6314 *J. Org. Chem.* 1993, *58*, 6314-6318

Silanol Reactivity: Evaluation of Silanolate as a Metalation-Directing Group

Scott McN. Sieburth* and Louis Fensterbank

Department of Chemistry, State University of New York at Stony Brook,
Stony Brook, New York 11794-3400

Received June 29, 1993[*]

Alkali metal salts of dimethylarylsilanol and di-*tert*-butylphenylsilanol were treated with organometallic reagents to determine the viability of silanolates as ortho-metalation-directing groups. When dimethylphenylsilanol was treated with an excess of *n*-butyllithium, metalation was not observed. Heating these reactions led to substitution of the methyl and phenyl groups on silicon by *n*-butyl groups. When a *m*-methoxy group was present, metalation of the aromatic ring was observed between the two substituents. The more hindered di-*tert*-butylphenylsilanol was inert to excess *n*-butyllithium, but treatment of the potassium salt of this silanol with *n*-butyllithium results in metalation largely at the meta and para positions, with only traces of ortho products. Calculated deprotonation enthalpies of arylsilanes using AM1 can explain some of the observed acidities from this study as well as observations made in a related study of arylsilane metalation by Schlosser et al.

Metalation of organic compounds through complex-induced proximity effects[1] has become a prominent synthetic method.[2,3] Many functional groups, including amides, amines, alcohols, ethers, halogen, and oxazolines, have been reported to be ortho-metalation directors and a number of studies have ranked their directing effects.[2] We sought to define a new metalation-directing group, one that could be easily introduced and then easily removed.[4] Ideally this group could be introduced via an aryllithium and would provide a method for "walking" a site of metalation around an aromatic ring (Figure 1).

With the criteria that this metalation-directing group be removable, an organosilane was a clear choice. Trimethylsilyl groups have been routinely used in metalation sequences as an acid or fluoride-labile group for blocking an undesired site of metalation,[5] and simple attachment of a ligating substituent on silicon might be expected to change this blocking group into a metalation director. Ideally, this substituted silicon group would be readily available, stable to metalation conditions, and compatible with use in a single-operation reaction sequence.

With this stringent set of requirements in mind, we focused on dimethylsilanolate (Me$_2$SiO$^-$, e.g. 1). This unit contains a ligating oxy anion and would mimic the metalation-directing hydroxymethyl group (2).[6] It also seemed plausible that the oxy anion would inhibit nucleophilic attack at silicon. At the inception of this project, the only study of arylsilane metalation was a short report from Gilman concerning triphenylsilanol[7] in which metalation was not observed (vide infra). Whereas the most powerful metalation-directing groups are inductively electron withdrawing, an organosilane metalation-directing group would be uniquely electropositive. Metalation directors derived from other second row elements have been described (sulfones, sulfonates, and phosphonates, and their amides), however these are all inductively electron-withdrawing groups.[8] Nevertheless, even when the inductive effect of a ligating group is insulated from the aromatic ring by saturated carbon atom(s), as in the case of (dimethylamino)methyl and 2-(dimethylamino)ethyl, the group can still be a strong metalation director.[9] It therefore seemed plausible that the electropositive nature of a silicon could be superseded by proximity effects. Recent studies by Schlosser[10] and Tamao[11] have provided additional data on these points and these are discussed below.

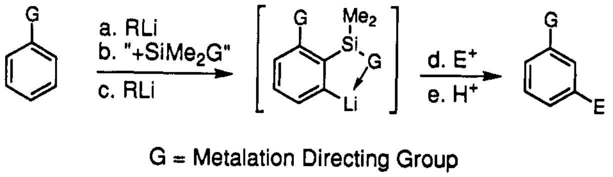
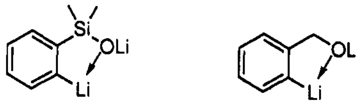


Figure 1. A functionalized silicon could serve as a removable metalation-directing group.



1 2

Figure 2. Proposed silanolate metalation director 1 and the known metalation director 2.

Results and Discussion

Attachment of the Silanolate Group. Critical to the proposed chemistry in Figure 1 was the ready introduction of the silanolate group. A simple method for this trans-

---

[*] Abstract published in *Advance ACS Abstracts*, October 1, 1993.

(1) Beak, P.; Meyers, A. I. *Acc. Chem. Res.* 1986, *19*, 356-363.

(2) Snieckus, V. *Chem. Rev.* 1990, *90*, 879-933.

(3) Gschwend, H. W.; Rodriguez, H. R. *Org. React.* (*N.Y.*) 1979, *26*, 1-360.

(4) Figuly, G. D.; Martin, J. C. *J. Org. Chem.* 1980, *45*, 3728-3729.

