Simple, low-cost synthetic route to potentially polymerizable silatranes

Hengqin Cheng and Richard M. Laine

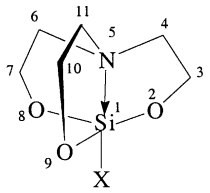
Departments of Chemistry, Materials Science and Engineering, and the Macromolecular Science and Engineering Center, University of Michigan, Ann Arbor, MI 48109-2136, USA

Received 22nd June 1999, Accepted 18th October 1999

Silatrane glycol, **2**, can be synthesized in kilogram quantities in one step from silica. Compound **2** is unusual for a silicon alkoxy compound as it is water soluble and water stable. Silatrane glycol **2** can be reacted with acetic anhydride to produce 1-acetoxysilatrane, **4**. Compound **4** undergoes facile ligand exchange allowing the synthesis of a number of reactive compounds including: 1-methacryloxysilatrane **5**, 1-allyloxysilatrane **6** and 2-[(propen-2-yloxy)ethanoxy]silatrane **7** all of which are potentially useful for producing silatrane-containing polymers.

Introduction

Silatranes (5-aza-2,8,9-trioxa-1-silabicyclo[3.3.3]undecanes) are a unique class of silicon-containing compounds with the general structure shown in **1** below. The structural features include a tricyclic ring and a dative Si–N bond. Thus, silatranes are neutral compounds that contain a pentacoordinate, trigonal bipyramidal silicon.



1

Silatrane compounds have received extensive attention because of their novel structures[1] and biological/pharmacological properties[2,3] (*e.g.* antitumor effects,[4–6] hypocholesterolemic effects,[7,8] and hair and fur growth stimulation[9,10]). Their effects on wound healing and hair growth have led to new medicines and medical treatments in the clinical trial phase in Russia.[11] Silatrane toxicity has also been examined[12] and a novel silatrane containing rodenticide [1-(*p*-chlorophenyl)silatrane] has been commercialized.[13] Because of these interests, considerable research on the syntheses[14–18] and characterization[19–27] of this class of compounds has been carried out.

Silatrane compounds were first synthesized by Frye in 1961.[28] The general synthetic approaches to silatranes are illustrated in reactions (1)–(5):

$$XSi(OC_2H_5)_3 + N(CH_2CH_2OH)_3 \rightarrow N(CH_2CH_2O)_3SiX + 3C_2H_5OH \quad (1)^{29}$$

$$Si(OR)_4 + N(CH_2CH_2OH)_3 + R'OH \xrightarrow[\text{distillation}]{\text{MOH (cat.)}} N(CH_2CH_2O)_3SiOR' + 4ROH \quad (2)^{29}$$

$$1/n[RSiO_{1.5-m}(OH)_{2m}]_n + N(CH_2CH_2OH)_3 \xrightarrow[\text{distillation}]{\text{KOH (cat.)}} N(CH_2CH_2O)_3SiR + (1.5+m)H_2O \quad (3)^{30}$$

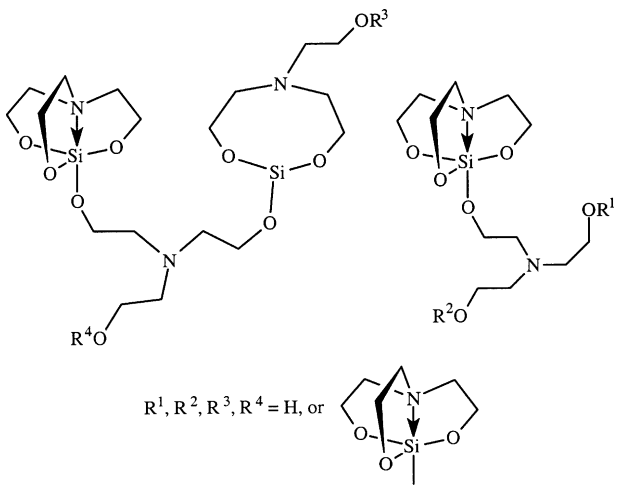
$$1/n(RSiO_{1.5})_n + N(CH_2CH_2OH)_3 \xrightarrow[\text{heat}]{\text{KOH (cat.)}} N(CH_2CH_2O)_3SiR + 1.5H_2O \quad (4)^{31}$$

$$N(OCH_2CH_2)_3SiOR + R'OH \rightleftharpoons N(OCH_2CH_2)_3SiOR' + ROH\uparrow \quad (5)^{31}$$

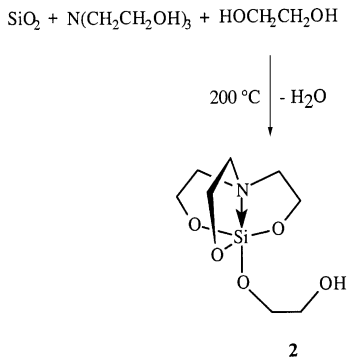
It has been suggested[31] that ligand exchange reactions [*i.e.* reaction(5)] form equilibria that can be driven to completion *only* by removing the exchanged alcohol. Thus it is preferable that the R′OH boiling point be higher than that of ROH so that the reaction can be driven by simple distillation.

