

After 15 min at 175° with occasional swirling the sublimation tower was separated from the test tube, brought out of the dry-box, allowed to cool, and weighed. The contents were rinsed off the indentations with chloroform and subjected to glc as well as spectral analysis. The melt was allowed to cool, then pulverized and continuously extracted for 24 hr with ether. After 3 × 100 ml water washes the organic layer was dried over magnesium sulfate and concentrated on a Roto-Vap. Whenever 1-Ad-X reacted with the melt a tarry gold substance resulted which proved to be a complex mixture of substituted aliphatic hydrocarbons.

Gaseous products were detected by attaching an evacuated 10-cm Perkin-Elmer demountable gas cell to the sublimation tower via a short length of Tygon tubing. The observed  $\nu_0$  values for hydrogen chloride and carbon monoxide agreed with published data.<sup>22</sup>

**Cyclic Voltammetry.** Cyclic voltammograms were recorded with a PAR Model 170 electrochemistry system. The reference electrode was an aluminum wire (Alfa, m5N) separated from the working and counter electrodes by a fine glass frit. The melt in the reference compartment was saturated with sodium chloride. The working electrode, isolated in its own fritted compartment, was a 30-mil tungsten wire (Alfa, m3N8) sealed into a Pyrex tube with a bead of uranium glass, ground flat on an emery wheel and polished with 600 grit silicon carbide powder. The counter electrode was an aluminum wire.

Cyclic voltammograms were run at approximately 10<sup>-3</sup> M substrate concentrations at 50, 100, 200, and 500 mV/sec.  $E_p$  values are quoted for rates of 200 mV/sec.

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## Silalactones from Hydrosilyl Derivatives of Toluic Acids

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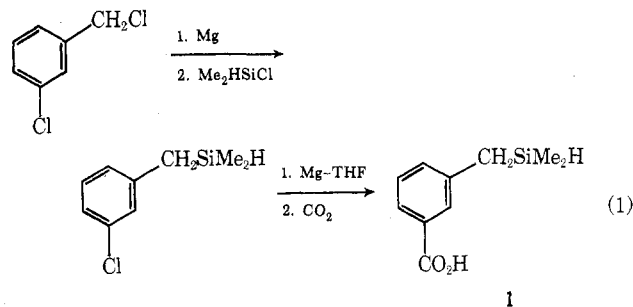
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The preparation of 3- and 4-carboxybenzyl dimethylsilane is reported, along with conversion of the acids under pyrolytic and hydrolytic conditions to dimeric or polymeric silalactones and to silanols and disiloxanes. In some cases, rather complex equilibria involving the various products can be displaced to result in virtually exclusive formation of one product. Of particular interest is a novel macrocyclic lactone dimer in the meta series which can be obtained in good yield. A general method for the preparation of silalactones is proposed, and the monomeric lactone from 2-carboxybenzyl dimethylsilane is reported. Spectral properties of the products are reported and discussed.

The possible interactions between an aromatic ring and a Si atom  $\beta$  to the ring have been the subject of intense investigation in recent years. Two types of interactions have been proposed, first, a 1,3 p-d bonding in which electron density is donated from the phenyl ring to an empty d orbital on Si,<sup>1</sup> and second, a hyperconjugative interaction involving a C-Si  $\sigma$  bond.<sup>2</sup> Either type of interaction could give rise to hindered rotation about the ring to benzyl carbon bond. This restriction to rotation of the side chain could in principle be observed by variable-temperature nmr, since the methylene protons or the methyl groups on silicon would become diastereotopic and potentially distinguishable when an ortho or meta substituent is present. To investigate this possibility, 3-carboxybenzyl dimethylsilane (1) was prepared. The carboxy group was chosen because of its anticipated ease of synthesis and because of the relatively large effects of carbonyl groups on chemical shifts of nearby protons. We chose to study the meta derivative first so that we could be sure that we would not be observing a steric interaction between the carboxyl and silylmethyl groups.