(5) Mills, R. J.; Taylor, N. J.; Snieckus, V. *J. Org. Chem.* 1989, *54*, 4372-4385.

(6) Gilman, H.; Brown, G. E.; Webb, F. J.; Spatz, S. M. *J. Am. Chem. Soc.* 1940, *62*, 977-979. Meyer, N.; Seebach, D. *Angew. Chem. Int. Ed. Engl.* 1978, *17*, 521-522. Perozzi, E. F.; Martin, J. C. *J. Am. Chem. Soc.* 1979, *101*, 1591-1593. Meyer, N.; Seebach, D. *Chem. Ber.* 1980, *113*, 1304-1319.

(7) Gilman, H.; Benkeser, R. A.; Dunn, G. E. *J. Am. Chem. Soc.* 1950, 72, 1689-1691.

(8) Bowden, K. In *Comprehensive Medicinal Chemistry*; C. Hansch, Ed.; Pergamon: New York, 1990; Vol. 4, pp 205-239.

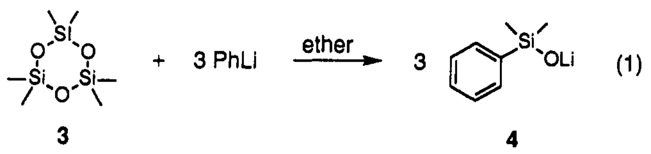
(9) Simig, G.; Schlosser, M. *Tetrahedron Lett.* 1988, *29*, 4277-4280.

(10) Schlosser, M.; Choi, J. H.; Takagishi, S. *Tetrahedron* 1990, *46*, 5633-5648.

(11) Tamao, K.; Yao, J.; Tsutsumi, Y.; Abe, H.; Hayashi, T.; Ito, Y. *Tetrahedron Lett.* 1990, *31*, 2925-2928.

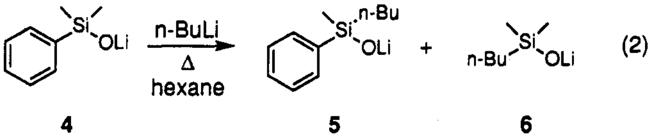
0022-3263/93/1958-6314$04.00/0

formation was found in the work of Ruidisch and Schmidt[12] who reported that treatment of polymeric dimethylsiloxanes with methyllithium gave lithium trimethylsilanolate. We have found that aryllithium reagents can also be used in place of methyllithium (eq 1). For example, reaction of the commercially available hexamethylcyclotrisiloxane **3** with 3 equiv of phenyllithium results in the quantitative formation of lithium dimethylphenylsilanolate **4**. A comprehensive study of this chemistry will be reported separately.[13] This simple, high-yield method for the preparation of **4** set the stage for silanolate metalation studies.



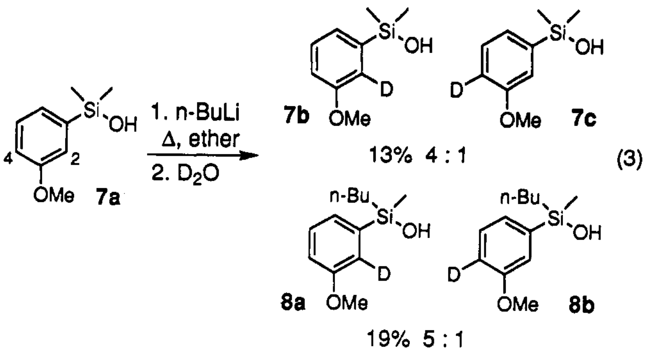
Reaction of Dimethylphenylsilanolate with Lithium Reagents. A wide range of conditions for metalation of **4** were examined. Generally, dimethylphenylsilanol in an appropriate solvent (hexane, ether, THF) at 0 °C was treated with 2–10 equiv of a lithium reagent (*n*-butyllithium, *sec*-butyllithium, *tert*-butyllithium), with and without the addition of TMEDA, and then stirred at ambient temperature for periods up to several days. After addition of an electrophile (Me_3SiCl, Me_2S_2, CO_2, PhCHO), the only silicon-containing product was the starting silanol or the siloxane derived from self-condensation (formed during workup). No evidence could be formed for metalation of the aromatic ring or the methyl groups on silicon.

Several analogous reactions were heated to reflux for periods ranging from hours to days. Following addition of an electrophile, several new species were found, however these products did not result from metalation of **4**, but from substitution of a phenyl or methyl group on silicon with an *n*-butyl group (eq 2). Adducts derived from reaction of phenyl and methyl anions with the added electrophiles were also isolated. Once again, metalation of the methyl groups on silicon was not observed.