In addition to the above methods, the direct synthesis of silatranes from SiO_2 has also been explored. In a brief 1971 report,[29] Frye described the reaction of silica with neat triethanolamine [reaction (6)] to produce oligomeric "triethanolamine silicate, which may be represented by the somewhat idealized structure, $(HOCH_2CH_2)_nN$-$[CH_2CH_2OSi(OCH_2CH_2)_3N]_{3-n}$".[29]

$$(3-n)SiO_2 + N(CH_2CH_2OH)_3 \text{ (excess)} \rightarrow (HOCH_2CH_2)_nN[CH_2CH_2OSi(OCH_2CH_2)_3N]_{3-n} + 2(3-n)H_2O \quad (6)$$



In addition to Frye's work, we recently reported the synthesis of silatrane glycol from silica in one step:[32]



(7)

2

Our goal in this work was to develop low cost routes to processable ceramic precursors. We were able to demonstrate that silatrane glycol can be used to formulate precursors to mullite ($3Al_2O_3 \cdot 2SiO_2$), cordierite ($2MgO \cdot 5SiO_2 \cdot 2Al_2O_3$),[33] barium aluminosilicate ($BaO \cdot 2SiO_2 \cdot Al_2O_3$), strontium aluminosilicate ($SrO \cdot 2SiO_2 \cdot Al_2O_3$),[34] and porous silicon oxynitride particles.[35]

The discovery of a facile route to silatrane glycol prompted us to further explore the utility of silatranes for other materials applications. Silatrane precursors offer numerous advantages compared with other silicon alkoxides because of their relatively high environmental stability (see below) which makes them easy to process. Because silatranes have well-defined structures and their physical and chemical properties can be controlled by simply varying the **1** – X substituents, new derivatives with diverse applications may be accessible. Specifically, besides their utility in formulating ceramic precursors, we are also interested in making silatrane-containing polymers. These polymers have potential application as flame resistant materials for aircraft interiors. To make such polymers, we need to make polymerizable silatrane monomers. We believe this can be achieved by introducing polymerizable **1** – X substituents into silatranes. To be attractive for industrial applications, the synthetic route must be simple and low-cost. Here we describe a novel, low-cost synthetic route to polymerizable silatrane monomers.

Results and discussion

Synthesis of silatrane glycol 2

As noted above, we have discovered that various forms of silica (SiO_2) will react with equivalent amounts of triethanolamine ($TEAH_3$) in ethylene glycol (EGH_2) as per reaction (7) to form silatrane glycol **2** quantitatively. We recently determined that this reaction could be easily scaled to kilogram quantities (using 1 kg SiO_2 in a 12 L reactor).

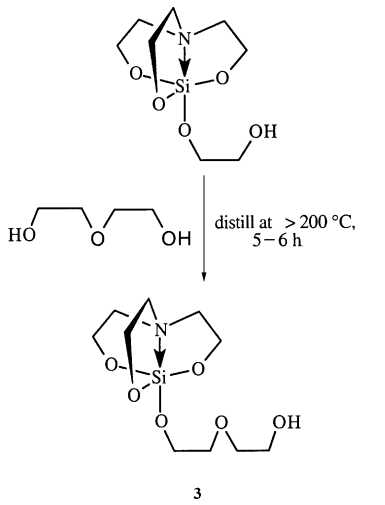
As part of these scale-up studies, we found that **2** is soluble and stable in neutral water at room temperature for periods of up to one week, this contrasts with our initial assessment that **2** was water sensitive. (It is likely that trace amounts of $TEAH_3$ catalyze hydrolysis.) Furthermore, aqueous solutions of **2** survive brief boiling (10–20 min) in air. However, **2** has a relatively low solubility in water, ≈ 50 mg ml^{-1}.

Resistance to hydrolysis likely arises because the transannular Si–N bond creates a penta-coordinate silicon which, when coupled with the protection offered by the bulky tricyclic ring, reduces the potential for attack at Si by hydroxide/water to form the intermediates necessary for hydrolysis. The water solubility may be attributed to the potential of the TEA oxygens and the glycol hydroxyl to form hydrogen bonds with water.

