NMR spectroscopy or by GC.

eration is most likely due to better solubilization of $KMnO_4$ in sonicated THF, and improved mass transport to and from the solid surface in the heterogeneous system.

2.2. $^tBu_2Si(OH)_2$

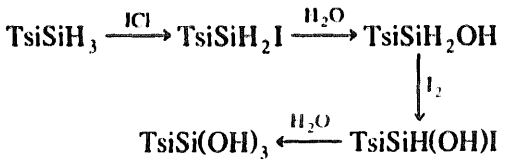
After stirring $^tBu_2SiH_2$ and $KMnO_4$ for 23 h in THF, the products were identified by GC/GC-MS and ^1H NMR spectroscopy as $^tBu_2Si(OH)_2$ (51%) and $^tBu_2SiH(OH)$ (3%). The same reaction in MeOH for 23 h at room temperature gave $^tBu_2Si(OH)_2$ (40%) with $^tBu_2SiH(OH)$ (6%). A net acceleration is achieved when using the cleaning bath and THF, as only 10 h is needed to obtain a similar yield; use of the probe increased the yield further (see Table 1). The improvement due to the probe corresponds to an approximate six-fold rate of increase with respect to the silent reaction, and gave a 72% yield in 5 h at room temperature. A previous preparation of $^tBu_2Si(OH)_2$ by hydrolysis of the fluoride $^tBu_2SiF_2$ required 20 h under reflux in 1/1 (v/v) Me_2SO/H_2O and gave only a 16% yield [10].

2.3. $TsiSi(OH)_3$

Silane triols are usually only stable if prepared under critically controlled conditions and if the organic group is relatively large [10]. Phenylsilane triol (m.p. 128–130°C) results from the hydrolysis of $PhSi(OMe)_3$, it dehydrates readily to cross-linked polysiloxanes and ultimately to the three-dimensional polymer $(PhSiO_{1.5})_n$ [11]. The very bulky ligand $(Me_3Si)_3C$ allows a stable silanetriol $TsiSi(OH)_3$ (m.p. 285–290°C) to be prepared by the route shown in Scheme 1 [1]. It was therefore of interest, to see if oxidation with $KMnO_4$ would give a direct route from $TsiSiH_3$ to $TsiSi(OH)_3$, to investigate potential rearrangements involving 1,3-migrations of silyl groups from C to O [12] in the presence of $KMnO_4$ and to check the influence of the quantity of oxidising agent used on the reaction rate.

(i) When $TsiSiH_3$ and 3 mol equivalents of $KMnO_4$ were stirred in THF, the solution became immediately pale yellow and gradually darkened. The absence of a violet colour suggested that the solubilized salt reacts immediately with the silane. The stirring was stopped after 1 h and 83% $TsiSi(OH)_3$ was isolated.

(ii) It has been shown that rearrangements involving 1,3-migrations of silyl groups from C to O, e.g. $(Me_3Si)_2C(SiMe_3)(SiR_2OH) \rightarrow (Me_3Si)_2CH(SiR_2OSiMe_3)$,



Scheme 1.

(R = Me or Ph) can occur on treatment of suitable silanols with base [12]. The influence of the solvent on the reaction was therefore investigated because of possible MeOK formation when using methanol. The course of the reaction between $TsiSiH_3$ and ca. 3 equivalents of $KMnO_4$ in methanol was monitored by ^1H NMR spectroscopy and no further change was detected after 45 min. Integration of the singlets corresponding to the protons of the Tsi groups in $TsiSi(OH)_3$ (0.240 ppm) and $TsiSi(OH)H_2$ (0.207 ppm) gave a 9/1 ratio. Although a slight excess of salt had been used (5%), the oxidation appeared to be incomplete, probably due to consumption of $KMnO_4$ by the solvent. In a second experiment a 20% excess of $KMnO_4$ was used and, after stirring (45 min) and work-up, silanetriol was isolated (77%) and characterised by MS(CI), suggesting that there is a competition between oxidation of the solvent and oxidation of the silane. In neither THF nor methanol was any rearrangement product detected.

(iii) The last investigation of the oxidation of $TsiSiH_3$ by $KMnO_4$ was on the influence of the $KMnO_4$: silane stoichiometry and the possibility of forming $TsiSiH_2(OH)$ only. The stirred reaction carried out in THF at room temperature with 1.0 equivalent of $KMnO_4$ gave back the starting material with only less than 5% $TsiSiH_2(OH)$ after 24 h. When the ultrasonic probe was used under the same conditions during 1 h at 25°C and using 1.5 equivalents of $KMnO_4$, three singlets due to the Me_3Si protons in $TsiSiH_3$ (0.165 ppm), $TsiSiH_2(OH)$ (0.207 ppm) and $TsiSi(OH)_3$ (0.240 ppm) were visible by ^1H NMR spectroscopy in a ratio of 1 : 0.75 : 0.70 respectively. A further addition of 1 equivalent of $KMnO_4$ (total 2.5 equivalents) to the reaction mixture, followed by another 5 min of sonication, gave a ratio of 0.1 : 3 : 5 for the same compounds. At this point a very small peak showed the presence of TsiH. Addition of a further molar equivalent of oxidising agent (total 3.5 equivalents) resulted in the complete disappearance of the starting material and formation of $TsiSi(OH)_3$ (86%) plus TsiH (14%). No by-products due to intramolecular rearrangements were detected.