Attempts to employ Lochmann–Schlosser conditions,[14] by addition of potassium *tert*-butoxide or initial deprotonation of the silanol with potassium hydride (see below), also gave attack at silicon without formation of metalation products.

Metalation with a *m*-Methoxy Substituent. The effect of a second metalation-directing substituent at the meta position is normally cooperative and results in metalation between metalation-directing groups.[2,3] We therefore treated 3-methoxy silanol **7a** with *n*-butyllithium in ether at reflux followed by quenching with D_2O (eq 3). Several products were formed and these were purified by column chromatography. In addition to products derived from loss of the phenyl group (13%), two deuterated arylsilanes were isolated. These two products were determined to be dimethyl-(3-methoxyphenyl)silanol (**7**) (13%) and *n*-butyl-(3-methoxyphenyl)methylsilanol (**8**) (19%), the latter resulting from replacement of a methyl group in **7** with an *n*-butyl group. The mass spectrum of both of these compounds showed greater than 95% incorporation of deuterium, and the MS fragmentation placed the position of deuteration on the aromatic ring. The proton NMR, in which each of the aromatic protons are clearly resolved, allowed the determination of the two sites of deuteration as well as an estimate of their ratio. For both products **7** and **8**, protons at C2 and C4 of the aromatic ring were reduced in size. The residual protons at C2 lacked the meta coupling found in **7a**, indicating deuterium incorporation at C4. Similarly, residual protons at C4 showed only ortho coupling, indicating deuterium at C2. For both **7** and **8**, 80–85% of the deuterium was incorporated at C2 between the two groups (**7b**, **8a**). These results are quite similar to metalation results reported for 3-methoxybenzyl alcohol[15] and indicate that the silanol can perform as a metalation-directing group despite the susceptibility of silanolate to nucleophilic attack.



Reaction of Di-*tert*-butylphenylsilanolate with Lithium Reagents. To inhibit substitution at silicon, di-*tert*-butylphenylsilanol (**9a**) was examined. Treatment of **9a** with an excess of *n*-butyllithium or *tert*-butyllithium in hexane, at ambient temperture or at reflux followed by quenching with CO_2, gave only recovered silanol. Utilizing the potassium salt, however, proved to be more interesting. Deprotonation of the silanol in hexane with potassium hydride was followed by addition of *n*-butyllithium. The resulting mixture was then stirred overnight at ambient temperature to give a tan suspension. Carboxylation[16] and esterification[17] gave a 1% yield of silalactone **10**, a 44% yield of methyl benzoates **11** and **12** (in a ratio of 1.7:1), and a 42% recovery of silanol **9a**. The suspended solid formed during this metalation was found to be the metalated intermediate: on settling, the supernatant gave only silanol **9a** and valeric acid (derived from *n*-butyllithium or *n*-butylpotassium) whereas the solids gave **11** and **12**. Performing this metalation reaction at reflux consumed more of starting silanol **9a** but did not yield additional **10**–**12**. Instead, new products resulting from dimetalation of **9** were found (eq 4).

Metalation of Aryltrialkylsilanes. Our results complement the metalation studies of Schlosser et al.[10] with aryltrialkylsilanes. They found that phenyltriisopropyl-

---

[12] Ruidisch, I.; Schmidt, M. *Angew. Chem. Int. Ed. Engl.* **1963**, *2*, 328.

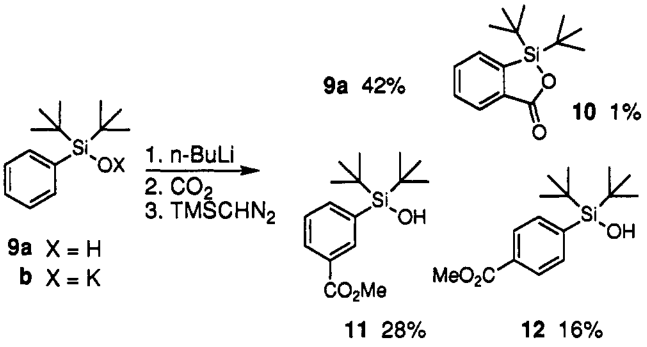
[13] Sieburth, S. McN.; Mu, W. *J. Org. Chem.*, in press.

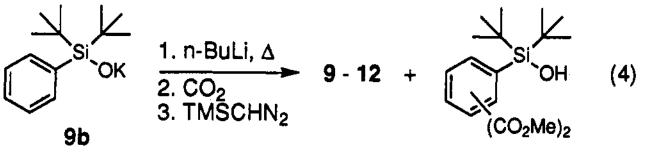
[14] Schlosser, M. *Pure Appl. Chem.* **1988**, *60*, 1627–1634. Bauer, W.; Lochmann, L. *J. Am. Chem. Soc.* **1992**, *114*, 7482–7489.

