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# A disiloxane equilibration approach to the preparation and characterization of 5,5′-(1,1,3,3-tetramethyldisiloxane-1,3-diyl)bisbicyclo[2.2.1]heptane-2,3-dicarboxylic anhydride

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**Abstract**

The preparation of 5,5′-(1,1,3,3-tetramethyldisiloxane-1,3-diyl)bisbicyclo[2.2.1]heptene-2,3-dicarboxylic anhydride, **3**, by a novel synthetic approach was found to be an effective method to isolate this disiloxane which is difficult to purify. The structure of the diastereomerically mixed product was confirmed by a combination of nuclear magnetic resonance spectroscopic and liquid chromatographic studies and correlated to the X-ray structure from the D,L-isomer. The hydrosilation of bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic anhydride **1** by 1,1,3,3-tetramethyldisiloxane and pentamethyldisiloxane is compared.

## Introduction

This laboratory has recently been interested in various silicone containing anhydrides as they allow greater synthetic flexibility in the preparation of various copolymers than do the traditional 3-aminopropylsiloxane systems. The first $\alpha,\omega$-dianhydride substituted polydimethylsiloxanes with the anhydride fragment connected to the silicone via a Si–C bond were those prepared from 5,5′-(1,1,3,3-tetramethyldisiloxane-1,3-diyl)bisbicyclo[2.2.1]heptene-2,3-dicarboxylic anhydride, **3** [1]. They have the been used to prepare silicone modified polyimides [2,3] and polyamides [4]. Two methods for the synthesis of **3** have been reported [1,5]. Although these syntheses produce **3** in good yield, the purification of the product from these reaction mixtures is difficult.

The chloroplatinic acid catalyzed hydrosilation reaction of 1,1,3,3-tetramethyldisiloxane and bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic anhydride **1** [1] (Scheme 1) yield a number of products as observed by chromatographic analysis. Though as many as 36 stereoisomers of **3** are, in principle, possible from this reaction mixture, these products were not simply diastereomeric forms of **3**. Approximately 85% of

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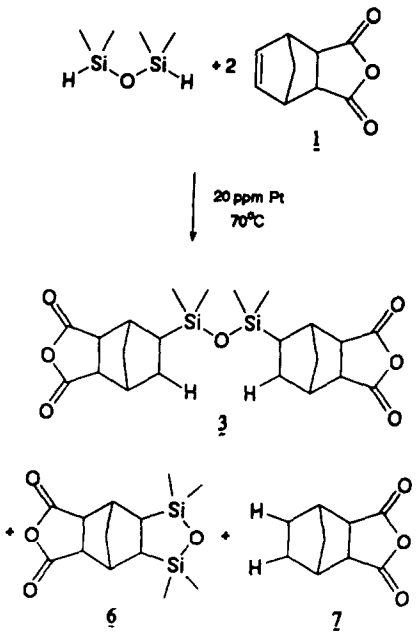
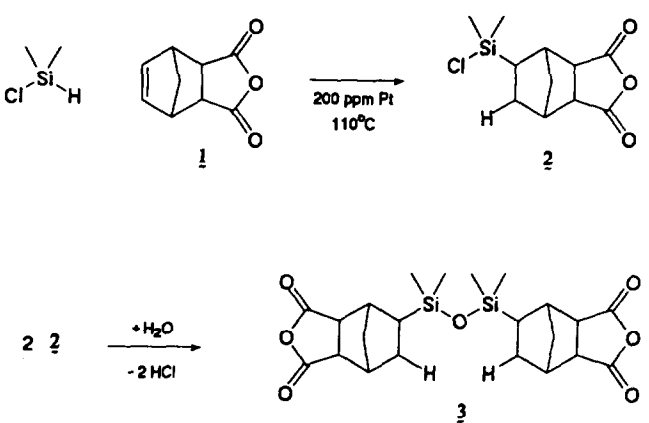


