Kinetic Control in the Cleavage of Unsymmetrical Disilanes

Làszlò Hevesi,* Michael Dehon, Raphael Crutzen, and Adriana Lazarescu-Grigore

Department of Chemistry, Facultés Universitaires Notre-Dame de la Paix, 61, rue de Bruxelles, B-5000 Namur, Belgium

Received September 30, 1996 (Revised Manuscript Received January 15, 1997[⊗]*)*

A series of 12 phenyl-substituted arylpentamethyldisilanes **1a**−**l** have been synthesized in order to examine the regioselectivity of their nucleophilic Si,Si bond cleavage reactions under Still's conditions (MeLi/HMPA/0 °C). It has been found that the sensitivity of these reactions to the electronic effects of the substituents in the phenyl ring could be described by the Hammett-type equation $\log(k_A/k_B) = 0.4334 + 2.421(\Sigma\sigma)$; (correlation coefficient $R = 0.983$). The k_A/k_B ratio represents the relative rate of attack at silicon atom A (linked to the aryl ring) or at silicon atom B (away from the aryl ring) of the unsymmetrical disilanes. Thus, the present investigation shows that the earlier belief according to which the nucleophilic cleavage of unsymmetrical disilanes always produces the more stable silyl anionic species (thermodynamic control) should be abandoned, or at least seriously amended: kinetic factors appear to exert a primary influence on the regioselectivity of such reactions. Since the two major kinetic factors (i.e., electrophilic character of and steric hindrance at a given silicon atom) have opposite effects on the orientation of the reaction, it may happen that kinetic and thermodynamic control lead to the same result. For some of the unsymmetrical disilanes studied, the major reaction path was not the Si,Si bond cleavage; instead, Si−aryl bond breaking occurred, producing the corresponding aryl anions.

Introduction

Silyl anionic species have become of increasing importance in various fields of organic chemistry,[1] as well as in materials sciences.[2]

Although the reaction of disilanes with alkali metals is a well-known method for the production of silylmetal species,[3] the less economic but considerably faster cleavage of the same disilanes by strongly nucleophilic reagents, such as alkoxides,[4,5] methyllithium,[6a] or fluoride ion,[7] has often been preferred as an alternative method. Almost invariably, symmetrical disilanes have been considered for this latter type of reaction, and the scarce data reported for unsymmetrical disilanes[5,7] indicate that the Si,Si bond is cleaved in such a way as to generate the more stable silyl metal species (thermodynamic control of the reaction). However, in the conceptually related Sn,Si bond cleavages it has been observed that kinetic factors, such as the steric bulk of the goups attached to silicon and to tin, can play a dramatic role as to the preferential formation of silyl or stannyl anionic species. Thus, tributylstannyl anion was efficiently produced by the "naked" cyanide ion-mediated cleavage of tributylstannylsilanes when the silyl moiety was Me_3-Si, $PhMe_2Si$, or *n*-$BuMe_2Si$, whereas stannylsilanes having Et_3Si or *t*-$BuMe_2Si$ groups were completely unreactive.[8] Even more remarkably, trialkylstannyl or trialkylsilyl mixed cuprates could be formed selectively from appropriately substituted stannylsilanes upon cleavage with a higher order cuprate.[9]

These and other observations[10] led us to undertake a systematic investigation of the nucleophilic cleavage reaction of unsymmetrical disilanes such as the series **1a**−**l** (Scheme 1) where both electronic and steric effects will alter the reactivity of one of the silicon atoms, the other one being held constant. From the results reported here we conclude that in the compounds studied under the chosen conditions, the Si,Si bond cleavage is overwhelmingly controlled by kinetic factors.

Results and Discussion

Disilanes **1a**−**l** have been prepared in a straightforward manner by reacting pentamethylchlorodisilane with the corresponding aryllithiums, themselves obtained by bromine/lithium exchange (ArBr/2 equiv of *t*-BuLi/Et_2O/−78 °C/1 h). These disilanes were then subjected to the cleavage reaction described by Still[6a] (1 equiv of MeLi/HMPA/0 °C/15 min) followed by quenching of the reaction mixtures with aqueous ammonium chloride. The so-obtained product mixtures have been analyzed by gas chromatography.

