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Preliminary communication

Preparation of novel hetero polyfunctional disiloxanes by Lewis/Brønsted acid catalyzed equilibration of *sym*-tetramethyldisiloxane or *sym*-divinyltetramethyldisiloxane with polychlorosilanes☆

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Abstract

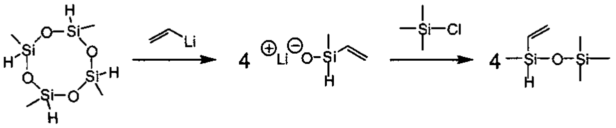
1,1-Dichloro-1,3,3-trimethyldisiloxane, 1,1-dichloro-3,3-dimethyl-1-phenyl- disiloxane, 1,1-dichloro-3,3-dimethyl-3-vinyldisiloxane, 1-chloro-3,3-dimethyl-3-vinyl- disiloxane, and 1,1-dichloro-3,3-dimethyldisiloxane have been prepared by Lewis/Brønsted acid catalyzed equilibration reactions. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Polyfunctional disiloxanes; Si–H; Si–C; Si–vinyl

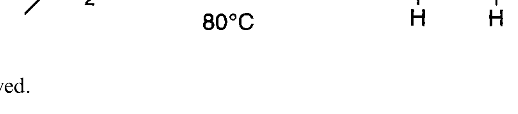
1. Introduction

There are comparatively few commercially available hetero polyfunctional silicon compounds. Among these are trichlorosilane, dichlorosilane and methyldichlorosilane which contain both Si–Cl and Si–H reactive functional groups. The Si–H of these is reactive in Pt catalyzed hydrosilation reactions, while the Si–Cl bond is susceptible to nucleophilic substitution reactions.

While siloxanes are economically the most important type of organosilicon derivatives, only a few symmetrical polyfunctional siloxanes are commercially available. Among these are 1,3-dichlorotetramethyldisiloxane, *sym*-tetramethyldisiloxane, *sym*-divinyltetramethyldisiloxane, 1,3,5,7-tetramethylcyclotetrasiloxane, *tetrakis* (dimethylsiloxy)silane, hexachlorodisiloxane and 1,3,5,7-tetravinyl-1,3,5,7-tetramethylcyclotetrasiloxane [1]. Recently, several unsymmetrical hetero polyfunctional disiloxanes have been prepared by reaction of lithium methylvinylsilanolate with chlorosilanes [2,3].



As far as we are aware, there are only four examples of di or trisiloxanes which contain both Si–H and Si–Cl bonds previously reported. *bis*(Trimethylsiloxy)chlorosilane has been prepared by photochemical or Pd catalyzed chlorination of *bis*(trimethylsiloxy)silane [4]. 1,3-Dichloro-1,3-dimethyldisiloxane has been formed by reaction of methyldichlorosilane with ferric oxide [5], while 1,3-dichloro-1,3-dimethyl-3-vinyldisiloxane has been prepared by partial co-hydrolysis of methyldichlorosilane and methylvinyldichlorosilane [6]. Finally, 1,1-dichloro-1,3,3-trimethyldisiloxane has been mentioned in a patent [7].



☆ All our best wishes to Professor Dietmar Seyferth on his 70th birthday. A most productive scientist, whose work we have long admired. As Editor of both the Journal of Organometallic Chemistry and Organometallics, he has insisted on a high standard of quality.

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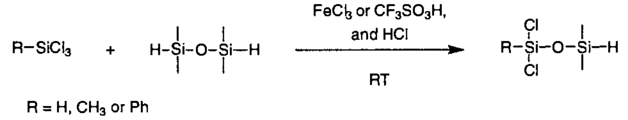
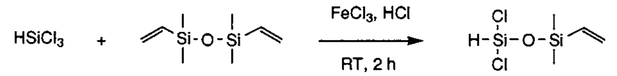
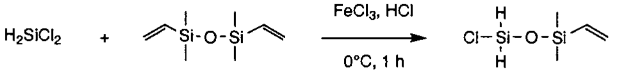
2. Results and discussion

We should like to report a new route to hetero polyfunctional disiloxanes which contain both reactive Si–H and Si–Cl bonds. We have found that ferric chloride or triflic acid in conjunction with anhydrous HCl catalyzes equilibration reactions between methyltrichlorosilane, phenyltrichlorosilane, or trichlorosilane and *sym*-tetramethyldisiloxane (I). The products of these exchange reactions are dimethylchlorosilane and disiloxanes which contain both reactive Si–H and Si–Cl bonds.



Successful equilibration reactions have also been carried out between trichlorosilane or dichlorosilane and *sym*-divinyltetramethyldisiloxane (II). These reactions yield disiloxanes which contain not only reactive Si–H and Si–Cl bonds but also Si–vinyl bonds. These are among the most highly functionalized hetero disiloxanes yet reported.