## Results and Discussion

All attempts to prepare 1 by using standard Grignard preparations (eq 1) were unsuccessful. Although there is

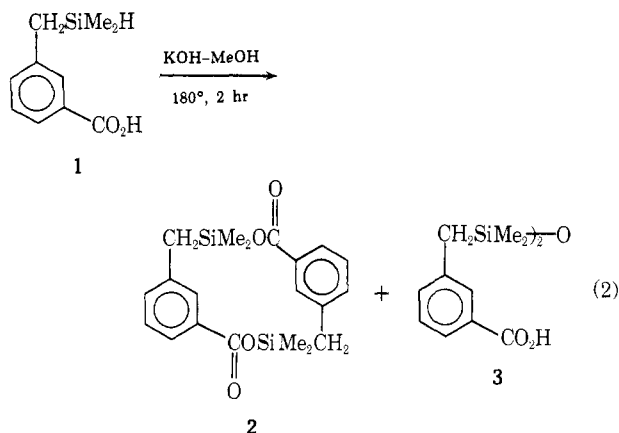


ample precedent for the generation of a C-Mg bond in the presence of a Si-H bond,<sup>3</sup> it is usually necessary to use forcing conditions to generate Grignards from aryl chlorides. Indeed, the only method that resulted in the formation of the Grignard reagent from *m*-chlorobenzyl dimethylsilane involved the use of powdered Mg,<sup>4</sup> prior activation

of the Mg with dibromoethane, high chloride concentrations, and prolonged heating of the reaction mixture. No reaction occurred when Mg turnings were substituted for powdered Mg. This procedure gave a fairly high yield of acid 1 (80–90%)<sup>5</sup> in the crude reaction mixture, indicating no apparent difficulties from involvement of the Si–H bond. However, decomposition of 1 during the vacuum distillation resulted in a lower yield of the pure compound.

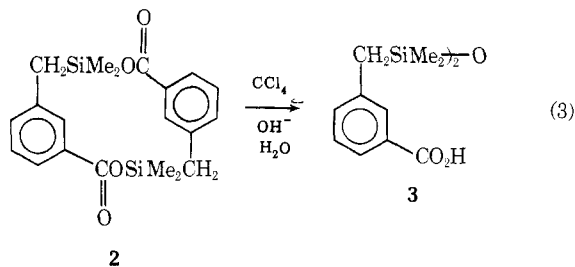
During the distillation of 1 the first time it was prepared, relatively high pot temperatures (>200°) were reached and partial solidification of the pot mixture occurred. On further investigation into the nature of the solid, which showed spectroscopically the absence of a Si–H linkage, we were able to determine that heating acid 1 with base results in formation of a novel silalactone dimer, 2.<sup>6</sup> Several silalactones with silyl ester linkages and one example of a dimer have been reported in the literature;<sup>7–10</sup> however, none have been prepared in this manner. Disilalactone 2 is unusual in several respects. It is the largest dimer reported in the literature, it reacts differently than previously reported silalactones, and it is the only silalactone that contains phenyl groups in the heterocyclic ring. Owing to the novelty of this system, we decided that it merited further study.

In the absence of base, the conversion of acid 1 to disilalactone 2 proceeded very slowly at 180°. Under these conditions, approximately 10% of 1 had been converted to 2 after heating for 4 hr. Upon addition of methanolic KOH, complete conversion of the acid was achieved after heating at 180° for 2 hr.

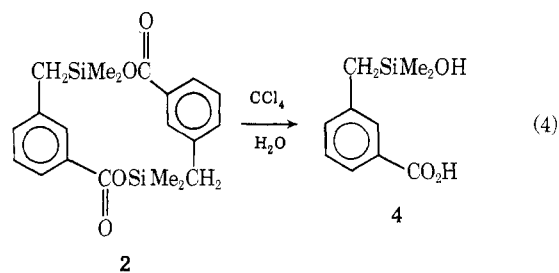


The product mixture contained 78% of 2 and 22% of (3-carboxybenzyl)dimethyldisiloxane (3). The silalactone dimer could be readily purified by subliming it directly from the latter reaction mixture at 170° (0.5 mm). A white, crystalline solid was obtained which became a viscous oil when exposed to atmospheric moisture.