When the solvent was changed to methanol, stirring of $TsiSiH_3$ with 1.0 equivalent of $KMnO_4$ gave a brown colouration immediately. The reaction mixture, worked-up after 45 min, gave an oil which ^1H NMR spectroscopy and GC/GC-MS analysis showed to be a mixture of compounds (Eq. (2) and see Table 1). Two singlets at 0.376 and 0.330 ppm in the ^1H NMR spectrum could not be identified but might correspond to rearranged products containing $Si-O-SiMe_3$ groups

$$TsiSiH_3 + 1\ KMnO_4 \xrightarrow{MeOH} TsiSiH_3 + TsiSiH_2OH + TsiH + \text{unknown} \quad (2)$$

TsiH has often been found as a cleavage product of reactions between $TsiSiX_3$ compounds and a base, and

$TsiSiH_3$ has previously been found to break down on treatment with 1.5 M NaOMe in MeOH at 50°C for 3 days to give five main products, one of them being TsiH [1]. The formation of TsiH from reactions of Tsi–Si compounds is probably due to an initial nucleophilic attack at the silicon centre, followed by expulsion of the Tsi^- anion, which then acquires a proton from the solvent [13].

2.4. $TsiSiMe_2OH$

$TsiSiMe_2OH$ has been studied in detail by Eaborn and coworkers [12] and it can be prepared by the reaction of $TsiSiMe_2I$ with an H_2O/dioxane mixture at reflux for 16 h [1]. In a similar way to $TsiSiH_2(OH)$, $TsiSiMe_2OH$ is also prone to intramolecular rearrangements (Eq. (3)) and cleavage reactions (Eq. (4)) [14]

$$TsiSiMe_2OH + K \xrightarrow{C_6H_6} (Me_3Si)_2CHSiMe_2OSiMe_3 \quad (3)$$

$$TsiSiMe_2OH + NaOMe \xrightarrow{MeOH} (Me_3Si)_2CHSiMe_2OMe \quad (4)$$

(i) When THF was used as solvent, the stirred solution first went pink–violet and after 5 min turned brown. The course of the reaction, monitored by ^1H NMR spectroscopy, showed the complete disappearance of the starting material after 6 h. The silanol was isolated as a white solid (84%). When using the cleaning bath, at around 25°C and during 1.5 h, 82% $TsiSiMe_2OH$ was isolated.

(ii) Using methanol with 20% excess $KMnO_4$ resulted in an incomplete reaction. After 4.5 h the oxidation stopped and $TsiSiMe_2OH$ (54%) plus $TsiSiMe_2H$ (46%) were detected by ^1H NMR spectroscopy. It is likely that the slower rate of oxidation of $TsiSiMe_2H$, due to an increase in steric hindrance at silicon, results in more $KMnO_4$ being consumed by the solvent. Sonication improved the results, as the cleaning bath at around 20°C and during 1.5 h gave 67% $TsiSiMe_2OH$ and 33% starting material. Under the same conditions using the probe, all the starting material was consumed in 0.5 h giving 92% of the silanol. When the course of the reaction in methanol was monitored by GC analysis to check more carefully for the presence of rearranged silanols, 11% of the rearranged $(Me_3Si)_2CHSiMe_2(OSiMe_3)$ was identified by GC/GC-MS from the neat reaction mixture. Surprisingly, after filtration and isolation of the product, the ^1H NMR spectrum and the GC trace showed only the presence of $TsiSiMe_2OH$. It is possible that the intramolecular rearrangement occurred in the oven of the GC instrument, which is heated at 300°C, in the presence of KOH or KOMe when samples are taken from the neat reaction mixture. The proportion of rearranged product increased on the GC trace when the concentration of reactants was doubled, which suggests that the rearrangement process is linked with the concentration of the base [13]. Again, after work-up of the more concentrated reaction solution, the silanol was isolated pure. This is also consistent with a thermolytic rearrangement occurring in the GC oven, possibly by the mechanism known to occur in solution [12].