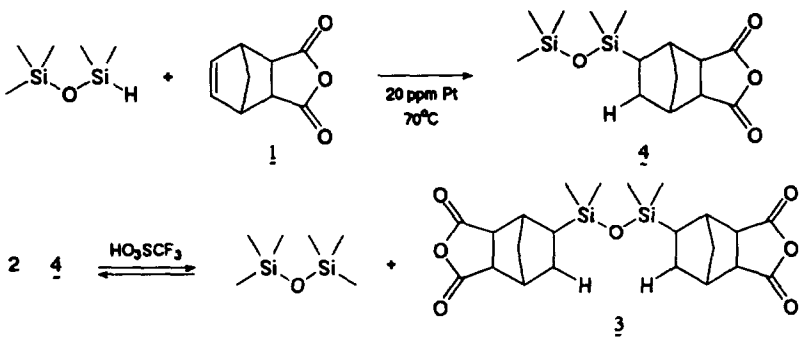

Scheme 1. Synthesis of **3** via tetramethyldisiloxane.

the mixture was the desired disiloxane. Due to its low volatility and the inability to crystallize it in pure form with a high yield, it was isolated by simply trituration in ether. The purity of the product is quite variable by this technique.

An alternative to the direct synthesis of **3** is the preparation of 5-chloro-dimethylsilylbicyclo[2.2.1]heptene-2,3-dicarboxylic anhydride **2** and its subsequent hydrolysis and condensation [4] (Scheme 2). A high yield of **2** was achieved and it was distilled under vacuum. Unfortunately, the reaction rate was slow and the quantity of platinum catalyst required was high [6]. The reaction of **2** with water yields **3** almost quantitatively but must be stripped of all of the HCl generated to be used effectively in many applications.




Scheme 2. Synthesis of **3** via chlorodimethylsilane.




Scheme 3. Synthesis of **3** via **4**.

To prepare $\alpha,\omega$-dianhydride substituted polydimethylsiloxanes from **3**, it was necessary to examine the acid catalyzed polymerization of octamethylcyclotetrasiloxane with **3** as an end-capping chain transfer agent. These polymerization studies indicated that the equilibration reaction was free of side reactions and would rapidly proceed to the statistical distribution of homologues defined by the mixture of reagents [7]. This suggested an approach to the preparation of **3** by first preparing the asymmetric disiloxane, 5-(pentamethyldisiloxanyl)bicyclo[2.2.1]heptane-2,3-dicarboxylic anhydride **4**, and equilibrating this disiloxane while removing hexamethyldisiloxane (Scheme 3). This method combines the high rate and low catalyst loading of the direct approach (Scheme 1) while efficiently employing the strategy of isolating a pure intermediate in high yield and converting it into the desired product in nearly quantitative yield (Scheme 2).

We now wish to report this synthesis and the characterization of the stereoisomers of **3** produced in the reaction. The hydrosilation of **1** by pentamethyldisiloxane is compared to the hydrosilation of **1** by 1,1,3,3-tetramethyldisiloxane. This synthetic strategy should be useful with other disiloxanes which are difficult to purify.

## Experimental

*Pentamethyldisiloxane*

The synthesis of pentamethyldisiloxane was carried out by the trifluoromethanesulfonic acid catalyzed equilibration of a 3 : 1 molar ratio of hexamethyldisiloxane with 1,1,3,3-tetramethyldisiloxane at room temperature overnight. An aliquot was withdrawn, the acid quenched with an excess of MgO, and the sample analyzed by gas chromatography. The observed ratio of 1 : 6 : 9 for 1,1,3,3-tetramethyldisiloxane : pentamethyldisiloxane : hexamethyldisiloxane agreed with that predicted assuming a completely random process. No further change was observed with time. An excess of MgO was added to the reaction mixture and pentamethyldisiloxane was isolated in greater than 99.9% pure form in a 90% yield by distillation at 84 °C using a standing plate fractionating column.