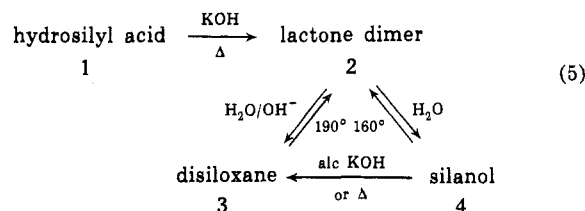
When the reaction mixture from eq 2 was dissolved in hot CCl<sub>4</sub> and exposed to moisture, 3, the disiloxane, crystallized out of the solution (eq 3). This reaction was not surprising, since disiloxanes have been observed to form from silalactones upon the addition of moisture.<sup>7,9</sup> Mironov, *et al.*, also observed that a disiloxane was converted to a silalactone on heating. Indeed, heating compound 3 at



190° for 1 hr gave 20% of the disilalactone with 80% of 3 unconverted. Further heating caused no appreciable change in the composition of the product mixture. Since other workers reported that silalactones could be converted to disiloxanes by moisture alone, the sublimed disilalactone was dissolved in hot CCl<sub>4</sub> and exposed to moisture in the absence of any base. Instead of the expected disiloxane, (3-carboxybenzyl)dimethylsilanol (4), was obtained (eq 4).



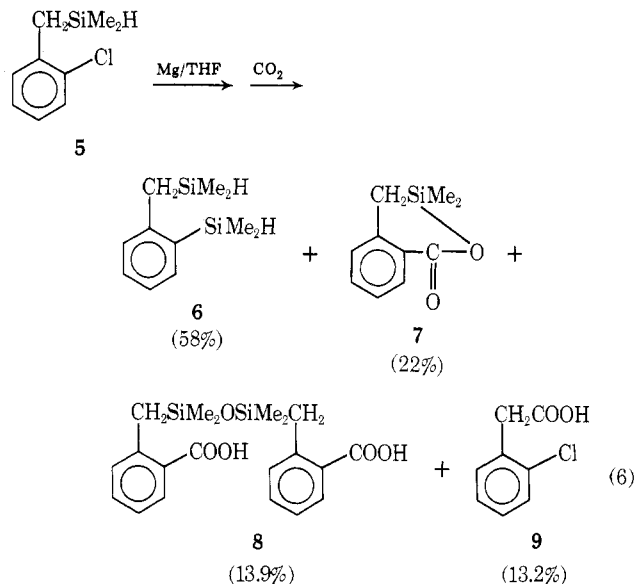
The formation of a silanol from a silalactone has not been previously reported, and we are somewhat surprised at the reluctance of 4 to yield disiloxane in protic media. Silanol 4 did react in the usual manner with base to give disiloxane 3. However, heating the silanol in the absence of base gives disilalactone 2 and disiloxane 3 in approximately equal quantities. The interconversions involving all of the species mentioned so far are summarized in eq 5. The system is, so



far as we are aware, unique in allowing the formation of all of these related compounds under conditions where any one can be obtained as the almost exclusive product by appropriate minor adjustment of reaction conditions.

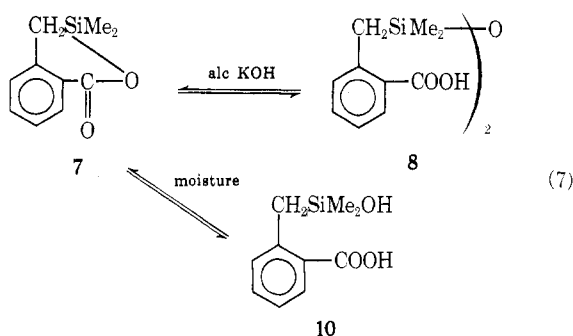
The literature with respect to preparation of  $\omega$ -silalactones is very sparse, and the present work gives promise of affording a general method for their preparation from readily available starting materials. The essence of a preparative method for  $\omega$ -silalactones is the generation of silanol and carboxylic acid functions together; then, if ring size is appropriate, silalactone formation should follow. The present method involves generation of the acid function by a Grignard route in the presence of Si–H, followed by hydrolysis of hydride to silanol. In order to have some evidence of the generality of the synthesis, and also because we were still interested in the spectroscopic properties of the hydroxysilyl acids, we extended our investigations to the corresponding ortho and para derivatives.