[⊗] Abstract published in *Advance ACS Abstracts,* March 15, 1997.

(1) (a) Fleming, I. In *Comprehensive Organic Chemistry*; Barton, D. H. R., Ollis, W. D., Eds.; Pergamon Press: Oxford, 1979; Vol. 3. (b) Colvin, E. W. *Silicon in Organic Synthesis*; Butterworths: London, **1981**. (c) Weber, W. P. *Silicon Reagents for Organic Synthesis*; Springer Verlag: Berlin, **1983**. (d) Colvin, E. W. *Silicon Reagents in Organic Synthesis*; Academic Press: London, **1988**. (e) *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, **1991**. (f) Lipshutz, B. H. In *Organometallics in Synthesis*; Schlosser, M., Eds.; John Wiley & Sons: Chichester, U.K., 1994. (g) Hevesi, L. In *Comprehensive Organic Functional Group Transformations*; Katritzky, A. R., Meth-Cohn, O., Rees, C. W., Eds.; Pergamon: Oxford, 1995; Vol. 2, Ley, S. V., Ed., Chapter, 2.18.

(2) (a) West, R. In *The Chemistry of Organic Silicon Compounds;* Patai, S., and Rappoport, Z.,Eds.; John Wiley & Sons: Chichester, U.K., 1989; Vol. 2, p 1207. (b) Jones, R. G.; Benfield, R. E.; Cragg, R. H.; Swain, A. C.; Webb, S. J. *Macromolecules* **1993**, *26*, 4878. (c) *Organosilicon Chemistry II, From Molecules to Materials*; Auner, N., Weis, J., Eds.; VCH: Weinheim, Germany, 1996.

(3) See, for example: Davis, D. D.; Gray, C. E. *Organomet. Chem. Rev. A* **1970**, *6*, 283 and references cited therein.

(4) (a) Sakurai, H.; Okada, A.; Kira, M.; Yonezawa, K. *Tetrahedron Lett.* **1971**, 1511. (b) Sakurai, H.; Okada, A. *J. Organomet. Chem.* **1972**, *35*, C13. (c) Sakurai, H.; Kondo, F. *Ibid.* **1975**, *92*, C46.

(5) Buncel, E.; Venkatachalam, T. K.; Edlund, U. *J. Organomet. Chem.* **1992**, *437*, 85.

(6) (a) Still, W. C. *J. Org. Chem.* **1976**, *41*, 3063. (b) Still, W. C.; Mitra, A. *Tetrahedron Lett.* **1978**, 2659.

(7) Hiyama, T.; Obayashi, M.; Mori, I.; Nozaki, H. *J. Org. Chem.* **1983**, *48*, 912.

(8) Chenard, B. L.; Laganis, E. D.; Davidson, F.; RajanBabu, T. V. *J. Org. Chem.* **1985**, *50*, 3666.

(9) Lipshutz, B. H.; Reuter, D. C.; Ellsworth, E. L. *J. Org. Chem.* **1989**, *54*, 4975.

(10) Dispa, J.-F.; Hevesi, L. Unpublished work on the cleavage by methyllithium of (*N*-methyl-2-pyrrolyl)pentamethyldisilane.