[15] Uemura, M.; Tokuyama, S.; Sakan, T. *Chem. Lett.* **1975**, 1195–1198.

[16] Brandsma, L. *Preparative Polar Organometallic Chemistry*; Springer-Verlag: New York, 1990; Vol. 2.

[17] Hashimoto, N.; Aoyama, T.; Shioiri, T. *Chem. Pharm. Bull.* **1981**, *29*, 1475–1478.





(4)

silane was more difficult to metalate than benzene itself. Metalation with the "LiCKOR" mixture of potassium *tert*-butoxide and *n*-butyllithium[10] gave metalation only at the meta and para positions, favoring the latter and suggesting that silicon was inductively deactivating. Under comparable conditions, metalation of di-*tert*-butylsilanolate **9b** (eq 3) yields a more statistical ratio of meta and para products that suggests that the silanolate group may be less deactivating than the trialkylsilanes. Interestingly, Schlosser also reported that the methyl groups of phenyltrimethylsilane are rapidly metalated,[18] whereas we have not observed methyl metalation with silanolates.

The Ligating Substituent. Ortho metalation with a silicon-directing group has recently been achieved by Tamao et al.[11] (Figure 3). This metalation required ethylenediamine ligands on silicon, and appropriate substitution of the diamine was critical. The deprotonation of methyl groups on silicon was a complicating feature,[18] although the use of *tert*-butyllithium minimized this pathway.

Substitution Reactions at Silicon. We are aware of two other reports describing substitution of organic groups on a silanolate by lithium reagents. As with the chemistry outlined in eq 2, these substitutions occurred in refluxing solvent. Gilman[7] found that treatment of triphenylsilanol with 3 equiv of *n*-butyllithium precipitated lithium triphenylsilanolate. Heating the suspension to reflux followed by addition of CO_2 gave only benzoic acid and *n*-butyldiphenylsilanol. Frye et al.[19] described a similar transformation for lithium *n*-butyldimethylsilanolate with excess *n*-butyllithium. In hexane at reflux, formation of lithium di-*n*-butylmethylsilanolate and methyllithium was observed.

Substitution of *n*-butyl for phenyl or methyl (eq 2) is presumably a metal exchange-like process that occurs through nucleophilic attack at silicon to give a dianionic, pentavalent silicon intermediate (or transition state) which then expels one of the four organic substituents. While many pentavalent silicon molecules are known,[20] species with more than two silicon–carbon bonds are rare.[21]

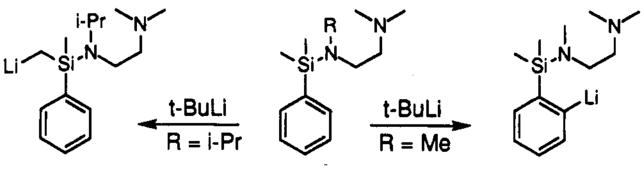
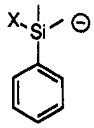
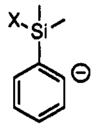
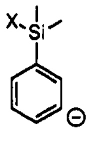
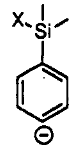


Figure 3. Tamao's metalation-directing silane.[11]

Table I. Relative Enthalpies of Deprotonation, in kcal/mol, Calculated Using AM1

entry	X				
1	CH_3	0	6.4	11.9	10.4
2	OH	0	6.1	15.8	14.0
3	$O^{\ominus}$	20.3	9.0	2.3	0
4	ONa	8.7	3.2	0.6	0
5	OLi	0	2.8	4.8	2.9
6	OLi_2	11.0	0	7.1	6.8

Enthalpies of Deprotonation. To gain further insight into the deprotonation of aryl silanes, the enthalpies of deprotonation for several arylsilanes were calculated using AM1.[22] Dewar and Dieter[23] and Meot-Ner and Kafafi[24] have shown that AM1 can reproduce experimentally determined acidities. The *relative* enthalpies for a series of arylsilanes, with the most acidic position defined as zero, are listed in Table I. The calculated results for phenyltrimethylsilane (entry 1) compare favorably with the empirical results for phenyltrimethylsilane and phenyltriisopropylsilane. Methyl groups are much more acidic than the aromatic protons, as was found for phenyltrimethylsilane.[10] The relative enthalpies of the meta and para positions clearly favor the latter as reported by Schlosser et al. for phenyltriisopropylsilane.[10] Ortho positions are calculated to be more acidic than the other ring positions, and in this case the bond from the silicon to the aromatic ring is distorted, a deformation that brings the electropositive silicon closer to the anion.[25] Replacement of a methyl group with a hydroxyl group leads to the same rank ordering of acidities (entry 2).