*o*-Carboxybenzyl dimethylsilane could be expected to be a precursor for a six-membered ring silalactone or conceivably a 12-membered ring dimer which could be compared with 2. The Grignard reagent of (2-chlorobenzyl)dimethylsilane (5) was prepared using the method developed for compound 1. The usual carbonation and work-up with mild acid hydrolysis gave a crude reaction mixture which apparently, from its nmr spectrum, contained none of the expected *o*-hydroxysilyl acid. Careful fractional distillation afforded the components of the mixture shown in eq 6. The silalactone 7 is obtained (in impure form) on distillation of the reaction mixture which has been subjected to hydrolysis in the presence of mild acid. Such conditions are normally not sufficient to result in Si–H hydrolysis, so that we presume that lactone is formed immediately on carbonation, with carboxylate anion displacing hydride. Simple propinquity



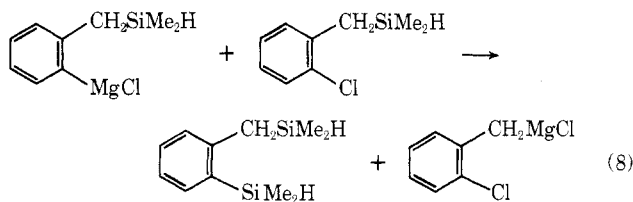
plus the reasonable stability of the silalactone apparently afford sufficient driving force to make the displacement proceed.

Pure disiloxane 8 was obtained only after distillation fractions were extracted with mild base. The yield quoted is derived from nmr spectra of the first distillation products. It is possible that some 8 may have been formed on hydrolysis of 7. Indeed, in a separate experiment, silalactone 7 in CCl<sub>4</sub> was treated with alcoholic KOH to reach an equilibrium mixture containing 7 and 8 in a 5:3 ratio, respectively. Exposing silalactone 7 to moisture gave an equilibrium mixture of 7 and a compound that could not be isolated in pure form but was tentatively identified as (2-carboxybenzyl)dimethylsilanol (10, eq 7). The reactions of



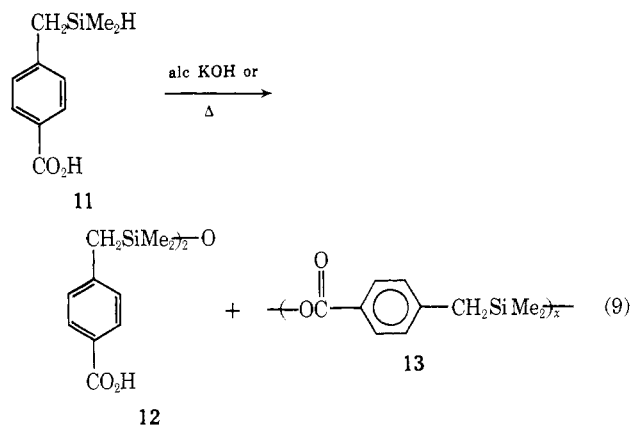
compound 7 were consistent with those observed for the silalactone dimer, 2; however, in contrast to the behavior of 2, 7 reacted more slowly and formed equilibrium mixtures that contained appreciable quantities of itself. The greater stability of 7 is probably due to the favorable six-membered ring geometry, while the macrocycle, 2, is more like a normal silyl ester.

The main product in eq 6 was a considerable surprise. The disilyl derivative, 6, was easily isolated by distillation and identified as the same compound previously prepared<sup>11</sup> by a standard procedure. The disilyl compound was apparently formed when one molecule of Grignard attacked the Si atom of another molecule of starting material, displacing the benzyl anion (eq 8). Cleavage of a benzyl



group from Si by a Grignard reagent has in fact been previously observed.<sup>12</sup> In agreement with eq 8, *o*-chlorophenylacetic acid, the carbonation product from the benzyl fragment, was also isolated. The observation of benzyl anion displacement with the ortho Grignard reagent, but not with the meta reagent, might be attributed to some kind of electronic effect. However, this seems unlikely, particularly since it is also not observed with the para reagent (*vide infra*). Perhaps Grignard and starting chloride complex with one another but only in the case of the ortho derivatives is there a reasonable steric disposition for nucleophilic attack on Si.

The Grignard reagent of *p*-chlorobenzyltrimethylsilane was prepared and carbonated to obtain a good yield of the expected para hydrosilyl acid, 11. This acid could not be anticipated to be the precursor for a monomeric silalactone, and models of the lactone dimer seem significantly strained. When the acid was heated in the presence of alcoholic KOH, a complex product mixture was formed. However, the most prominent Si-Me peak in the nmr spectrum of the mixture was a singlet at  $\delta$  0.4 ppm which (*vide infra*) we tentatively ascribe to a polymeric silyl ester. Also in agreement with this assignment is the observation that the peak eventually disappears on exposure to moisture. When the acid is heated without base, only two main products are formed, which we tentatively identify as polymer and disiloxane (eq 9).