Reaction (7) makes it possible to synthesize silatrane directly from silica in one step. If the ethylene glycol ligand can be exchanged easily with other ligands, this may offer a novel, simple and low-cost route to other silatranes. Thus, this synthetic possibility was explored.

Reactions of 2 with alcohols

Reaction of **2** with diethylene glycol ($diegH_2$) as per reaction (8) gives an oily mixture which contains the desired product, **3**.



(8)

3

However, diethylene glycol's very high boiling point (bp, 279 °C) makes it difficult to fully purify the product and further work on this route ceased. Note that because these reactions are conducted in a large excess of the exchanging diol, we do not see the formation of dimeric compounds.

Similarly, reaction of **2** with glycerol was also examined. Analysis of the reaction mixture indicated the presence of the desired product. However, attempts to isolate the product were again not successful, partly because of glycerol's very high boiling point and partly due to the formation of oligomeric products.

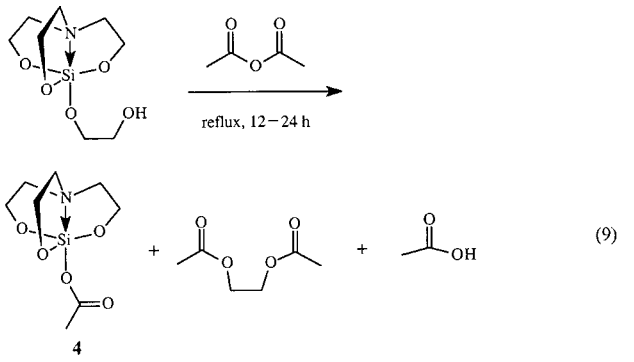
Reaction of **2** with allyl alcohol (allyl-OH, bp 97 °C) and 2-(propen-2-yloxy)ethanol (AllylEGH, bp 158 °C) gave only limited exchange. The reaction mixtures were refluxed at the boiling point of the corresponding alcohols. Because both alcohols have lower boiling points than ethylene glycol, the ethylene glycol byproduct does not distill out in either reaction. Thus, no driving force is available to effect completion.

Ligand exchange reactions of **2** with alcohols that have higher boiling points than EGH_2 appear to work but this approach suffers from purification problems. In contrast, reactions with alcohols that have lower boiling points do not go to completion. These results appear to confirm the general observations of other researchers, that silatrane **1** – X ligand exchanges reach equilibrium states that can only be driven to completion by removal of the exchanged ligand. Because the boiling point of ethylene glycol is high, we sought to drive the equilibrium by methods other than distillation.

Reaction of 2 with acetic anhydride

We now find that **2** will react with acetic anhydride under reflux to produce 1-acetoxysilatrane [**4**, reaction (9)]. This

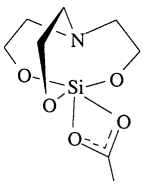
reaction can be followed visually and is judged to be complete when all of the solid **2** dissolves. Vacuum removal of the reaction solvent and byproducts, followed by washing with THF provides a white solid. In most cases, the product is analytically pure but can be recrystallized from dichloromethane–heptane. Spectroscopic studies show that the compound is the desired product, **4**. Likewise, both GC-MS and NMR analyses of the reaction solutions reveal the presence of ethlene glycol diacetate ($CH_3COOCH_2CH_2OCOCH_3$). The formation of the diacetate blocks the reverse reaction, thereby driving formation of **4**.



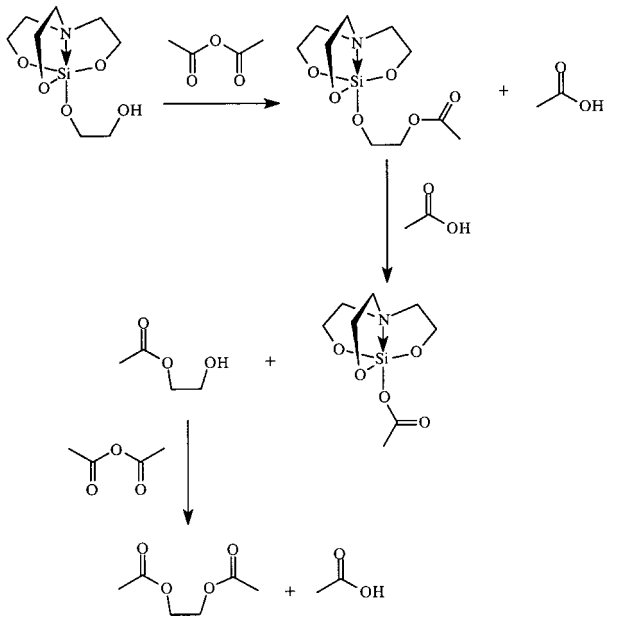
(9)

4

The IR spectrum of **4** shows a strong, sharp *ν*C=O band at 1710 cm^{-1}, typical of a simple carbonyl group, suggesting the absence of interactions between the carbonyl oxygen and silicon (that is, a bidentate structure as suggested below). The transannular Si–N bond is highly favored in silatranes, limiting the chance for forming bidentate structures.