3. Experimental

^{1}H-, ^{13}C- and ^{29}Si-NMR spectra were obtained on a Bruker AMX-500 MHz spectrometer operating in the FT mode. ^{1}H-NMR spectra were run on 5% w/v CDCl$_3$ solutions. Forty percent w/v solutions in acetone-d_6 were used to obtain ^{29}Si-and ^{13}C-NMR spectra. ^{13}C-NMR spectra were obtained with broad band proton decoupling. An inverse gated ^{1}H-decoupling pulse program with a 60 s delay was used to acquire ^{29}Si-NMR spectra [8]. The same program was used to obtain Si–H coupling constants with the proton decoupler turned off. Residual acetone-d_5 was used as an internal standard for ^{1}H- and ^{13}C-NMR. ^{29}Si-NMR spectra were referenced to an external TMS standard. IR spectra of neat films on NaCl plates were recorded on a Perkin–Elmer Spectrum 2000 FT-IR spectrometer.

Elemental analysis was obtained by Oneida Research Services Inc. Whitesboro, NY.

I and II were purchased from Gelest and were redistilled before use. Methyltrichlorosilane, phenyltrichlorosilane, trichlorosilane, dichlorosilane, and hexamethyldisilazane were obtained from Gelest and used as received. Ferric chloride hexahydrate and ammonium chloride were purchased from Mallinckrodt. Triflic acid was obtained from the 3 M Co.

3.1. *Ferric Chloride Catalyst*

Ferric chloride hexahydrate (1 g, 3.7 mmol) was dissolved in $\sim$ 5 ml dry acetone. Trimethylchlorosilane (2.5 g, 23 mmol) was added dropwise to the solution at 0°C. The green colored solution was allowed to warm to room temperature. During this time, the color turned slowly brown while two layers separated. The colorless upper layer was discarded.

3.2. *1,1-Dichloro-1,3,3-trimethyldisiloxane*

3.2.1. *Method 1*

Methyltrichlorosilane, (96 g, 0.64 mol) and I (57 g, 0.42 mol) were placed in a 200 ml round-bottomed flask equipped with a Teflon covered magnetic stirrbar and sealed with a rubber septum. The catalyst solution (500 µl) was injected into the flask at room temperature. An exothermic reaction occurred when dry HCl gas was bubbled into the solution. Excess pressure was relieved through a syringe needle attached to a drying tube filled with Drierite. The contents of the flask warmed to $\sim$ 35°C in 10 min. Addition of HCl was continued for 2 h. The reaction mixture was distilled through a 50 cm vacuum jacketed column which was packed with stainless steel saddles. A fraction, b.p. 116°C/760 mm, 33.6 g (42% yield) was collected. ^{1}H-NMR δ: 0.32(d, 6H, $J = 3$ Hz), 0.84(s, 3H), 4.77(septet, 1H, $J = 3$ Hz). ^{13}C-NMR δ: -0.17, 5.97. ^{29}Si-NMR δ: -17.10(1Si), 0.94 (1Si). IR ν: 2966, 2151, 1414, 1258, 1088, 904, 797 cm^{-1}.

3.2.2. *Method 2*

Methyltrichlorosilane (25.5 g, 0.17 mol) and I (15.1 g, 0.11 mol) were placed into a 50 ml round-bottomed flask which was sealed with a rubber septum. Triflic acid (150 µl, 1.7 µmol) was injected into the flask at 20°C. A rapid increase in temperature ($\sim$ 20°C) occurred when dry HCl gas was bubbled into the solution for 5 min. After 15 min, hexamethyldisilazane (500 µl, 4.1 µmol) was added to neutralize the reaction mixture. Distillation gave 8.1 g (39%) of 1,1-dichloro-1,3,3-trimethyldisiloxane.

3.3. *1,1-Dichloro-3,3-dimethyl-1-phenyldisiloxane*

Phenyltrichlorosilane, (63 g, 0.30 mol) and I (40 g, 0.30 mol) were allowed to react with 200 µl of catalyst solution and dry HCl gas as above. After 5 h, the reaction mixture was distilled and a fraction, b.p. 71–

73°C/1.8 mm, 22.3 g (30% yield) was collected. ^{1}H-NMR δ: 0.30(d, 6H, $J = 3$ Hz), 4.90(septet, 1H, $J = 3$ Hz), 7.30–7.75(m, 5H). ^{13}C-NMR δ: 0.24, 128.80, 132.40, 133.59, 134.18. ^{29}Si-NMR δ: -30.26(1Si), 2.28(1Si, $J_{\text{Si-H}} = 213$ Hz). IR ν: 2964, 2149, 1593, 1431, 1257, 1130, 1083, 898, 838, 774, 695 cm^{-1}.