*5-exo-(Pentamethyldisiloxane-yl)bicyclo[2.2.1]heptane-endo-2,3-dicarboxylic anhydride* **4**

To a mechanically stirred suspension of bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic anhydride **1** (recrystallized one from toluene) in 1.1 molar equivalents of pentameth-

yldisiloxane at 70 °C, Karsteadt's [9] formulation of chloroplatinic acid was added such that the resulting mixture was 30 ppm in Pt. After an induction period of approximately 20 min the exothermic hydrosilation occurred to yield **4** (99% by GC) within 30 min. During conversion, the temperature of the reaction mixture increased slowly to approximately 100 °C while the suspended **1** dissolved. The pure **4** was isolated in a 97% yield by distillation at 136–137 °C and 0.2 mmHg from MgO. Upon standing the colorless liquid crystallized (m.p. 49–50 °C). $^1$H NMR (200 MHz, $C_6D_6$): $\delta$ −0.09 (s, 3 H), −0.02 (s, 3 H), 0.12 (s, 9 H), 0.72 (AXYZ, 9.8, 7.2, 2.0 Hz, 1 H), 0.84 ($AXY_2Z$, 10.1, 2.6, 2.0, 1.5 Hz, 1 H), 1.35 (m, 1 H), 1.37 ($AXY_2$, 10.1, 1.5 Hz, 1 H), 1.64 (AXYZ, 13.8, 9.8, 2.6 Hz, 1 H), 2.35 (m, 1 H), 2.51 (m, 1 H), 2.54 (m, 1 H), 2.55 (m, 1 H); $^1$H NMR (200 MHZ, $CDCl_3$): $\delta$ 0.00 (d, 3 H), 0.04 (s, 9 H), 0.05 (s, 3 H), 0.61 (AXYZ, 9.1, 7.8, 1.8 Hz, 1 H), 1.57 (m, 3 H), 1.73 ($AXY_2$, 9.9, 1.6 Hz, 1 H), 2.77 (m, 1 H), 2.83 (m, 1 H), 3.39 (m, 2 H); $^{13}$C NMR (75 MHz, $C_6D_6$): $\delta$ − 1.62, −1.35, 1.47, 25.58, 26.53, 40.04, 40.90, 41.01, 49.18, 52.36, 171.57, 171.77; $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ −1.15, −0.95, 1.73, 25.72, 26.63, 40.28, 41.13, 41.42, 49.51, 52.62, 172.07, 172.36; IR film cast from $CDCl_3$: 2930 (s), 2855 (m), 1855 (s), 1770 (s), 1255 (s), 1220 (s), 1080 (s) 975 (m), 960 (m), 940 (m) 910 (s), 895 (m), 837 (s), 750 (m) cm$^{-1}$. Anal. Found: C, 53.36; H, 7.74; Si, 18.17. $C_{14}H_{24}Si_2O_4$ calcd.: C, 53.81; H, 7.91; Si, 17.97%.

*5-*exo*-(1,1,3,3-Tetramethyldisiloxane-yl)bicyclo[2.2.1]heptane-*endo*-2,3-dicarboxylic anhydride* **5**

The synthetic procedure was equivalent to that of **4** using 1.0 molar equivalents of 1,1,3,3-tetramethyldisiloxane for each equivalent of **1**. After removal of a forecut consisting primarily of **7**, distillation at 126–131 °C and 0.2 mmHg from MgO yielded **5** contaminated with 5,6-*exo*-(1,1,3,3-tetramethyldisiloxane-diyl)bicyclo-[2.2.1]heptane-*endo*-2,3-dicarboxylic anhydride **6**. **5**: $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 0.00 (doublet, 8.0 Hz, 6 H), 0.10 (s, 3 H), 0.11 (s, 3 H), 0.58 (AXYZ, 9.1, 7.8, 1.8 Hz 1 H), 1.55 (m, 3 H), 1.67 ($AXY_2$, 9.9, 1.6 Hz, 1 H), 2.73 (m, 1 H), 2.78 (m, 1 H), 3.39 (m, 2 H) 4.61 (heptet, 8.0 Hz, 1 H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ −1.27, 0.65, 25.69, 26.65, 40.23, 40.99, 41.43, 49.50, 52.64, 172.26, 172.52; IR (neat film on NaCl): 2930 (vs), 2855 (m), 2100 (s), 1860 (s), 1775 (s), 1255 (s), 1220 (s), 1080 (s), 1030 (s), 975 (m), 960 (m), 940 (m) 900 (s), 830 (m), 765 (m), 730 (m) cm$^{-1}$. **6**: $^1$H NMR (200 MHz, $CDCl_3$): $\delta$ 0.13 (s, 3 H), 0.17 (s, 3 H), 1.21 (d, 2.0 Hz, 2 H), 1.46 ($AXY_2$, 10.3, 1.8 Hz, 1 H), 1.65 ($AXY_2Z_2$, 10.3, 2.0, 1.5 Hz, 1 H), 2.81 (AWXYZ, 3.3 1.8, 1.8, 1.5 Hz, 2 H), 3.42 (AXY, 3.3, 1.8 Hz, 2 H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ −2.4, 1.4, 28.3, 41.8, 41.9, 51.6, 172.2.