S0022-3263(96)01131-0 CCC: $14.00

Scheme 1

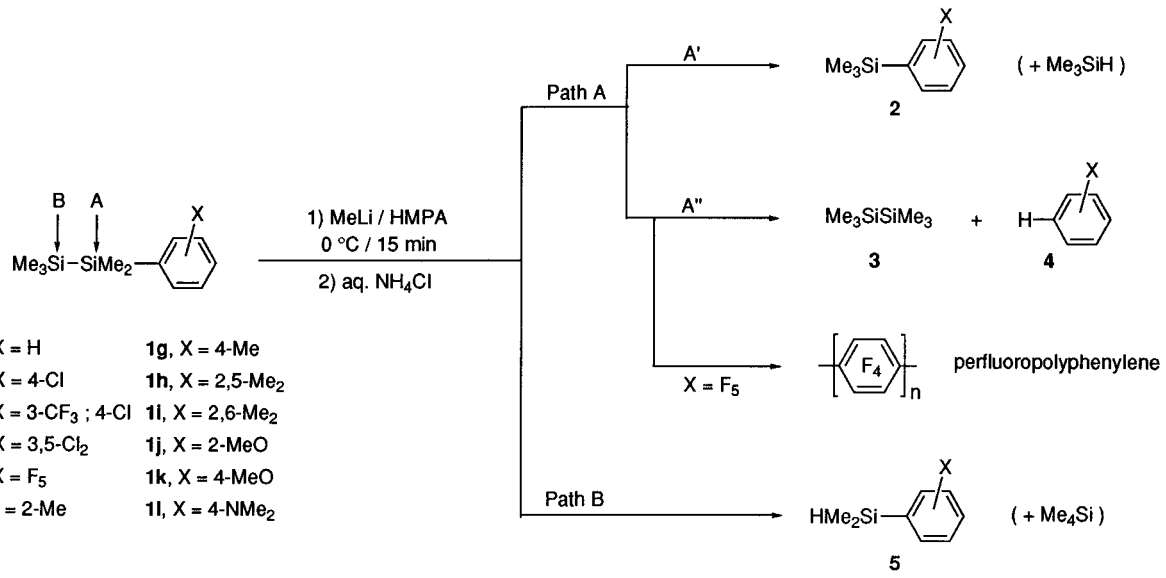


Table 1. Competition between paths A and B (Scheme 1) in the cleavage of unsymmetrical disilanes 1

entry	disilane **1**	X	k_A/k_B	$\log(k_A/k_B)$	$\Sigma\sigma$
1	**1a**	H	95/5 = 19	1.28	0.0
2	**1b**	4-Cl	93/7 = 13.3	1.12	0.24
3	**1c**	3-CF_3; 4-Cl	99.5/0.5 = 199[a]	2.3	0.70
4	**1d**	3,5-Cl_2	99/1 = 99	1.99	0.74
5	**1e**	F_5	99.6/0.4 = 250[a]	2.4	1.13[b]
6	**1f**	2-Me	52/48 = 1.08	0.033	−0.14[b]
7	**1g**	4-Me	59/41 = 1.44	0.16	−0.14
8	**1h**	2,5-Me_2	47/53 = 0.9	−0.046	−0.20[b]
9	**1i**	2,6-Me_2	68/12 = 5.7	0.76	−0.28[b]
10	**1j**	2-OMe	73.5/26.5 = 2.8	0.44	−0.12[b]
11	**1k**	4-OMe	62/38 = 1.63	0.21	−0.12
12	**1l**	4-NMe_2	26/74 = 0.35	−0.46	−0.32

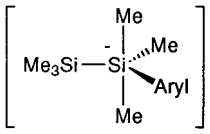
[a] Estimated approximate value. [b] Hammett σ for *ortho* substituents taken equal to σ_{para}.

According to the two possible sites of attack A and B of the nucleophile methyllithium, the expected cleavage products are the silanes **2** and **5** (Scheme 1, paths A′ and B). Therefore, in order to facilitate the analysis of the chromatograms, authentic silanes **2** and **5** have also been prepared. Nevertheless, with the exception of compounds **1a**−**c** and **1l**, the results obtained for all of the other disilanes were complicated by the presence in the reaction mixtures of unexpected products arising either from cleavage of the aryl−silicon bonds (Scheme 1, path A″) or from other side reactions. However, since most of the byproducts did arise from attack of methyllithium at one or the other of the two silicon atoms of the starting disilanes **1**, the total of the products originating from each site has to be considered rather than just the amounts of silanes **2** and **5**. For this reason, Table 1 lists the total amounts of products generated by attack of the nucleophile at sites A and B.