**Spectral Properties.** The nmr spectra of the compounds described are quite simple (see Experimental Section), a fact which made it possible to follow spectrally some of the complex hydrolysis equilibria encountered. In the hydrosilyl acids and their precursors, the Si-H proton appeared with the septet pattern from coupling with Si-Me protons, but further broadened by coupling with the benzylic protons. Disappearance of the Si-H signal was one major clue to the transformations taking place. The lactone dimer<sup>12</sup> had several notable features. As is well known and was observed throughout our series of compounds, aromatic protons ortho to a carbonyl function are shifted downfield. The dimer 2, however, showed a resonance even further downfield in the aromatic region ( $\delta$  8.4) which we assign to the aromatic proton contained in the heterocyclic ring. Models indicate that this proton can come quite near the aromatic nucleus across the ring, thus being further deshielded. The second feature of interest in 2 is the chemical shift of the Si-Me protons. At  $\delta$  0.4 they are substantially further downfield than the Si-Me protons of the silanol 4 ( $\delta$  0.2), or disiloxane 3 ( $\delta$  0.1), which also have Si attached to oxygen.<sup>13</sup> We suggest that this chemical shift will be found to be characteristic of Si-Me protons in silyl esters, as an identical position is observed for the ortho silalactone 7. The Si-Me chemical shift also serves as one basis for our assignment of the polymeric silyl ester structure to

the product, **13**, of pyrolysis of the para hydrosilyl acid **11**.

Determination of the variable-temperature nmr spectral properties of the meta hydrosilyl acid **1** was one of the original goals of the research. At temperatures as low as  $-80^{\circ}$  in acetone- $d_6$ , however, no splitting of either benzylic or Si-Me signals could be observed. The observation is, of course, no direct proof against the existence of a hyperconjugative or other interaction. We simply cannot see evidence of one in this system using this technique.

We have not yet been able to obtain good mass spectra of all of the products identified, but both lactone dimer **2** and lactone **7** gave spectra in which the parent peak is prominent. The tentatively identified silanol, **10**, and the disiloxane, **8**, in the ortho series both gave mass spectra essentially identical with that of the lactone **7**, indicating quite facile dehydration, perhaps occurring thermally, prior to ionization. The disiloxane in the para series, **12**, also shows the fragment at  $m/e$  192,  $O_2CC_6H_4CH_2SiMe_2$ , and this peak grows as inlet temperature is raised, again indicating the possibility of pyrolysis.

### Experimental Section

Unless otherwise stated, all Grignard reagents were prepared in three-neck round-bottom flasks equipped with a reflux condenser, a magnetic stirrer, and an addition funnel. The glassware was flame dried and flushed with nitrogen prior to conducting the reaction under a nitrogen atmosphere. Tetrahydrofuran (THF) was dried by distilling from calcium hydride and then shaking with Linde 5A molecular sieves. The low-temperature nmr study was run on a Varian HA-100 and routine nmr spectra were recorded using a Varian A-60A spectrometer. Chemical shifts reported are relative to internal TMS. Infrared spectra were obtained using a Perkin-Elmer 137 Infracord spectrophotometer. Mass spectra were obtained using a Hitachi Perkin-Elmer RMS-4 mass spectrometer operating at 70 eV, and data are reported as  $m/e$  (relative intensity). Melting points are corrected.