Attaching a negatively charged oxygen to silicon (entry 3) does not yield useful calculated acidities, as the calculated enthalpies clearly reflect the charge proximity: the greatest distance between charges yielding the most stable dianion. To circumvent this problem, counterions

---

[18] For other examples of methylsilane deprotonation see: Imanieh, H.; Quayle, P.; Voaden, M.; Conway, J.; Street, S. D. A. *Tetrahedron Lett.* **1992**, *33*, 543–546. Hosomi, A.; Kohra, S.; Tominaga, Y.; Shoji, M.; Sakurai, H. *Chem. Pharm. Bull.* 1987, *35*, 1663–1665. Macdonald, J. E.; Poindexter, G. S. *Tetrahedron Lett.* **1987**, *28*, 1851–1852. Friesen, R. W.; Sturino, C. F.; Daljeet, A. K.; Kolaczewska, A. *J. Org. Chem.* **1991**, *56*, 1944–1947. Carey, F. A.; Court, A. S. *J. Org. Chem.* **1972**, *37*, 939–943. Marumo, K.; Inoue, S.; Sato, Y.; Kato, H. *J. Chem. Soc., Perkin Trans. 1* **1991**, 2275–2276.

[19] Frye, C. L.; Salinger, R. M.; Fearon, F. W. G.; Klosowski, J. M.; DeYoung, T. *J. Org. Chem.* **1970**, *35*, 1308–1314.

[20] Reviews: Tandura, S. N.; Voronkov, M. G.; Alekseev, N. V. In *Topics In Current Chemistry*; F. L. Boschke, Ed.; Springer-Verlag: New York, 1986; Vol. 131, pp 99–189. Corriu, R. J. P.; Young, J. C. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Ed.; John Wiley & Sons: New York, 1989; pp 1241–1288. Corriu, R. J. P.; Young, J. C. In *The Silicon-Heteroatom Bond*; Patai, S., Rappoport, Z., Ed.; John Wiley & Sons: New York, 1991; pp 49–66.

[21] Examples: Stevenson, W. H., III; Wilson, S.; Martin, J. C.; Farnham, W. B. *J. Am. Chem. Soc.* **1985**, *107*, 6340–6352. Damrauer, R.; Burggraf, L. W.; Davis, L. P.; Gordon, M. S. *J. Am. Chem. Soc.* **1988**, *110*, 6601–6606. Dixon, D. A.; Hertler, W. R.; Chase, D. B.; Farnham, W. B.; Davidson, F. *Inorg. Chem.* **1988**, *27*, 4012–4018.

[22] Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am.* Chem. *Soc.* **1985**, *107*, 3902–3909.

[23] Dewar, M. J. S.; Dieter, K. M. *J. Am. Chem. Soc.* **1986**, *108*, 8075–8086.

[24] Meot-Ner, M.; Kafafi, S. A. *J. Am. Chem. Soc.* **1988**, *110*, 6297–6303.

[25] Minimized structures and their calculated heats of formation can be found in the supplementary material.

were introduced (entries 4–6): the numbers in entry 4 are derived from the use of a simple hard sphere with a positive charge representing a sodium atom, entry 5 is identical to 4 except the counterion is lithium, entry 6 employs two lithium ions. During initial attempts to determine values for entries 4 and 5, Coulombic interactions continued to figure prominently in the calculated structures and, in the absence of constraints, the minimized structures had the cation equidistant between the anions (these calculated values are not shown). Particularly for the meta and para cases, these final structures contained benzene rings that were highly distorted and high in energy. To eliminate this unrealistic distortion, some constraints were placed on the structure optimization. The starting structure, optimized with only the oxygen carrying a negative charge, had a linear arrangement of the cation, oxygen, and silicon atoms. This linearity was maintained during subsequent calculations. In addition, the bond between the silicon and the aromatic ring was allowed to rotate, but not to bend. The numbers in entry 6 result from optimization with no geometric constraints.

In all three sets of the calculations using counterions, the meta position continues to be less acidic than the para position which is consistent with our results and those of Schlosser.[10] Within these three sets, entry 5 is the least consistent with the other two and does not reflect our observed acidities, particularly the acidity of the methyl groups. Entries 4 and 6 both show the methyl groups to be the least acidic of the protons. The difference in the acidity order for these two entries results from the relative acidity of the ortho position, a result most likely due to the presence of two counterions in entry 6 and the minimization constraints imposed on entry 4. Both of these would exert their most pronounced effect on the ortho anion calculations, as the charged centers are brought into proximity. While calculations of deprotonation enthalpies, particularly for multiply charged species, must be interpreted with caution, the results shown in Table I suggest that correlation with experiment is possible.