In the cases of disilanes **1a**−**c** and **1l** very clean cleavage reactions were observed, leading only to the corresponding silanes **2** and/or **5**. However, it was surprising to find that electron-attracting substituents such as those present in **1b** and **1c** did not induce the formation of substantial amounts of **5b** or **5c**. Similarly, up to 95% of the attack of the unsubstituted **1a** occurred at site A forming **2a** and the less stable trimethylsilyl anion after Si,Si bond breaking. In all three cases, the aryldimethylsilyl anions corresponding to **5a**−**c** would be anticipated to be more stable. On the other hand, site A of disilanes **1a**−**c** is certainly the more electrophilic one, suggesting thereby that these reactions are governed by kinetic control.

On the other extreme of our disilanes series, cleavage of compound **1l** led to the quantitative formation of a 26/74 mixture of silanes **2l** and **5l**. This result would also appear surprising in terms of the relative stability of trimethylsilyl and [4-(dimethylamino)phenyl]dimethylsilyl anions, since now the former one would be predicted to be more stable, and yet, the latter one has been formed predominantly. If, however, we admit that the strongly electron-releasing 4-(dimethylamino) group is able to reduce the electrophilicity of site A below that of site B, then the observed **2l/5l** = 26/74 ratio can again be explained by kinetic control of the reaction.

As judged from the nature of the products, the cleavages of disilanes **1d** and **1e** may appear quite different; in fact, these reactions took place in a very similar manner. In both cases methyllithium attacked at silicon atom A leading eventually to a negatively charged pentacoordinate silicon species[11] of type **I** that could in principle expel trimethylsilyl anion or an aryl anion.



(I)

Due to the better leaving-group abilities of 3,5-dichlorophenyl and pentafluorophenyl anions as compared to that of trimethylsilyl anion, the silicon−aryl bond of **1d** and **1e** was cleaved predominantly. The relative amounts of primary products formed from **1d** were as follows: 1,3-dichlorophenyl anion 91% (detected as *m*-dichlorobenzene (**4d**)), (3,5-dichlorophenyl)trimethylsilane (**2d**) 8%, and

(11) For the mechanisms of nucleophilic substitution on silicon, see, for example: (a) Corriu, R. J. P.; Guerin, C.; Moreau, J. J. E. In *The Chemistry of Organic Silicon Compounds;* Patai, S., Rappoport, Z., Eds.; John Wiley & Sons: Chichester, U.K., 1989; Vol. 1, p 305. (b) Bassindale, A. R.; Taylor, P. G. *Ibid.* p 839.

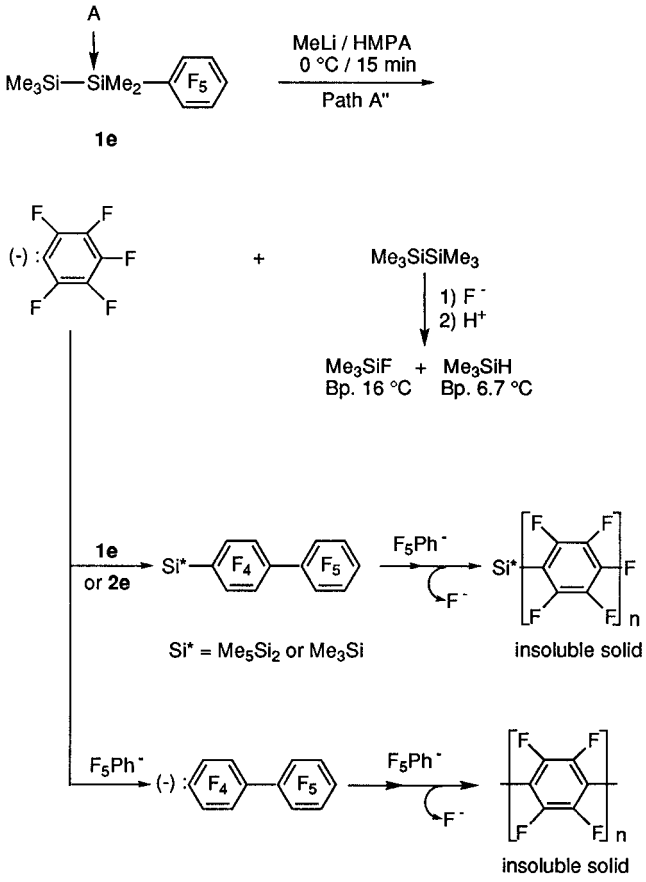
(3,5-dichlorophenyl)dimethylsilyl anion 1% (detected as (3,5-dichlorophenyl)dimethylsilane (**5d**)). Thus, the ratio of total attack at site A to that at site B is $k_A/k_B = 99/1$ (Table 1, entry 4).