The ^1H and ^{13}C NMR spectra of **4**, Table 1, are also consistent with a monodentate structure. The ^{29}Si NMR spectrum gives a signal at δ −99.9, which represents a slight upfield shift from **2** (δ −97.6) likely resulting from the acetoxy group being more electron withdrawing than EGH. The literature suggests that the greater the electronegativity of the **1** − X group, the shorter the Si–N transannular bond length.[24] This usually causes an upfield shift of the ^{29}Si NMR signal.[25]



Scheme 1

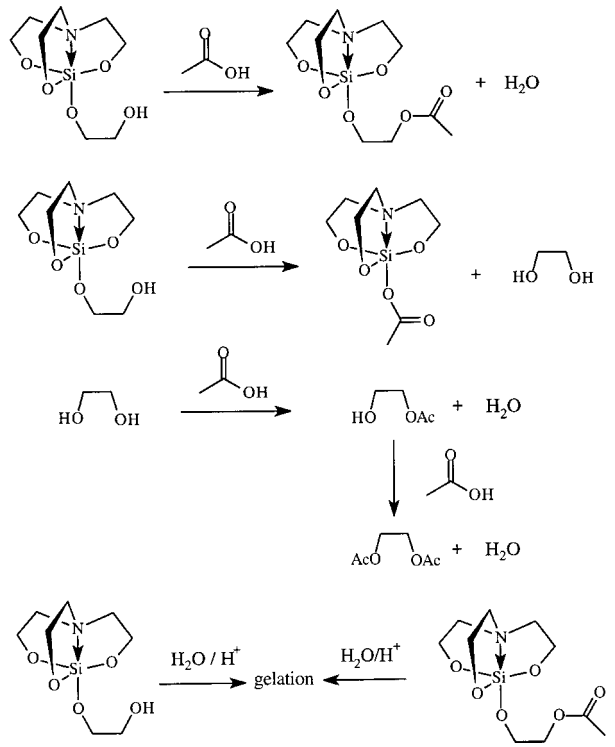
Scheme 1 provides a proposed sequence of reactions whereby **2** transforms to **4**. A detailed analysis of the kinetics of reactant loss and product formation remains to be done to verify the validity of the proposed sequences.

In the proposed sequence of reactions, acetic acid produced in the first step is suggested to react with a monoacetate intermediate to form **4**. However, replacing acetic anhydride with acetic acid in reaction (9) does not work. One explanation is that water is generated as shown in Scheme 2.

Since there is no way to trap this water, it will probably hydrolyze **2** (especially in the hot, strongly acidic environment), leading to gelation. However, when acetic anhydride is used, the same esterification step generates acetic acid as the byproduct instead of water, and hydrolysis is avoided.