Conclusions

Silicon, a versatile element in synthetic organic chemistry, can be used as an anchoring element for ortho-metalation directors, both as aminosilanes as shown by Tamao et al.[11] and as silanolates in concert with other directing groups. It is apparent, however, that the electropositive nature of silicon and competition from deprotonation of alkyl substituents on silicon complicate this application. In the current study, it was shown that an oxy anion on silicon significantly lowers the acidity of attached methyl groups, but that the potential for using the readily prepared dimethylsilanolates as metalation-directing groups is complicated by nucleophilic attack at silicon.

Experimental Section

General. Melting points were obtained by using a Thomas-Hoover capillary mp apparatus and are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Inc. NMR spectra were recorded on a GE QE-300 (300 MHz ^{1}H) or a Bruker AC-250 (250 MHz ^{1}H). Column and thin-layer chromatography were performed on silica gel with the indicated solvent system. Ether and THF were distilled from sodium benzophenone ketyl and hexane was distilled from calcium hydride. All reactions requiring anhydrous conditions were performed under a positive pressure of nitrogen. Hexamethylcyclotrisiloxane was purified by sublimation at 55 °C (55 torr).

Dimethyl-(3-methoxyphenyl)silanol (7a): To a solution of 3-bromoanisole (0.50 g, 2.67 mmol) in ether (5 mL) at −78 °C was added dropwise *tert*-butyllithium (3.46 mL of a 1.7 M solution in pentane, 5.9 mmol). After stirring for 20 min a solution of hexamethylcyclotrisiloxane (**3**) (0.198 g, 0.89 mmol) in ether (2 mL) was added dropwise. The reaction mixture was then stirred at −78 °C for 1 h and at rt for 2 h. The reaction was poured into 10% HCl and extracted with ether. The combined organics were dried over $MgSO_4$ and concentrated to give 460 mg of an oil. Flash chromatography (3:1 hexane/ethyl acetate) gave silanol **7a** (356 mg, 73%): ^{1}H NMR ($CDCl_3$) δ 0.35 (s, 6 H), 2.99 (s, 1 H), 3.77 (s, 3 H), 6.94 (dd, 1 H, $J = 8.2, 2.7$ Hz), 7.13 (d, 1 H, $J = 2.7$ Hz), 7.17 (d, 1 H, $J = 7.3$ Hz), 7.33 (bt, 1 H, $J = 8$ Hz); ^{13}C NMR ($CDCl_3$) δ 0.1, 55.0, 114.9, 118.3, 125.3, 129.1, 140.8, 158.9; IR (neat) 3330, 3058, 2956, 2833, 1573, 1482, 1120, 1042 cm^{-1}; MS (EI) 182 (M^+, 20), 167 (100), 152 (4), 137 (15). HRMS calcd for $C_{12}H_{14}O_2Si$: 182.0763, found: 182.0766.

Metalation of Dimethyl-(3-methoxyphenyl)silanol (7a): To a solution of silanol **7a** (350 mg, 1.92 mmol) in ether (3 mL) was added *n*-butyllithium (3.17 mL of a 1.39 M solution in hexanes). The reaction mixture was heated to reflux for 19 h, cooled to rt, and quenched with excess D_2O. The reaction was poured into 10% HCl and extracted with ether. The combined organics were dried over $MgSO_4$. Flash chromatography (85:15 hexane/ether) gave four products:

Di-*n*-butylmethylsilanol (30 mg, 9% yield): ^{1}H NMR ($CDCl_3$) δ 0.09 (s, 3 H), 0.58 (t, 4 H, $J = 7.8$ Hz), 0.88 (t, 6 H, $J = 6.8$ Hz), 1.32 (m, 8 H), 1.71 (bs, 1 H); ^{13}C NMR ($CDCl_3$) δ −2.1, 13.4, 15.8, 24.9, 28.3; MS (EI) 159 ($M^+ - 15$, 2), 117 (77), 61 (100).[19]

Dimethylbutylsilanol (10 mg, 4% yield): ^{1}H NMR ($CDCl_3$) δ 0.1 (s, 6 H), 0.59 (m, 2 H), 0.88 (m, 6 H), 1.3 (m, 8 H), 1.72 (bs, 1 H).[26]

Dimethyl-(2-deuterio-3-methoxyphenyl)silanol (7b) plus dimethyl-(4-deuterio-3-methoxyphenyl)silanol (7c) (44 mg, 13%): ^{1}H NMR ($CDCl_3$) δ 0.39 (s, 6 H), 3.82 (s, 3 H), 6.94 (d, 0.8 H, $J = 8.2$ Hz), 7.13 (s, 0.2 H), 7.17 (d, 1 H, $J = 7.2$ Hz), 7.32 (dd, $J = 8.2, 7.2$ Hz, 1H); GC/MS (EI) 183 (19), 168 (100), 153 (3), 138 (10).