Under the same conditions the cleavage reaction of disilane **1e** occurred in a peculiar manner: a deep purple-black precipitate formed upon dropwise addition of methyllithium (eventually accompanied by the appearance of a few gas bubbles), and by the end of the addition the whole reaction mixture solidified. Quenching with aqueous ammonium chloride and warming to room temperature led to a more aboundant gas evolution and bleaching of the mixture. Conventional workup gave a light beige solid (insoluble in all common solvents) and a small amount of liquid. Gas chromatographic analysis of the latter showed the presence of traces of (pentafluorophenyl)trimethylsilane (**2e**) and (pentafluorophenyl)-dimethylsilane (**5e**). On the other hand, because of its insolubility the light beige solid could not be analyzed by conventional spectroscopic methods. However, XPS spectroscopy has revealed carbon (57 atomic %) and fluorine (40 atomic %) as major constituents; nitrogen, oxygen, and silicon are present in the amounts of 1 atomic % each. Furthermore, the carbon peak could be resolved into two components, one corresponding to carbons bound to fluorine (65%) and one of the type *C*−C−F (35%). Since these figures are very close to those of perfluoropoly-*p*-phenylene, we assign this structure to the beige solid. In a preliminary account[12] of this work we erroneously proposed poly(dimethyl)silane as the structure of this solid material. On the basis of reported precedents[13] it was assumed that methyllithium might have abstracted a methyl group from **1e**. The silyl anion produced would have decomposed with generation of tetramethyldisilene, which would then have polymerized. In light of the present data this pathway can be ruled out.

Therefore, the apparent differences between the reactions of **1d** and **1e** arise from the different fates of the aryl anions formed in the cleavage steps: 1,3-dichlorophenyl anion is stable under the reaction conditions and gives *m*-dichlorobenzene on protonation, whereas pentafluorophenyl anions polymerize by an S_NAr-type mechanism[14] (Scheme 2). This process liberates fluoride ions, which are known to react instantly with hexamethyldisilane[7] to give trimethylsilyl fluoride and trimethylsilyl anion (converted into trimethylsilane upon protonation). These low-boiling compounds may have been the origin of the observed gas bubbles. On the other hand, formation of perfluoropolyphenylene has been confirmed by generating pentafluorophenyl anions from pentafluorobromobenzene (1 equiv of *n*-BuLi/THF/−78 °C, 1 h, then 2 equiv of HMPA/0 °C, 1 h). The XPS spectrum of the so-obtained off-white solid was identical to that described above.

The members of the next group of disilanes, **1f**−**h**, have in common that their sites A and B display quite similar reactivities toward methyllithium under the presently used conditions; as a result, the corresponding k_A/k_B ratios all have values close to unity (Table 1, entries 6−8).