2.5. $TsiSiPh_2(OH)$

$TsiSiPh_2(OH)$ can be synthesised in 60 days by hydrolysis of $TsiSiPh_2I$ in H_2O–MeCN (5 vol.%) under reflux, or 24 h in H_2O–Me_2SO under reflux [3]. As the oxidation was expected to be more difficult than for $TsiSiMe_2H$, because of a greater steric hindrance at silicon, only the most efficient method, i.e. the probe, was used. When the sonication was carried out in methanol for 4 h or in THF for 2 h, with the temperature inside the reaction vessel at around 25°C, ^1H NMR spectroscopy showed that only the starting material was present, neither silanol nor TsiH was detected. It would thus seem that $KMnO_4$ is an unsuitable oxidising agent, even under the influence of ultrasound, for the most hindered silanes.

2.6. $[(HO)Me_2Si]_4Si$

Tetrakis(dimethylsilyl)silane is a low melting solid (m.p. 40–42°C) with four very reactive Si–H bonds [15]. It is readily oxidised and tends to form polysiloxanes if not stored under an inert atmosphere. The tetrasilanol $[(HO)Me_2Si]_4Si$ is unknown, and the attempted oxidation of $(HMe_2Si)_4Si$ was carried out in THF with the probe on power level 7 for 2 h at 25°C. The reaction mixture was then filtered and the solvent removed under vacuum, yielding an oil instead of the expected solid. ^1H NMR spectroscopy showed that the septet and doublet resonances due to the starting material had disappeared, giving place to two sets of broad resonances in the 0.0–0.5 ppm region. IR spectroscopy showed a broad absorption between 1030 and 1120 cm^{-1}, typical of a siloxane linkage. Given the complicated product obtained, probably a mixture of siloxanes formed by a base-catalysed rearrangements, the reaction was not repeated. The carbon centred analogue $(HOMe_2Si)_4C$ is known to be both temperature and base sensitive, and it is likely that the silicon centred compound is even more sensitive to rearrangements [16].

3. Conclusions

Sterically hindered silanols containing ^tBu, Ph or $(Me_3Si)_3C$ groups can be readily synthesised directly from the corresponding silicon hydrides and $KMnO_4$. The rate of oxidation is generally accelerated by ultrasound, but the efficiency of the method depends on various factors: cleaner reactions occur in THF as $KMnO_4$ is partially consumed by reaction with the

solvent in methanol when the reaction is slow, no oxidation occurs when steric hindrance is too great as in $(Me_3Si)_3CSiPh_2H$, and side reactions can take place when the product is sensitive to base-catalysed rearrangements.

4. Experimental section

The ^1H and ^{29}Si NMR spectra were recorded at 90 and 17.9 MHz respectively on a JEOL EX-90 FT-NMR spectrometer, chemical shifts are in parts per million relative to TMS. The IR spectra were recorded on a Perkin-Elmer 1710 FT-IR spectrometer, using Nujol mulls between KBr plates. Analyses by gas liquid chromatography were recorded on a Perkin-Elmer 8320 capillary GC instrument with a flame ionisation detector having a 25 m non-polar BP1 column. Mass spectra were obtained by chemical ionisation (CI, NH_3) or electron impact (EI) at 70 eV on a Finnigan 4500 quadrupole mass spectrometer. For analysis by linked GLC–mass spectrometry, a Varian GC 3400 gas chromatograph with a 25 m BP1 non-polar column was used.

All reactions involving a bath were carried out in a rectangular Pulsatron 125H ultrasonic cleaner from Kerry Ultrasonics, using a frequency of 38 ± 10 kHz. All reactions in the bath were carried out in round-bottomed flasks or Schlenk tubes, and the reaction vessel was placed in the position of maximum intensity (or agitation in the reaction vessel), which was generally found to be between the two transducers in the centre of the cleaning tank. Temperature control for reactions in the bath was achieved by periodic changing of the water, giving the following temperature accuracy: $T \pm 3°C$. In all cases the water level was kept between 2 and 4 cm below the top level of the tank, depending on the activity visible in the reaction vessel.

A Sonic and Materials VC 300 sonifier consisting of a 20 kHz ultrasound generator with a variable power output up to 300 W was used to drive a converter, kept in a sound-proof box (all reactions were carried out in the dark) with a lead zirconate titanate transducer. A stepped horn plus tip, 14 cm long with a 12 mm diameter at the radiating surface, was used. The horn was equipped with a joint to allow sonication in glass vessels in an inert atmosphere. A Suslick cell (15 ml) was used for all reactions using the probe, and temperature control was carried out by immersing the reaction vessel, fitted to the probe, partially into a coolant. The inside of the sonicated vessel was generally found to be between 20 and 25°C.

Tetrahydrofuran was heated under reflux with sodium wire and benzophenone until a deep purple colouration was obtained, and it was freshly distilled before use. Anhydrous methanol was obtained from the Aldrich Chemical Company and was used as received.