***n*-Butyl-(2-deuterio-3-methoxyphenyl)methylsilanol (8a) plus *n*-butyl-(4-deuterio-3-methoxyphenyl)methylsilanol (8b)** (84 mg, 19% yield): ^{1}H NMR ($CDCl_3$) δ 0.38 (s, 3 H), 0.87 (m, 6 H), 1.35 (m, 4 H), 2.1 (bs, 1 H), 3.82 (s, 3 H), 6.93 (d, 0.85 H, $J = 7.9$ Hz), 7.12 (s, 0.15 H), 7.15 (d, 1 H, $J = 7.3$ Hz), 7.31 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 1.7, 13.7, 16.2, 25.2, 26.3, 55, 114.9, 118.4, 125.4, 129.1, 140.0, 158.9; IR (neat) 3284, 2920, 1564, 1464, 1257, 1043 cm^{-1}; MS (EI) 225 (6), 210 (2), 168 (100), 154 (25), 138 (13); HRMS calcd for $C_{12}H_{19}DO_2Si$: 225.1294, found: 225.1297.

Di-*tert*-butylphenylsilanol (9a). To a solution of di-*tert*-butyldifluorosilane (1 g, 5.54 mmol)[27] in THF (10 mL) at 0 °C was added dropwise a solution of phenyllithium (5 mL of a 1.8 M solution in 7:3 cyclohexane/ether, 9 mmol). The reaction mixture was allowed to warm up to rt overnight. Following addition of a 10% aqueous NaOH solution (3 mL), the mixture was heated to reflux for 10 h. The resulting mixture was poured into a saturated aqueous NH_4Cl solution (60 mL) and extracted with ether (2 × 50 mL) and then CH_2Cl_2 (2 × 40 mL). The combined organics were dried over $MgSO_4$ and concentrated *in vacuo* to give 1.40 g of a yellow oil. Flash chromatography (4:1 hexane/ethyl acetate) gave **9a** (1.1 g, 84%): ^{1}H NMR ($CDCl_3$) δ 1.05 (s, 18 H), 1.75 (bs, 1 H), 7.36 (m, 3 H), 7.63 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 20.3, 27.9, 127.3, 128.9, 134.4, 136.0; IR (neat) 3450, 2964, 2857, 1470, 1364, 1108, 822 cm^{-1}; MS (EI) 236 (M^+, 1.4), 179 (52), 137 (100), 123 (14), 97 (21), 84 (38), 75 (100); HRMS calcd for $C_{14}H_{24}OSi$: 236.1597, found: 236.1600.

Metalation of Di-*tert*-butylphenylsilanol (9a) at Room Temperature. To a suspension of oil-free KH (175 mg, 4.37 mmol) in hexane (2 mL) at ambient temperature was added

---

(26) Cundy, C. S.; Lappert, M. F.; Dubac, J.; Mazerolles, P. *J. Chem. Soc., Dalton Trans.* **1976**, 910–914.

(27) Dexheimer, E. D.; Spialter, L.; Smithson, L. D. *J. Organomet. Chem.* **1975**, *102*, 21–27. Marans, N. S.; Sommer, L. H.; Whitmore, F. C. *J. Am. Chem. Soc.* **1951**, *73*, 5127–5130. Eaborn, C. *J. Chem. Soc.* **1952**, 2846–2849.

dropwise a solution of di-*tert*-butylphenylsilanol (**9a**) (688 mg, 2.9 mmol) in hexane (3 mL). Gas evolution was observed. After 15 min, *n*-butyllithium (1.8 mL of a 2.5 M solution in hexane, 4.5 mmol) was added dropwise, instantly yielding a brown precipitate. The mixture was then stirred for an additional 15 h. After cooling to 0 °C, THF (6 mL) was added, resulting in a clear brown solution. This solution was then transferred to a vigorously stirred, saturated solution of CO_2 in THF at −78 °C, with continuous bubbling of CO_2 for 10 min.[16] The reaction mixture was allowed to warm up to room temperature and then quenched with 10% HCl (50 mL). The aqueous layer was extracted with ether (1 × 25 mL) and CH_2Cl_2 (4 × 20 mL), dried over $MgSO_4$, and concentrated *in vacuo*. The crude product (900 mg) was dissolved in a mixture of MeOH (8 mL) and benzene (30 mL), and (trimethylsilyl)diazomethane[17] (3.25 mL of a 2 M solution in hexanes, 6.5 mmol) was added. After stirring for 2 h at rt, glacial acetic acid was added dropwise until the yellow color disappeared, and the reaction mixture was then concentrated *in vacuo*. Chromatography of the product (95:5 hexane/ethyl acetate) gave silalactone **10** (6 mg, 1%), silanol **9a** (290 mg, 42%), and an inseparable mixture of esters **11** and **12** (377 mg, 44%, in a ratio of 1.7:1).