Scheme 2

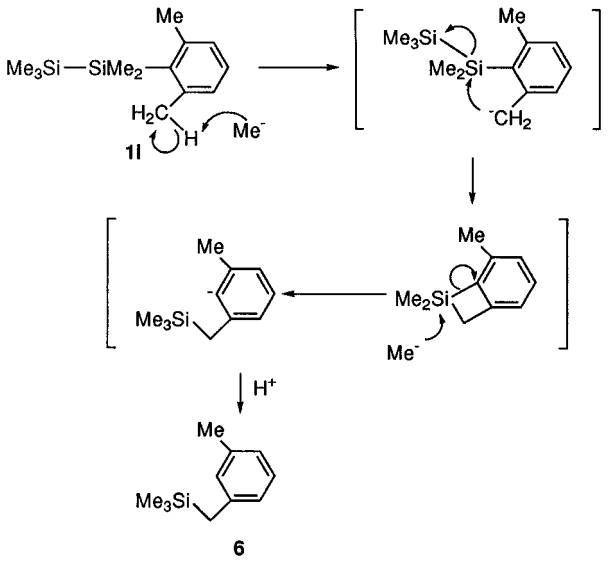


Analyses of the cleavage reaction mixtures have been slightly complicated by the presence in these mixtures of various but substantial amounts of silanols arising from silanes **5f**−**h**. Indeed, hydrosilanes are known to undergo nucleophilic substitution reactions by strong nucleophiles leading to displacement of hydride ions.[15] In our case, we have noted that uncontrolled quenching of the cleavage reactions of **1f**−**h** with aqueous ammonium chloride led to basic media where hydroxide ions could partially transform **5f**−**h** into the corresponding silanols.[16]

Surprisingly, the cleavage behavior of disilane **1i** differed from that of **1f**−**h** in that attack of site A was seen to be predominating: $k_A/k_B = 5.7$ (Table 1, entry 9). The apparently complex product mixture consisted of *m*-xylene (62%), (2,6-dimethylphenyl)trimethylsilane (**2i**) (6%), (2,6-dimethylphenyl)dimethylsilane (**5i**) (5.5%), (2,6-dimethylphenyl)dimethylsilanol (6.5%), as well as another silane identified as [(3-methylphenyl)methyl]-trimethylsilane (**6**) (20%). Silanes **2i** and **5i** are the normal Si−Si bond cleavage products arising from attack at sites A and B, respectively. Since the major 3,5-dimethylphenyl anion can only have been formed by attack at site A followed by Si−aryl bond cleavage, it remains intriguing why this process is the most favored one. Indeed, the cases of **1f**−**h** show that, due to the

(12) Hevesi, L.; Dehon, M. *Tetrahedron Lett.* **1994**, *35*, 8031.
(13) Nadler, E. B.; Rappoport, Z. *Tetrahedron Lett.* **1990**, *31*, 555.
(14) We thank one of the reviewers for pointing out that in the polymerization reactions attack of a neutral species such as **1e** or **2e** by the pentafluorophenyl anion should be a more favorable process than the latter's self-condensation. The same remark pertains for the synthesis of perfluoropolyphenylene from pentafluorobromobenzene. A more detailed study of these reactions will be reported in due course.
(15) Reaction of hydrosilanes with nucleophiles: (a) Grignard and organolithium reagents: Gilman, H.; Zuech, E. A. *J. Am. Chem. Soc.* **1959**, *81*, 5925 and references cited therein. (b) Hydroxides: Sommer, L. H.; Korte, W. D.; Frye, C. L. *J. Am. Chem. Soc.* **1972**, *94*, 3463 and references cited therein.
(16) In a control experiment the reaction of dimethyl-*o*-tolylsilane **5f** with 1 equiv of lithium hydroxide in aqueous HMPA at room temperature for 10 min gave essentially complete conversion into dimethyl-*o*-tolylsilanol.

Scheme 3



electron-donating effect of methyl substituents on the phenyl ring, the electrophilic character of the two silicon atoms became roughly equal. From a kinetic point of view, steric hindrance by the two *o*-methyl groups present in **1i** should have further diminished the chances of attack at site A. On the other hand, in spite of their unfavorable electronic effects, steric hindrance by the same *o*-methyl groups in the pentacoordinate intermediate of type **I** should favor the expulsion of 2,6-dimethylphenyl anion. This decomposition might well be faster than that of the pentacoordinate intermediate resulting from attack at site B. Thus, as long as formation from **1i** of the two possible pentacoordinate intermediates are equilibrium processes the overall equilibrium can be driven in the observed direction.