*5,5-*exo*-(1,1,3,3-Tetramethyldisiloxane-1,3-diyl)bisbicyclo[2.2.1]heptene-2,3-*endo*-dicarboxylic anhydride* **3**

A 0.005 *N* solution of trifluoromethanesulfonic acid in **4** at 70 °C was stirred at a pressure of 60 mmHg. Hexamethyldisiloxane which bubbled from the mixture was trapped at dry ice temperatures in a pretared flask. After 2 h the reaction mixture was noticeably more viscous and 92% of the maximum yield of hexamethyldisiloxane had been collected. An aliquot removed under $N_2$ rapidly solidified to a glass. It was then dissolved in acetone, the acid quenched with MgO and analyzed by gas chromatography and $^1$H NMR and determined to be 95% **3**. Vacuum was again applied and the temperature increased to 120 °C. After two more hours little

additional hexamethyldisiloxane was collected, and an aliquot was analyzed and determined to be 98% **3**. Upon cooling, the reaction mixture solidified. An excess of MgO was placed on top of the glassy solid, the solid was dissolved in an equal volume of acetone, and the solution was filtered. The solution was then poured into rapidly stirring hexane to precipitate **3** in a 96% yield and 99.5% purity by GC analysis. A second precipitation yielded pure **3** in an isolated yield of 93% from **4**. The white solid had a melting range of 126–153° C. Analysis by LC exhibited two peaks of equal area. $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ 0.067 (s, 6 H), 0.081 (s, 3 H, D,L), 0.085 (s, 3 $H_{meso}$), 0.69 (AXYZ, 9.4, 7.3, 1.9 Hz, 2 H), 1.56 (m, 4 H), 1.64 (m, 4 H), 2.77 (m, 1 $H_{meso}$), 2.80 (m, 1 H, D,L), 2.88 (m, 2 H) 3.41 (m, 4 H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ −1.38, −1.15, 25.55, 26.53, 40.09, 40.77, 41.42, 49.25, 52.42, 171.90, 172.16.

Fine white crystals formed upon cooling of a hot concentrated toluene solution of **3**. LC analysis of these crystals indicated a 7 : 3 ratio of the two peaks. A second recrystallization of these crystals gave an 85 : 15 mixture of the two components. A third recrystallization from a mixed acetone : heptane solution yielded a few fine white needles which melted at 171–173° C and eluted as single component by LC. When further cooled, the original toluene mother liquor yielded additional small crystals which were approximately 55% the high melting isomer. The remaining mother liquor was approximately 75% of the other diastereomer. After removal of the toluene, the powdery residue was dissolved in an acetone:water mixture. Many small crystals and a few large colorless crystals were formed upon standing over night. The large crystals melted sharply at 131–132° C and gave a single peak by LC analysis. An X-ray analysis was carried out on a crystal isolated from this mixture and shown to be the D,L isomer [10*].

Spectral grade toluene (Aldrich), acetone (Aldrich), and LC grade hexane (EM) were used as received. Trifluoromethanesulfonic acid was prepared from the anhydride (Aldrich distilled from $CaH_2$) and 0.5 equivalents of water. The conversion of anhydride occurred with stirring for one week, at which time the lower density $H_2O$ layer was converted to a higher density acid layer. Portions of dry acid were removed from under the anhydride layer using a syringe.