3.4. 3,3-Dichloro-1,1-dimethyl-1-vinyldisiloxane

Trichlorosilane, (56 g, 0.42 mol) and II (42 g, 0.22 mol) were allowed to react as above. Distillation gave 9.0 g (20% yield) of the desired product, b.p. 56°C/40 mm. ^{1}H-NMR δ: 0.31(s, 6H), 5.66(s, 1H), 5.86(dd, 1H, $J = 20$ and 4 Hz), 6.06(dd, 1H, $J = 15$ and 4 Hz), 6.19(dd, 1H, $J = 20$ and 15 Hz). ^{13}C-NMR δ: -0.04, 134.02, 137.03. ^{29}Si-NMR δ: -39.58 (1Si), 5.77(1Si). IR ν: 3058, 2965, 2248, 1598, 1409, 1261, 1098, 1007, 845, 811, 792, 714, 570 cm^{-1}. Elemental Anal. Calc. for $C_4H_{10}OSi_2$: C, 23.88; H, 5.01; Cl, 35.24. Found: C, 24.43; H, 4.99; Cl, 37.03.

3.5. 1-Chloro-3,3-dimethyl-3-vinyldisiloxane

Dichlorosilane (32 g, 0.31 mol) and II (60 g, 0.32 mol) were mixed at 0°C and 500 µl of catalyst solution was added. The flask was maintained at 0°C throughout the reaction. Dry HCl gas was bubbled into the solution for 1 h. The reaction mixture was separated by fractional distillation. A fraction, b.p. 107°C/760 mm, 9.2 g (18% yield) was collected. ^{1}H-NMR δ: 0.19(s, 3H), 5.11(s, 2H), 5.74(dd, 1H, 20 and 3.5Hz), 5.94 (dd, 1H, $J = 15$ and 3.5 Hz), 6.08 (dd, 1H, $J = 20$ and 15 Hz). ^{13}C-NMR δ: -0.31, 133.14, 137.35. ^{29}Si-NMR δ: -33.29 (1Si, $J_{\text{Si-H}} = 271$ Hz), 3.72 (1Si). IR ν: 2964, 2202, 1597, 1409, 1259, 1086, 969, 905, 821, 790, 711, 523, 644 cm^{-1}.

3.6. 1,1-Dichloro-3,3-dimethyldisiloxane

Trichlorosilane (54 g, 0.40 mol) and I (30 g, 0.23 mol) were placed into a 100 ml round-bottomed flask. Fifty microliters of triflic acid was added. The temperature rapidly increased when dry HCl gas was bubbled through the solution. After 15 min, hexamethyldisilazane (500 µl, 4.1 µmol) was added to neutralize the reaction mixture. The product was distilled. A fraction, b.p. 79–82°C/760 mm, 5.20 g (13% yield) was obtained. ^{1}H-NMR δ: 0.30(d, 6H, $J = 2.5$ Hz), 4.82 (septet, 1H, $J = 2.5$ Hz), 5.60 (s, 1H). ^{13}C-NMR δ: 0.02. ^{29}Si-NMR δ: -38.54 (1Si, $J_{\text{Si-H}} = 352$ Hz), 2.00 (1Si, $J_{\text{Si-H}} = 215$ Hz). IR ν: 2966, 2249, 2155, 1421,1259, 1103, 907, 830, 813, 775, 629, 573, 491 cm^{-1}.

4. Results and discussion

The mechanism of this reaction is not known. In some cases, we have been able to replace ferric chloride with triflic acid. However, in both reactions anhydrous HCl is essential. Ferric chloride and HCl combine to form $HFeCl_4$ which is a superacid ($H_o \leq -12$) like triflic acid ($H_o = -14.1$) [9,10]. In the case of the reactions of methyltrichlorosilane, phenyltrichlorosilane, and trichlorosilane with I, we suggest the following mechanism. Protonation of the oxygen of I leads to an oxonium ion. Nucleophilic attack by chloride ion on a dimethylsilyl center of the oxonium ion leads to dimethylchlorosilane and dimethylsilanol, which reacts with methyltrichlorosilane, for example, giving 1,3,3-trimethyl-1,1-dichlorodisiloxane and HCl. In these reactions, triflic acid alone is ineffective. The low nucleophilicity of the trifluoromethane sulfonate anion may prevent its attack on the dimethylsilyl centers of the oxonium ion. The equilibration reactions with II may occur by a similar pathway.

While the procedure is both simple and the reactions rapid, the yields reported for isolated distilled materials are low. Yields based on spectroscopic analysis of reaction mixtures are significantly higher. Changes in reaction stoichiometry can lead to different products. For example, ferric chloride/HCl catalyzed reaction of methyltrichlorosilane with three equivalents of I yields *tris*(dimethylsiloxy)methylsilane [11].

5. Conclusions

A simple method for the preparation of novel hetero polyfunctional disiloxanes from commercially available starting materials is reported.

Acknowledgements

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