While (2,6-dimethylphenyl)dimethylsilanol most probably was produced as above by further transformation of silane **5i** by fortuitous hydroxide ions, rationalization of the benzylic silane **6** requires a new reaction pathway (Scheme 3). Besides being an excellent nucleophile, methyllithium in HMPA solution should also be a very strong base capable of extracting a proton from one of the *o*-methyl groups of **1i** generating a benzylic anion. Intramolecular nucleophilic attack of this anion on silicon atom A would lead to a silabenzocyclobutene intermediate[17] that upon ring opening by another methyl anion followed by protonation would give silane **6** whose structure has been confirmed by independent synthesis (see the Experimental Section).

Quantitative evaluation of the two competing cleavage pathways A and B of the methoxy-substituted disilanes **1j** and **1k** has met with some difficulty due to the diversity of observed products. The more complex mixture has been obtained from **1j** in which five different compounds could be identified: 2-(trimethylsilyl)anisole (**2j**) (42%), 2-(trimethylsilyl)phenol **7** (48%), anisole (6%), phenol (3%) and (2-methoxyphenyl)dimethylsilane (**5j**) (1%). The mixture produced by cleavage of disilane **1k** was more simple: 4-(trimethylsilyl)anisole (**2k**) (26%), 4-(trimethylsilyl)phenol (**8**) (72%) and (4-methoxyphenyl)-dimethylsilane (**5k**) (2%).

The presence of large amounts of phenolic compounds in both reaction mixtures strongly suggested that demethylation reactions of the methoxy groups must have occurred. The primary products, silyl anions, appeared to be good candidates for effecting these nucleophilic demethylation reactions. Control experiments established indeed that trimethylsilyl and dimethylphenylsilyl anions are able to transform anisole as well as 4-(trimethylsilyl)anisole (**2k**) into the corresponding phenolate anions. Furthermore, it was noted that the reactions of the two above-mentioned silyl anions with anisole proceeded with quite comparable rates (approximately 50% conversion after 0.5 h of reaction). Therefore, we assumed that all phenolic products arose from demethylation of the corresponding methoxy compounds in equal amounts by trimethylsilyl, (2-methoxyphenyl)dimethylsilyl, or (4-methoxyphenyl)dimethylsilyl anions. This means that the 48% of 2-(trimethylsilyl)phenol (**7**) obtained in the cleavage of **1j** derived from demethylation of **2j** by Me_3Si and Me_2(2-MeOPh)Si anions to the extent of 24% each (Scheme 4). However, since demethylation of **2j** by (2-methoxyphenyl)dimethylsilyl anion (**5j′**) restores **2j**, only those 24% have to be added to the observed 42% of **2j** that have been demethylated by trimethylsilyl anion (Scheme 4, path A′). This increases the amount of initially formed **2j** to 66%, which has to be complemented by the amount of Si−aryl bond cleavage to get the grand total of attack at site A. Indeed, anisole may have originated from this route and phenol from the demethylation of the so-formed anisyl anion by the two silyl anions present (to the extent of 1.5% each; Scheme 4 path A″). Thus, the total of attack at site A of **1j** equals $42 + 24 + 9 - 1.5 = 73.5\%$ and at site B to $1 + 24 + 1.5 = 26.5\%$ (Table 1, entry 10). An alternative to the scenario of Si−aryl bond cleavage leading to the presence of anisole and phenol might consist in the desilylation of **2j** by its own demethylation product 2-(trimethylsilyl)-phenolate anion. Regardless of which one (or both) of these pathways were operative, the final figures would not be changed appreciably.