Gas chromatography was performed using a Shimadzu GC-9 with a six foot 10% OV-101 column. A temperature gradient from 40 to 320° C with an initial time of one minute and heating rate of 5° C $min^{-1}$ was used. The liquid chromatographic analysis was carried out using a Varian 500 with three 25 cm × 4.6 mm Zorbax SIL (Dupont) columns in series, 2 mL per minute of a 85 : 15 hexane : tetrahydrofuran solvent mixture, and a UV detector at 230 nm. Structural analysis by NMR spectroscopy was carried out using either a Varian XL-200, XL = 300, GE QE-300 or a Bruker 500. Melting points were determined on a Thomas Hover melting point apparatus and are uncorrected.

## Results and discussion

The hydrosilation of **1** by 1,1,3,3-tetramethyldisiloxane (Scheme 1) in a 2 : 1 molar ratio produces approximately seven mole percent of bicyclo[2.2.1]heptane-

* Reference number with asterisk indicates a note in the list of references.

*endo*-2,3-dicarboxylic anhydride **7**, and approximately seven mole percent of 5,6-*exo*-(1,1,3,3-tetramethyldisiloxane-diyl)bicyclo[2.2.1]heptane-*endo*-2,3-dicarboxylic anhydride **6**, as well as **3**. The distillation of **3** was very difficult even at very low pressures ( < 0.01 mmHg). It could not be crystallized in pure form in good yield.

When the reaction was carried out with equimolar amounts of **1** and 1,1,3,3-tetramethyldisiloxane, the products **5**, **6** and, **7** were formed in the same proportion throughout the course of the reaction. Furthermore, there was almost no **3** formed. Once all of the 1,1,3,3-tetramethyldisiloxane was consumed, only the formation of **3** from **5** was observed. There was no further generation of **6** or **7**.

When the hydrosilation was carried out with the reaction mixture from the synthesis of pentamethyldisiloxane, all of the tetramethyldisiloxane was converted to the products, **5**, **6**, and **7**, before a significant portion of **4** or **3** formed. The ratio of **5**, **6**, and **7** formed was the same as that observed when using pure tetramethyldisiloxane. The production of **3** and **4** occured at the same rate.

Hydrosilation of norbornene is known to be *syn* facial and results in *exo* substitution [6,11]. Hence, the mechanism for formation of **6** is not clear. As seen in Fig. 1, the compound is symmetric. If the isomer resulted via dehydrogenationsilation followed by normal *syn* facial hydrosilation, the strained asymmetric *exo endo* substituted product would be expected. No evidence of a dehydrogenationsilation product could be observed at any time in the reaction by either GC or $^1$H NMR analysis. The other obvious alternatives, *syn* addition with epimerization and disilanation, are not documented for such systems. The formation of disilane platinum species is known [12,13], hence the formation of disilanation and hydrogenation catalysts could account for the formation of **6** and **7**.

In contrast, the hydrosilation with pentamethyldisiloxane proceeded with complete conversion of **1** to **4** as indicated by GC analysis. Upon standing, **4** slowly disproportionated to **3**. When the mixture was kept at room temperature overnight, more than 10% of the mixture was **3** by GC analysis [14–16]. Adding MgO powder to the mixture immediately after the complete conversion of **1** prevented the formation of **3** upon storage. Distillation resulted in pure **4** in high yield.

The trifluoromethanesulfonic acid catalyzed equilibration of **4** to **3** was conveniently carried out without a solvent. The temperature was increased with conversion as the viscosity of the disiloxane mixture increased significantly. Within four hours 98% conversion of **4** to **3** was easily achieved. Although the equilibration could be carried to more than 99.5% **3**, the time required to do so was considerably longer. The addition of a second charge of acid at 98% conversion did not significantly enhance the rate of removal of hexamethyldisiloxane from the mixture. However, the solubility differences of the two disiloxanes was easily exploited for the final purification. The mixture of **3** and **4** was dissolved in an equal proportion of acetone after the addition of MgO to terminate the active species of equilibration. The solution was then filtered and poured into hexane with the selective precipitation of **3**. The remaining acetone: hexane solution contained little **3** by GC analysis, while the fine white precipitate was > 99.5% **3**. A second precipitation gave pure **3** in over 90% yield from **1**.