4.1. Starting materials

$TsiSiH_3$ [1], $TsiSiMe_2H$ [12], $TsiSiPh_2H$ [3] and $(HMe_2Si)_4Si$ [15] were synthesised according to the literature methods, $^tBu_2SiH_2$ was generously donated by FMC Ltd., Lithium Division.

4.2. Silent reactions at room temperature

The silane (0.40 mmol) and $KMnO_4$ (0.42 mmol) were charged in a 25 ml round-bottomed flask equipped with a magnetic stirrer bar under a stream of nitrogen followed by the solvent (7.5 ml). The heterogeneous reaction mixture was stirred, and the course of the reaction monitored by ^1H NMR and IR spectroscopy or by GC analysis. The reaction mixture was then removed from the bath and the solids were removed by filtration using a 2 cm layer of silica gel followed by washing with THF or MeOH (20 ml). The solvent was then removed from the combined filtrates under vacuum to yield the desired silanol.

4.3. Reactions using the cleaning bath

The silane (0.40 mmol) and $KMnO_4$ (0.42 mmol) were charged in a 25 ml round-bottomed flask under a stream of nitrogen followed by the solvent (7.5 ml). The flask was then positioned in a cleaning bath at 20°C for best agitation and the sonication started. The course of the reaction was monitored by ^1H NMR and IR spectroscopy or by GC analysis. The reaction flask was then removed from the bath and the silanol isolated as above for the stirred reactions.

4.4. Reactions using the probe

To a 15 ml reactor under nitrogen, charged with $KMnO_4$ (0.85 mmol) and silane (0.8 mmol) and fitted to the probe, was added the solvent (15 ml). The reaction mixture was cooled by an ice/water slush bath and sonication started on power setting 7. The course of the reaction was monitored by ^1H NMR spectroscopy and stopped upon complete disappearance of the silane. The reaction vessel was then removed from the probe and the silanol isolated as described above.

4.5. Product identification

The following data were used to identify the products in the various reactions.

Ph_3SiOH: δ(H) ($CDCl_3$) 2.48 (s, 1 H, SiOH), 7.36–7.70 (br, 15 H, Ph) m.p. 152–153°C (lit. 152–153°C [17]).

$^tBu_2Si(OH)_2$: δ(H) [$(CD_3)_2SO$] 0.99 (s, 18 H, ^tBu), 5.58 (s, 2 H, SiOH), m/z (E/I) 176 (3, $[M]^+$), 119 (14, $[M-Bu]^+$), 77 (100), 57 (8, $[Bu]^+$), 56 (11, $[C_4H_8]^+$).

$^tBu_2SiH(OH)$: δ(H) [$(CD_3)_2SO$] 0.97 (s, 18 H, ^tBu), SiH and SiOH not observed, m/z (E/I) 160 (5, $[M]^+$),

103 (15, $[M-Bu]^+$), 102 (14, $[M-Bu-H]^+$), 75 (100), 61 (60), 57 (29, $[Bu]^+$).

TsiSi(OH)$_3$: δ(H) ($CDCl_3$) 0.24 (s, 27 H, $SiMe_3$), 4.30 (s, 3 H, SiOH), *m/z* (CI) 328 (100, $[M + NH_3 + H]^+$), 295 (15, $[M-Me]^+$), 277 (10, $[M-Me-H_2O]^+$), ν_{SiO-H} 3381 cm^{-1} (br), m.p. 280–282°C (lit. 285–290°C [1]).

TsiSiH$_2$OH: δ(H) ($CDCl_3$) 0.207 (s, 27 H, $SiMe_3$), 4.55 (s, 2 H, SiH), *m/z* (EI) 277 (44, $[M-H]^+$), 217(5), 187 (25, $[M-SiMe_3-H_2O]^+$), 73 (100, $[SiMe_3]^+$).

TsiH: δ(H) ($CDCl_3$) 0.08 (s, 27 H, $SiMe_3$), −0.8 (s, 1 H, C–H), *m/z* (EI) 217 (45, $[M-Me]^+$), 114 (85) $[M-SiMe_3-3Me]^+$), 73 (100, $[SiMe_3]^+$).

TsiSiMe$_2$OH: δ(H) ($CDCl_3$) 0.236 (s, 27 H, $SiMe_3$), 0.322 (s, 6 H, $SiMe_2$), OH resonance not observed, *m/z* (CI) 291 (34, $[M-Me]^+$), 275 (44, $[M-2Me-H]^+$), 73 (100, $[SiMe_3]^+$), ν_{SiO-H} 3691 cm^{-1}, m.p. 322–324°C (lit. 325°C [1]).

Acknowledgements

We wish to thank the University of Salford Research Fund for financial support (to R.L.) and Dr. F. Reed (FMC Ltd., Lithium Division) for useful discussions.

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