**Preparation of (3-Carboxybenzyl)dimethylsilane (1).** Magnesium powder (0.16 mol, 3.9 g) and 50 ml of dry THF were placed in a round-bottom flask. The magnesium was activated by the addition of 1 ml of dibromoethane and refluxing for 15 min. (3-Chlorobenzyl)dimethylsilane (0.11 mol, 20.4 g) was added dropwise while refluxing the reaction mixture. An additional 25 ml of dry THF was added to the reaction vessel about 4 hr later. After refluxing for 24 hr, the Grignard reagent was poured into a slurry of Dry Ice in 50 ml of THF and stirred with a mechanical stirrer until the Dry Ice had sublimed. The organic layer was then hydrolyzed with dilute HCl, separated, and washed with  $H_2O$ . The solvent was removed using a rotary evaporator. Dry ether (25 ml) was added to the remaining material and this solution was dried over anhydrous  $MgSO_4$  for several hours. The solvent was removed and the remaining material was vacuum distilled to yield 9.55 g (31%) of **1**: bp  $109-110^{\circ}$  (0.3 mm); nmr ( $CCl_4$ )  $\delta$  0.05 (d,  $J = 4$  Hz, 6 H), 2.15 (d,  $J = 3$  Hz, 2 H), 3.9 (broadened septet, 1 H), 7.2-7.8 (m, 4 H), 11.7 (s, 1 H); ir (neat) 3000, 2600, 2100, 1675, 1600, 1400, 1260, 1240, 1200, 1150, 1060, 900, 850, 820, 780, 760, 750, and  $680\text{ cm}^{-1}$ . Anal. Calcd for  $C_{10}H_{14}SiO_2$ : C, 61.81; H, 7.26. Found: C, 61.81; H, 7.38.

**Preparation of Silalactone Dimer (2).** (3-Carboxybenzyl)dimethylsilane (0.0078 mol, 1.52 g) and 0.6 ml of 0.46 M KOH in anhydrous methanol were placed in a round-bottom flask and heated at  $170^{\circ}$  for 2 hr under a nitrogen atmosphere. An nmr spectrum indicated that approximately 78% of the acid had been converted to the disilalactone. The disilalactone was then sublimed from the product mixture at  $170^{\circ}$  (0.5 mm) to yield 1.00 g (67%) of **2**: mp  $152-155^{\circ}$ ; nmr ( $CDCl_3$ )  $\delta$  0.4 (s, 6 H), 2.4 (s, 2 H), 7.2-7.5 (m, 2 H), 7.7-8.0 (m, 1 H), 8.4 (s, 1 H); ir (Nujol) 1600, 1280, 1240, 1210, 1110, 1080, 930, 920, 840, 815, 790, 775, 755, and  $690\text{ cm}^{-1}$ ; mass spectrum  $m/e$  (rel intensity) 384 (30), 192 (18), 179 (13), 165 (14), 149 (18), 119 (16), 118 (70), 90 (100), 89 (25). Anal. Calcd for  $C_{20}H_{24}Si_2O_4$ : C, 62.46; H, 6.29. Found: C, 62.30; H, 6.37.

**Preparation of (3-Carboxybenzyl)dimethylsilanol (4).** The purified silalactone dimer obtained in the previous procedure was dissolved in hot  $CCl_4$  and left open to atmospheric moisture.<sup>14</sup> After 2 days, the silanol, a white, fluffy solid, precipitated from the solution. An nmr spectrum indicated that greater than 95% of the disilalactone had been converted to the silanol. The silanol was re-

crystallized from hot  $CHCl_3$  to give 0.6 g (50%) of **4**: mp  $115-117^{\circ}$ ; nmr ( $CDCl_3$ )  $\delta$  0.2 (s, 6 H), 2.3 (s, 2 H), 6.8 (s, 2 H), 7.2-7.4 (m, 2 H), 7.7-7.9 (m, 2 H); ir (Nujol) 3300, 2800, 2700, 1650, 1600, 1350, 1150, 1125, 1060, 1050, 900-750, and  $680\text{ cm}^{-1}$ . Anal. Calcd for  $C_{10}H_{14}SiO_3$ : C, 57.11; H, 6.71. Found: C, 56.96; H, 6.80.

**Preparation of (3-Carboxybenzyl)dimethyldisiloxane (3).** (3-Carboxybenzyl)dimethylsilane (1.27 g, 0.0067 mol) and 0.4 ml of 0.46 M potassium hydroxide in anhydrous methanol were placed in a round-bottom flask. The mixture was heated at  $166^{\circ}$  for 3 hr. The product mixture was then dissolved in hot  $CCl_4$  and left open to moisture. After 2 days, the disiloxane, a white, crystalline solid, precipitated from the solution. An nmr indicated that greater than 95% of the disilalactone had been converted to the disiloxane. After recrystallization from hot  $CCl_4$ , 0.70 g (54%) of pure disiloxane, mp  $143-145^{\circ}$ , was collected: nmr ( $CDCl_3$ )  $\delta$  0.1 (s, 6 H), 2.2 (s, 2 H), 7.2-7.4 (m, 2 H), 7.7-7.9 (m, 2 H), 10.2 (s, 1 H); ir (Nujol) 2800, 2600, 1650, 1575, 1400, 1260, 1240, 1200, 1150, 1060, 950, 900, 840-780, 750, and  $685\text{ cm}^{-1}$ . Anal. Calcd for  $C_{20}H_{26}Si_2O_5$ : C, 59.67; H, 6.51. Found: C, 59.22; H, 6.53.