The acid catalyzed equilibration of **5** did not proceed smoothly to **3**. The equilibration was accompanied by the formation of tri-, tetra-, and pentasiloxanes in addition to the desired product. The catalyst was also deactivated as the reaction progressed. By the introduction of a moist stream of $N_2$ during the reaction the

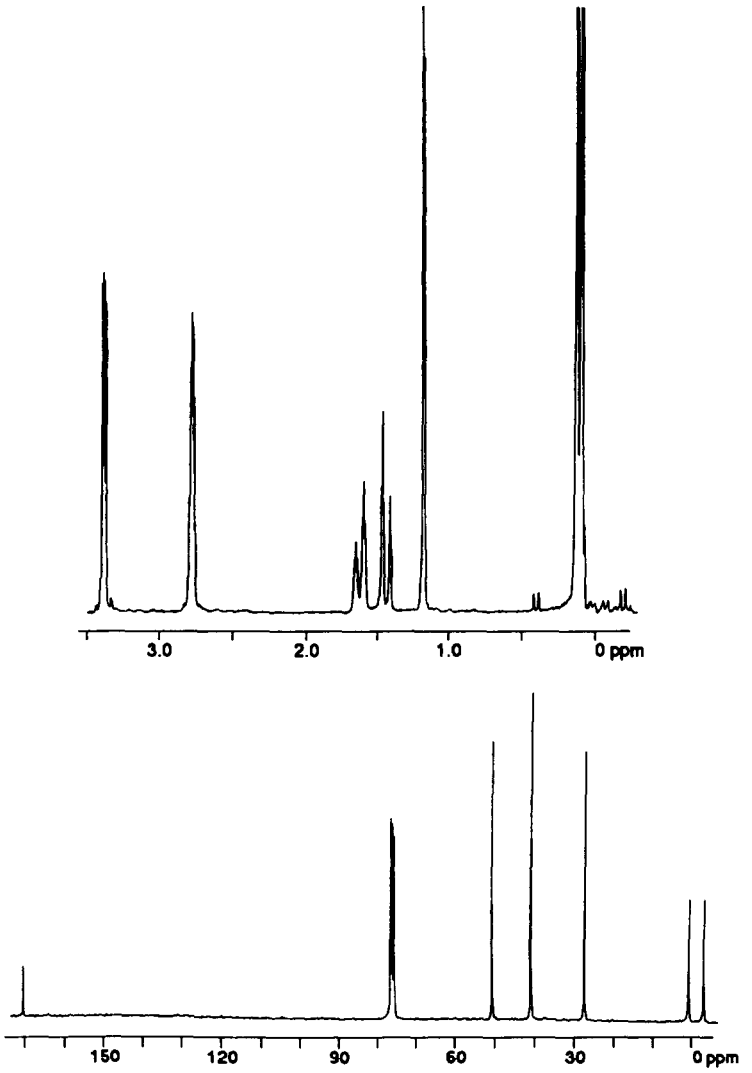



Fig. 1. NMR spectra of **6** in $CDCl_3$. $^1H$ top, $^{13}C$ bottom.

catalytic activity was maintained, however, the formation of higher molecular weight siloxanes increased.

Liquid chromatographic analysis of **3** suggested that two diastereomers were formed in equal proportions. The same mixture resulted when prepared by any of the three synthetic routes. As there was no evidence of diastereomers of **4**, a single mode of hydrosilation was indicated. The observation of two diastereomers of **3** can be attributed to a complete lack of diastereoselectivity in the kinetically controlled dihydrosilation, chlorosilane hydrolysis and condensation, and in the thermodynamically controlled siloxane equilibration. The NMR spectrum was also consistent with two isomers.