Table 1 NMR data for silatranes **2**, **4**–**7**

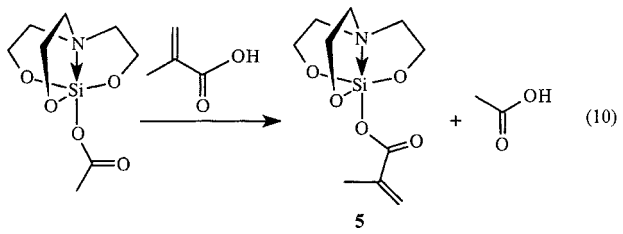
	2	**4**	**5**	**6**	**7**
^1H NMR (δ, ppm)	5.21 (1H, OH) 3.80 (6H, OCH_2CH_2N) 3.60 (2H, CH_2OH) 3.33 (2H, CH_2OSi) 2.98 (6H, NCH_2)	3.95 (6H, t, J = 6.0 Hz, OCH_2CH_2N) 2.99 (6H, t, J = 5.9 Hz, NCH_2) 2.06 (3H, s, CH_3)	6.07 (1H, CH_2=) 5.44 (1H, CH_2=) 3.9 (6H, t, J = 5.9 Hz, OCH_2CH_2N) 2.9 (6H, t, J = 5.9 Hz, NCH_2) 1.88 (3H, s, CH_3)	5.84–5.97 (1H, ddt, J = 17.0, 10.4, 4.7 Hz, CH_2=CH) 5.14–5.23 (1H, ddt, J = 17.0, 2.7, 1.9 Hz, CH_2=) 4.85–4.91 (1H, ddt, J = 10.4, 2.7, 1.9 Hz, CH_2=) 4.1 (2H, ddd, J = 4.7, 1.9, 1.9 Hz, =$CHCH_2O$) 3.7 (6H, t, J = 5.9 Hz, OCH_2CH_2N) 2.9 (6H, t, J = 5.9 Hz, NCH_2)	5.8–6.0 (1H, ddt, J = 17.3, 10.4, 5.5 Hz, CH_2=CH) 5.2–5.3 (2H, ddt, J = 17.3, 1.9, 1.4 Hz, CH_2=) 5.1–5.2 (1H, ddt, J = 10.4, 1.9, 1.4 Hz, CH_2=) 4.0 (2H, ddd, J = 5.5, 1.4, 1.4 Hz, $CHCH_2O$) 3.8 (8H, OCH_2CH_2N) 3.6 (2H, t, CH_2) 2.9 (6H, t, N–CH_2)
^{13}C NMR (δ)	63.6 (CH_2OH) 62.6 (CH_2OSi) 57.8 (NCH_2CH_2) 50.9 (NCH_2)	171.2 (C=O) 57.7 (CH_2CH_2O) 51.6 (NCH_2) 23.7 (CH_3)	167.2 (C=O) 138.7 (CH_2=) 124.6 ($(CH)_3C$=CH_2) 57.6 (NCH_2CH_2O) 51.6 (NCH_2) 18.5 (CH_3)	140.6 (CH_2=CH) 111.9 (CH_2=) 64.1 (=$CHCH_2O$) 58.1 (NCH_2CH_2O) 51.6 (NCH_2)	135.2 (CH_2=CH) 116.2 (CH_2=) 71.9 (=$CHCH_2O$) 71.5 (OCH_2CH_2O) 61.8 (OCH_2CH_2O) 57.5 (NCH_2CH_2O) 51.1 (NCH_2)
^{29}Si NMR (δ)	− 97.6	− 99.9	− 99.1	− 95.5	− 96.2



Scheme 2

Exchange reactions of 4

In contrast to **2**, **4** readily undergoes ligand exchange. Compound **4**, on stirring with methacrylic acid at $\leqslant 35\,^{\circ}C$ overnight, dissolves [reaction (10)] to give a clear solution. A new



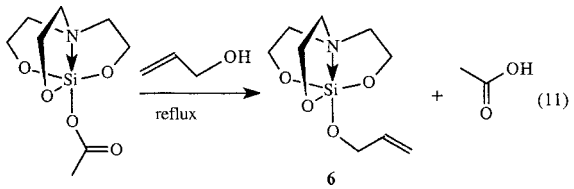
(10)

5

solid slowly precipitates out as mixing continues and can be isolated by filtration. The solid is soluble in chloroform and acetone, but not in hexane, diethyl ether or toluene; and thus can be recrystallized from acetone–heptane.

Analyses show that the solid is the desired compound **5**. The IR spectrum shows a strong, sharp νC=O absorption at 1694 cm^{-1} and another sharp νC=C absorption at 1646 cm^{-1}. The sharp νC=C band is also consistent with a monodentate carboxylate. ^{1}H and ^{13}C NMR data are given in Table 1 and are similar to those found for compound **4**. Similar to **4**, **5** exhibits a ^{29}Si peak at δ −99.1.

Reaction of **4** with allyl alcohol [reaction (11)] provides access to another potentially polymerizable silatrane, 1-allyloxysilatrane (compound **6**), which was unavailable from **2**



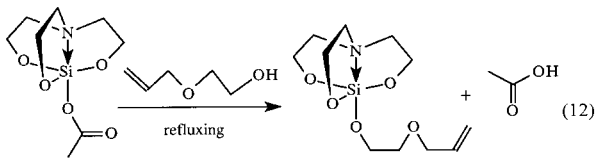
(11)

6

via exchange, as noted above. Compound **4** reacts slowly with excess allyl alcohol and after vacuum removal of solvent and byproduct, solid **6** can be recovered. Recrystallization from THF gives **6** as a pure white powder. The ^{1}H and ^{13}C NMR data are recorded in Table 1. The ^{29}Si peak appears at δ −95.5. In the IR spectrum, the νC=C band (weak) appears at 1630 cm^{-1}.