**Preparation of (2-Chlorobenzyl)dimethylsilane (5).** Magnesium turnings (0.68 mol, 16.5 g) and 400 ml of dry ether were placed in a round-bottom flask. The magnesium was activated by the addition of 2 ml of dibromoethane and stirring for 15 min. A mixture of 2-chlorobenzyl chloride (0.62 mol, 98.5 g) and 400 ml of dry ether was added dropwise. After all of the mixture had been added, the solution was refluxed for 1 hr. The Grignard reagent was then added dropwise to a mixture of dimethylchlorosilane (0.62 mol, 60.2 g) and 200 ml of dry ether. After the addition was completed, the solution was refluxed for 2 hr. The solution was then hydrolyzed with dilute HCl, separated, and washed with  $H_2O$ . The organic layer was dried over anhydrous  $MgSO_4$ , and then the ether was removed using a rotary evaporator. The remaining material was vacuum distilled to yield 67.6 g (59%) of **5**: bp  $59^{\circ}$  (2 mm); nmr ( $CCl_4$ )  $\delta$  0.0 (d,  $J = 4$  Hz, 6 H), 2.25 (d,  $J = 3$  Hz, 2 H), 3.95 (broadened septet, 1 H), 6.8-7.3 (m, 4 H); ir (neat) 3000, 2130, 1470, 1440, 1250, 1220, 1160, 1050, 1030, 900, 840, 785, 770, 750, 700  $cm^{-1}$ . Anal. Calcd for  $C_9H_{13}SiCl$ : C, 58.51; H, 7.09; Si, 15.20. Found: C, 58.27; H, 7.12; Si, 15.15.

**Preparation of  $\alpha,\alpha$ -Bis(dimethylsilyl)toluene (6).** The preparation was accomplished by using the procedure outlined in the preparation of (3-carboxybenzyl)dimethylsilane. The product was vacuum distilled to yield 7.46 g (65%) of **6**: bp  $57^{\circ}$  (0.3 mm); nmr ( $CCl_4$ )  $\delta$  0.0 (d,  $J = 4$  Hz, 6 H), 0.25 (d,  $J = 4$  Hz, 6 H), 2.25 (d,  $J = 3$  Hz, 2 H), 3.95 (broadened septet, 1 H), 4.55 (septet,  $J = 3$  Hz, 1 H), 6.8-7.4 (m, 4 H); ir (neat) 3000, 2150, 1600, 1460, 1450, 1260, 1200, 1150, 1120, 900, 840, 790, 750, 715,  $680\text{ cm}^{-1}$ . Anal. Calcd for  $C_{11}H_{20}Si_2$ : C, 63.38; H, 9.67; Si, 26.95. Found: C, 63.43; H, 9.61; Si, 27.04.

The residue from the vacuum distillation was further distilled at  $85-105^{\circ}$  (0.3 mm) and three fractions were collected. The fraction collected at  $85-95^{\circ}$  was dissolved in ether and washed twice with 5%  $NaHCO_3$ . The ether layer was dried over anhydrous  $MgSO_4$  and the ether was evaporated. The residue was vacuum distilled at  $91^{\circ}$  (0.3 mm) to yield pure lactone **7**: nmr ( $CDCl_3$ )  $\delta$  0.4 (s, 6 H), 2.31 (s, 2 H), 7.1-7.5 (m, 3 H), 8.0-8.4 (m, 1 H); mass spectrum  $m/e$  (rel intensity) 192 (25), 133 (74), 118 (67), 90 (100), 89 (68), 63 (20). Anal. Calcd for  $C_{10}H_{12}SiO_2$ : C, 62.45; H, 6.29. Found: C, 62.65; H, 6.14.