The two isomers were isolated in nearly pure form by recrystallization as described in the Experimental Section. The high field $^1H$ NMR spectra of the two

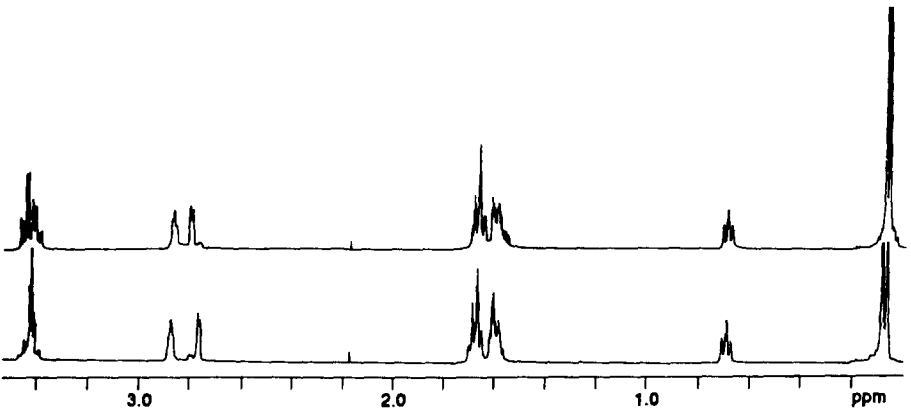
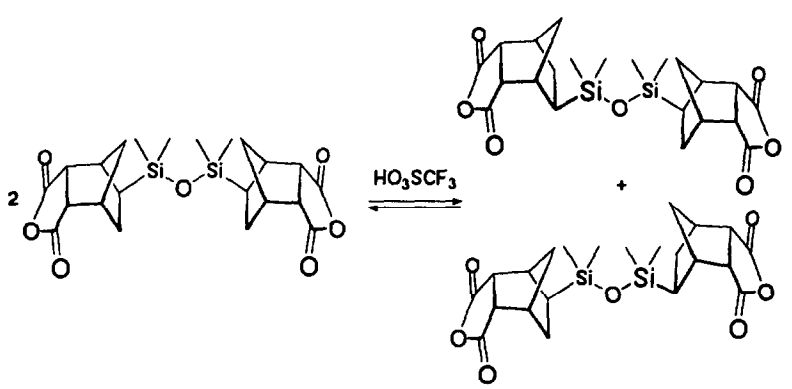



Fig. 2. 500 MHz $^1$H NMR spectra of the isolated diastereomers of **3** in $CDCl_3$. D,L top, *meso* bottom.

separated diastereomers clearly demonstrated that the spectrum of the mixture could be constructed from a mixture of the two isomers (Fig. 2). The single crystal X-ray analysis [10] of the lower melting isomer clearly indicated the presence of two enantiomers in the unit cell where hydrosilation occurred on the *exo* face, and "racemic" stereochemistry exists about the central oxygen. The higher melting isomer was proven to be the *meso* isomer, as it could be converted to the equimolar mixture of diastereomers by the addition of trifluoromethanesulfonic acid (Scheme 4).

In summary, we report a novel synthesis of **3**. This synthesis permits the isolation of the product in pure form via a simple acid catalyzed equilibration of an asymmetric disiloxane, **4**. The hydrosilations of **1** with tetramethyldisiloxane and pentamethyldisiloxane were found to be very different. This method is of potential use in the preparation of any disiloxane where the intermediate assymmetric disiloxane is easily purified and the substituents are inert to strong acids, strong bases, or both. This approach can also be used for the preparation [17] and the characterization [18] of polymers. The disiloxane equilibration reaction was used to aid in the characterization of the product by confirming the identity of the stereoisomeric disiloxanes formed.




Scheme 4. Equilibration of *meso* and D,L-**3**.

## Acknowledgments

We wish to thank S. Danishefski and his associates at Yale University for the 500 MHz NMR spectra. We wish to thank M. Garbauskas for the X-ray structural determination.

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