Control of the reaction time appears to be extremely important for this reaction. Short reaction times give poor conversion to the product, whereas long reaction times give an oil which is not the desired product, as indicated by NMR. It is likely that overlong reaction times result in decomposition of the silatrane compounds. Similar results are also observed in the reaction of **4** with 2-(propen-2-yloxy)ethanol as described below.

The reaction of **4** with 2-(propen-2-yloxy)ethanol [reaction (12)] gives an oil. Spectral analyses indicate that the desired



(12)

7

product **7** is obtained. Similar to **6**, a weak νC=C bond is observed at 1654 cm^{-1} in the FTIR spectrum and the NMR spectra contain all the desired signals as recorded in Table 1. The ^{29}Si NMR peak appears at δ −96.2. Table 2 contains mass spectral data for **2** and **4**–**7**.

As with reaction (11), reaction times must be controlled, a prolonged reaction time gives an oily product whose spectra have not been well interpreted, but clearly suggest something other than product **7**. It seems that longer reaction times in both reactions (11) and (12) destroy the product silatrane. It is possible that at prolonged reaction times, the byproduct acetic acid may react with the corresponding alcohol to produce ester and water, and the water then hydrolytically decomposes the silatrane. This suggests that the ligand exchange reactions of (11) and (12) proceed faster than the esterification reactions.

The above work describes initial efforts to use silica as a reactant in the syntheses of novel, stable alkoxysilane compounds at hundred gram to kilogram quantities. It demonstrates the feasibility of using a simple, silica-derived silatrane

Table 2 Mass spectral data for silatranes **2**, **4**–**7**

	2	**4**	**5**	**6**	**7**
HRMS (*m*/*z*)	236.0954 (obs. M + H)$^{+}$ (236.0954, calc.)	233.0709 (233.0720, calc.)	260.0948 (M + H)$^{+}$ (260.0954, calc.)	231.0925 (M)$^{+}$ (231.0927, calc.)	276.1266 (M + H)$^{+}$ (276.1267, calc.)
MS (*m*/*z*, intensity)		233(8.67%), 190(24.74%), 174(100%), 148(24.72%), 87(35.94%)	260(100%), 174(4.59%), 150(46.1%)	231(6.73%), 190(13.22%), 174(100%)	276(100%), 236(2.59%), 218(8.19%), 204(9.10%), 191(14.34%), 174(18.38%), 150(2.87%)

glycol to prepare sets of silicon-containing reactive monomers. These monomers offer the potential to form novel polymers of use as ceramic precursors and/or for the formulation of low cost, flame retardant materials. In addition, it may be that some of these simple derivatives or related compounds will offer potential in the areas of agriculture, pharmacology and/or biology.

Experimental

General procedures

All chemicals were reagent grade, purchased from standard vendors and used as received unless otherwise specified. Ethylene glycol (EGH_2) used in these experiments was: (1) purchased from standard vendors and used as received, (2) recycled from reaction distillate by double distillation under N_2, or (3) recovered from used antifreeze by double distillation under N_2. All reactions were carried out under N_2 to minimize the chances of exposure to air or moisture.

Analytical methods

Nuclear magnetic resonance (NMR). ^1H NMR and ^{13}C NMR studies were carried out on Varian 300 MHz and 400 MHz spectrometer using standard set ups. Samples (10–50 mg) were dissolved in $CDCl_3$ or acetone-d_6 and placed in 5 mm NMR tubes. Tetramethylsilane (TMS) was used as the chemical shift reference. ^{29}Si NMR studies were carried out on a Bruker 360 MHz spectrometer. Samples (200–500 mg) which were dissolved in 10–15 ml solvent were placed in a 10 mm NMR tube with an inner 5 mm NMR tube containing acetone-d_6 as the lock solvent and TMS as an external given reference.

Mass spectrometry (MS). Analyses were carried out by electronic ionization (EI) or by chemical ionization (CI) with ammonia on a VG 70-250-S (Micromass Corporation) machine. The instrument was calibrated with perfluorokerosene and scanned from m/z 1000 to m/z 35 at 10 s decade^{-1} and 6 kV accelerating voltage. Selected samples were analyzed by fast atom bombardment ionization in the positive ion mode (FAB +) using a VG 70-70-E mass spectrometer (Micromass Corporation). The instrument was calibrated using CsI salt clusters. The FAB atom gun was run with xenon gas, at settings of 1 mA and 8 kV voltage. The mass range was scanned from m/z 2800 to m/z 75 at 8 s decade^{-1} and run at 5 kV accelerating voltage.