Silalactone 10: ^{1}H NMR ($CDCl_3$) δ 1.08 (s, 18 H), 7.6–7.7 (m, 3 H), 8.07 (m, 1 H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 19.9, 27.1, 127.6, 130.1, 131.6, 132.9, 137.7, 139.3, 169.0; IR (neat) 2932, 2859, 1743, 1468, 1234, 1053, 744 cm^{-1}; MS (EI) 262 (M^+, 50), 207 (100), 163 (85), 150 (39), 119 (19); HRMS calcd for $C_{15}H_{22}O_2Si$: 262.1389, found: 262.1389.

Esters 11 and 12: bp 100 °C (0.06 torr); ^{1}H NMR ($CDCl_3$) δ 1.05 (s, 18 H), 2.15 (bs, 1 H), 3.9 (s, 3 H), 7.42 (bt, 0.6 H, J = 7.4 Hz), 7.74 (d, 0.8 H, J = 7.5 Hz), 7.84 (dd, 0.6 H, J = 7.4, 0.9 Hz), 7.99 (d, 0.8 H, J = 7.5 Hz) 8.03, (dd, 0.6 H, J = 8.1, 0.9 Hz), 8.33 (s, 0.6 H); ^{13}C NMR ($CDCl_3$) δ 20.3, 27.7, 27.9, 52.0, 127.9, 128.1, 129.2, 130.2, 130.5, 134.3, 134.4, 135.4, 136.8, 138.9, 142.6, 167.3, 167.5; IR (neat) 3511, 2950, 2890, 1726, 1707, 1470, 1437, 1364, 1012 cm^{-1}; GC/MS (CI) **11**: 295 (M^+ + 1, 100), 277 (13), 237 (68), 105 (40), **12**: 295 (M^+ + 1, 100), 277 (13), 237 (46), 105 (37). Anal. Calcd for $C_{16}H_{26}O_3Si$: C, 65.26; H, 8.90. Found: C, 65.09; H, 8.77.

Metalation of Di-*tert*-butylphenylsilanol (9a) at Reflux. A sample of silanol **9a** was treated in a manner identical to the procedure described above except the mixture was heated to reflux for 6.5 h. An identical workup procedure gave a complex mixture of esters. Chromatography of this mixture (95:5 hexane/ethyl acetate) gave one new isomer in pure form, identified as the symmetrical diester di-*tert*-butyl(3,5-dicarbomethoxyphenyl)silanol (7.5%): mp 75 °C; ^{1}H NMR ($CDCl_3$) δ 1.04 (s, 18 H), 1.78 (s, 1 H), 3.95 (s, 6 H), 8.50 (s, 2 H), 8.68 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 20.2, 27.3, 52.3, 130.1, 131.8, 134.6, 139.9, 168.2; IR 3477, 2930, 2855, 1727, 1467, 1245, 1141, 822 cm^{-1}; MS (EI) 352 (7), 321 (65), 295 (100), 253 (49), 189 (54), 145 (63); HRMS calcd for $C_{18}H_{28}O_5Si$: 352.1706, found: 352.1709.

Calculations. Initial structures were built and minimized using SYBYL 5.5[28] and the Tripos force field. AM1 calculations were performed using AMPAC, accessed through SYBYL. For all calculations the key work PRECISE was used. For calculations involving a lithium ion or a hard sphere ion (sodium), where AM1 parameters were not available, the key word PARASOK was also used.

Acknowledgment. Acknowlegment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research through grants 22739-G1 and 25375-AC1. The Bruker AC-250 NMR was obtained with instrumentation grants from the NIH (RR05547A) and the NSF (CHE 8911350) and with support of the Center for Biotechnology and from SUNY Stony Brook. We thank Dr. Richard Kondrat, Mr. Ron New, and Mr. Henry Ajie of the UCR Mass Spectrometry Laboratory for mass spectral analysis. We thank Professor James E. Jackson for helpful discussions.

Supplementary Material Available: The ^{1}H NMR spectra of **7** and **8** and a table of the calculated heats of formation and the optimized structures listed in Table I (10 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

---

(28) Tripos Associates, Inc. 1699 S. Hanley Drive, St. Louis, MO 63144.