The fraction collected at  $100-105^{\circ}$  was dissolved in ether and washed twice with 5%  $NaHCO_3$  solution. The aqueous layer was acidified and washed with ether. The ether was removed and the residue was recrystallized from an ethanol-water solution, and a white powder precipitated that was identified as disiloxane **8**: mp  $87-89^{\circ}$ ; nmr ( $CDCl_3$ )  $\delta$  0.0 (s, 6 H), 2.8 (s, 2 H), 7.0-8.2 (m, 4 H), 9.5 (s, 1 H). Anal. Calcd for  $C_{20}H_{26}Si_2O_5$ : C, 59.67; H, 6.51. Found: C, 59.92; H, 6.75.

The filtrate from the previous crystallization was washed with ether. The ether solution was concentrated and petroleum ether was added until the solution became cloudy. A white crystalline precipitate was collected and identified as (*o*-chlorophenyl)acetic acid (**9**): mp  $94-96^{\circ}$ ; nmr ( $CDCl_3$ )  $\delta$  3.85 (s, 2 H), 7.2-7.5 (m, 4 H), 11.4 (s, 1 H); mass spectrum  $m/e$  (rel intensity) 172 (18), 170 (51), 135 (69), 127 (35), 125 (100), 91 (61), 90 (22), 89 (31).

**Preparation of (4-Carboxybenzyl)dimethylsilane (11).** The preparation was accomplished using the procedure outlined in the preparation of **1**. The product was obtained by dissolving the reaction mixture in diethyl ether, adding petroleum ether until the solution became cloudy, and then cooling. The product precipitated as a white, fluffy solid to yield 16.49 g (78%): mp  $121-124^{\circ}$ ; nmr ( $CDCl_3$ )  $\delta$  0.05 (d,  $J = 4$  Hz, 6 H), 2.3 (d,  $J = 3$  Hz, 2 H), 3.9

(broadened septet, 1 H), 7.1–7.4 (m, 2 H), 7.9–8.2 (m, 2 H), 12.1 (s, 1 H); ir (Nujol) 3000, 2100, 1700, 1630, 1430, 1310, 1290, 1250, 1220, 1190, 1080, 950, 900, 870, 840, 750  $\text{cm}^{-1}$ . *Anal.* Calcd for  $\text{C}_{10}\text{H}_{14}\text{SiO}_2$ : C, 61.81; H, 7.26. Found: C, 61.71; H, 7.12.

**Preparation of (4-Carboxybenzyl)dimethyldisiloxane (12).** (4-Carboxybenzyl)dimethylsilane (0.87 g, 0.0046 mol) and 0.4 ml of 0.46 M KOH in anhydrous methanol were placed in a round-bottom flask. The mixture was heated at 150° for 1 hr. An nmr of the mixture indicated that about 50% of the acid had reacted. The reaction mixture was dissolved in ether and exposed to moisture for a few days. Petroleum ether was added to the ether solution until the solution became cloudy. A powdery precipitate was collected. The filtrate was concentrated and the disiloxane precipitated from solution yielding 0.1 g (10%) of pure product, mp 108–110°, after several recrystallizations: nmr (acetone- $d_6$ )  $\delta$  0.0 (s, 6 H), 2.0 (s, 2 H), 6.1 (s, 1 H), 7.0–7.2 (m, 2 H), 7.7–8.0 (m, 2 H). *Anal.* Calcd for  $\text{C}_{20}\text{H}_{26}\text{O}_5\text{Si}_2$ : C, 59.67; H, 6.51. Found: C, 59.63; H, 6.72.

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**Registry No.**—1, 51801-42-4; 2, 51801-43-5; 3, 51801-44-6; 4, 51801-45-7; 5, 51801-46-8; 6, 17867-29-7; 7, 51801-47-9; 8, 51801-48-0; 9, 2444-36-2; 11, 51801-49-1; 12, 51801-50-4; (3-chlorobenzyl)dimethylsilane, 27856-35-5; 2-chlorobenzyl chloride, 611-19-8; dimethylchlorosilane, 1066-35-9; (4-chlorobenzyl)dimethylsilane, 27856-36-6.

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- This feature of the nmr spectrum of **2**, along with the absence of the very characteristic Si–O–Si band in the infrared spectrum of **2**, led us to exclude the possibility that **2** could be the isomeric disiloxy anhydride.
- The reaction occurred during a period of very high humidity. With lower humidity, the dimer (**2**) may precipitate from solution.