Thermal gravimetric analysis (TGA). This was conducted using a TA Instruments 2950 thermal analysis instrument. Samples (30–60 mg) were loaded in platinum pans and heated under N_2 balance (40 cm^3 min^{-1}) with an air purge (60 cm^3 min^{-1}), using a high-resolution (Hi-Res 4) program with a maximum ramp rate of 50 °C min^{-1} to temperatures of 950 °C.

IR. IR spectra of the samples were recorded on a Mattson Galaxy Series FTIR 3000 spectrometer (Mattson Instruments, Inc., Madison, WI). Random cuttings of optical grade, single crystal potassium bromide (KBr, International Crystal Laboratories, Garfield, NJ) were ground using an alumina mortar and pestle. The ground KBr powder was used as the non-absorbing medium. IR samples were prepared in air by rigorously mixing 0.5 wt% analyte with ground KBr. The samples were then packed into sample holders, leveled off at the upper edge to provide a smooth surface, and transferred to the sample chamber, which was constantly flushed with N_2. 100 scans were collected for each sample at a resolution of ± 4 cm^{-1}.

Synthesis

Silatrane glycol 2. Fumed silica (240 g, 4.00 mol) and triethanolamine ($TEAH_3$) (565 ml, 4.25 mol) were mixed with about 3 L EGH_2 in a 5 L round-bottom flask equipped with a mechanical stirrer and distillation head. This mixture was heated to >200 °C to distill off EG and water produced during the reaction. All the silica dissolved within 10 h. The solution was kept heating at >200 °C under normal pressure to distill off EG until the solution was very viscous. Then the solution was heated at 150 °C under vacuum for further drying. The remaining solid was washed with freshly distilled ethanol and after filtration, 850 g of white solid was collected (90% yield).

1-Acetoxysilatrane 4. Silatrane glycol **2** (47 g, 0.20 mol) was mixed with acetic anhydride (200 ml) in a 500 ml round-bottom flask equipped with a magnetic stirring bar and refluxing column. The mixture was refluxed with stirring under N_2 for 12–24 h. Most of the silatrane glycol solid dissolved during reflux. The solution was then vacuum distilled to remove the liquid portion. The remaining solid was washed with THF and a white solid was obtained. This solid may be recrystallized from CH_2Cl_2–hepatane. The final product was a white solid (36 g, 78% yield).

1-Methacryloxysilatrane 5. 1-Acetoxysilatrane **4** (4.7 g, 0.020 mol) was mixed with methacrylic acid (5.0 ml) in a 50 ml flask with a magnetic stirring bar. The mixture was stirred under N_2 flow overnight. A white solid precipitated out. The remaining liquid was evaporated under vacuum at room temperature. The resulting solid was then washed with the minimum amount of ethanol. After drying, a white solid was obtained (4.2 g, 81% yield). The compound is pure judging from NMR spectra. Further purification may be carried out by recrystallization from acetone–heptane.

1-Allylsilatrane 6. 1-Acetoxysilatrane **4** (2.3 g, 0.010 mol) was mixed with 50 ml of freshly distilled allyl alcohol in a 100 ml flask with a magnetic stirring bar. The mixture was refluxed under N_2 flow with stirring until all of the solid had dissolved. Then the mixture was distilled under reduced pressure at <40 °C to remove all of the liquid. The resulting oily solid was recrystallized from dry THF and a white solid was obtained (*ca.* 50% yield).

1-(2′-propen-2-yloxy)ethoxysilatrane 7. 1-Acetoxysilatrane **4** (2.3 g, 0.010 mol) was mixed with 50 ml of 2-(propen-2-yloxy) ethanol in a 100 ml flask with a magnetic stirring bar. The mixture was refluxed under N_2 flow with stirring until all of the solid had dissolved. Then the mixture was distilled under reduced pressure at 50 °C to remove as much liquid as possible. A viscous oil was obtained (*ca.* 50% yield).

Acknowledgements

We would like to thank FAA for their generous support of this work through grant No. 95-G-026. This work was also supported in part through an NSF SBIR subcontract (Grant No. DMI 9661236) from Tal Materials, Inc. of Ann Arbor.

References

1 P. Hencsei and L. Parkany, *Rev. Silicon, Germanium, Tin Lead Compd.*, 1985, **8**, 191.
2 M. G. Voronkov, *Top. Curr. Chem.*, 1979, **84**, 77.
3 J. E. Casida, M. Eto, A. D. Moscioni, J. L. Engel, D. S. Milbrath and J. G. Vercade, *Toxicol. Appl. Pharmacol.*, 1976, **36**, 261.
4 A. Grna, P. Koo and J. Hogan, *Anticancer Res.*, 1992, **12**, 565.
5 F. Fazely, A. Grna and N. Ledinko, *Proc. Am. Assoc. Cancer Res.*, 1988, **29**, 526.
6 A. Grna, N. Ledinko, F. Fazely, S. Darling and J. Hogan, *Anticancer Res.*, 1988, **8**, 249.

7 P. Mehta, T. Ramasarma and C. Kurup, *Biochim. Biophys. Acta*, 1987, **920**, 102.
8 P. Mehta, T. Ramasarma and C. Kurup, *Mol. Cell. Biochem.*, 1990, **97**, 75.
9 G. A. Grigalinovich, Z. Atare, N. V. Miyakova, G. Zelcans and E. Lukevics, *Biol. Akt. Soedin. Elem. IV B Gruppy*, 1977, 113.
10 M. G. Voronkov, A. T. Platonova, L. A. Mansurova, I. G. Kuzentsov, G. I. Zelchan and V. M. Dyakov, *Ger. Offen.*, 1977, 2530255.
11 V. I. Sergeev and S. V. Irlyanova, *Biol. Akt. Soedin. Elem. IV B Gruppy*, 1977, 117.
12 M. G. Voronkov, G. I. Zelchan and E. J. Lukevits, *Silicon and Life*, Zinatne publishing house, Riga, 2nd edn., 1971.
13 C. B. Beiter, M. Schwarcz and G. Grabtree, *Soap. Chem. Spec.*, 1970, **46**, 38.
14 R. Zhuo, Z. Lu and J. Liao, *J. Organomet. Chem.*, 1993, **446**, 107.
15 R. E. Timms, *J. Chem. Soc. A*, 1971, 1969.
16 V. Gevorgyan, L. Borisova and E. Lukevics, *J. Organomet. Chem.*, 1997, **527**, 495.
17 R. J. Garant, L. M. Danies, S. K. Das, M. N. Janakiraman, R. A. Jacobson and J. G. Verkade, *J. Am. Chem. Soc.*, 1991, **113**, 5728.
18 R. J. P. Corriu, *J. Organomet. Chem.*, 1990, **400**, 81.
19 J. H. Iwamiya and G. E. Maciel, *J. Am. Chem. Soc.*, 1993, **115**, 6835.
20 M. S. Gordon, L. P. Davis and L. W. Burggraf, *Chem. Phys. Lett.*, 1989, **163**, 371.
21 J. W. Turley and F. P. Boer, *J. Am. Chem. Soc.*, 1968, **90**, 4026.
22 F. P. Boer, J. W. Turley and J. J. Flynn, *J. Am. Chem. Soc.*, 1968, **90**, 5102.
23 J. W. Turley and F. P. Boer, *J. Am. Chem. Soc.*, 1969, **91**, 4129.
24 A. Greenberg and G. Wu, *Struct. Chem.*, 1989, **1**, 79.
25 X. Zhang, S. Mao, L. Shen, C. Ye, R. Zhuo, Z. Lu and G. A. Webb, *J. Mol. Struct.*, 1995, **372**, 249.
26 V. F. Sidorkin, V. A. Pestunovich and M. G. Voronkov, *Russ. Chem. Rev.* (*Engl. Transl.*), 1980, **49**, 789.
27 J. B. Peel and D. Wang, *J. Chem. Soc., Dalton Trans.*, 1988, 1963.
28 C. L. Frye, G. E. Vogel and J. A. Hall, *J. Am. Chem. Soc.*, 1961, **83**, 996.
29 C. L. Frye, G. A. Vincent and W. A. Finzel, *J. Am. Chem. Soc.*, 1971, **93**, 6805.
30 M. G. Voronkov, *Pure Appl. Chem.*, 1966, **13**, 35.
31 M. G. Voronkov, V. M. Dyakov and S. V. Kirpichenko, *J. Organomet. Chem.*, 1982, **233**, 1.
32 R. M. Laine, P. Kansal and F. Babonneau, *J. Am. Ceram. Soc.*, 1997, **80**, 2597.
33 R. M. Laine, D. R. Treadwell, B. L. Mueller, C. R. Bickmore, K. F. Waldner and T. R. Hinklin, *J. Mater. Chem.*, 1996, **6**, 1441.
34 R. M. Laine, A. C. Sutorik, S. S. Neo and D. R. Treadwell, *J. Am. Ceram. Soc.*, 1998, **81**, 1477.
35 R. M. Laine and C. R. Bickmore, *J. Am. Ceram. Soc.*, 1996, **79**, 2865.

Paper 9/08291C