Similarly, but in a more straightforward manner, formation of 4-(trimethylsilyl)phenol (**8**) was attributed to demethylation of 4-(trimethylsilyl)anisole (**2k**) by Me_3-Si and dimethyl(4-methoxyphenyl)silyl anions in equal parts (36% each). Therefore, the total attack at site A of **1k** amounted in fact to $26 + 36 = 62\%$ and that at site B to $2 + 36 = 38\%$ (Table 1, entry 11). Interestingly, we have noted that purified 4-(trimethylsilyl)phenol (**8**) decomposed on standing into phenol and trimethyl[4-[(trimethylsilyl)oxy]phenyl]silane, which means that desilylation of this type of aromatic silanes can take place even under the action of the weakly nucleophilic phenolic hydroxy group.[18]

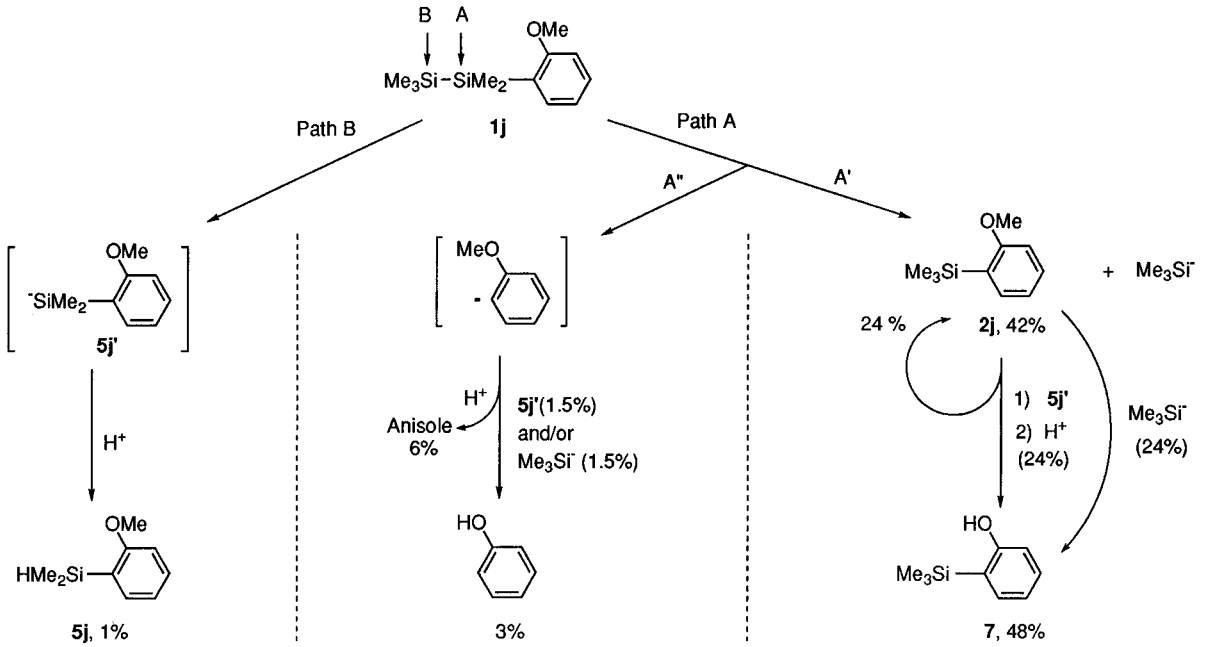
The results shown in Table 1 were correlated by a Hammett equation. For this purpose, Table 1 also includes the normal σ values, or when needed, their sums $\Sigma\sigma$. Figure 1 shows this correlation.

One can note that, while a fair number of points seem to fit into a linear relationship, others deviate substantially. It is worth specifying that among the latter we find **1a** with its unexpectedly high k_A/k_B value already

(17) Precedents for the formation of silabenzocyclobutene and stannabenzocyclobutene systems by closely resembling pathways have been reported: (a) Baines, K. M.; Groh, R. J.; Joseph B.; Parshotam, U. R. *Organometallics* **1992**, *11*, 2176. (b) Weidenbruch, M.; Schäfers, K.; Schlaefke, J.; Peters, K.; von Schnering, H. G. *J. Organomet. Chem.* **1991**, *415*, 343.

(18) For desilylation of 2-silylpyridines see: (a) Anderson, D. G.; Bradney, M. A. M.; Webster, D. E. *J. Chem. Soc, B* **1968**, 450. (b) Anderson, D. G.; Webster, D. E. *J. Chem. Soc. B* **1968**, 1008.

Scheme 4



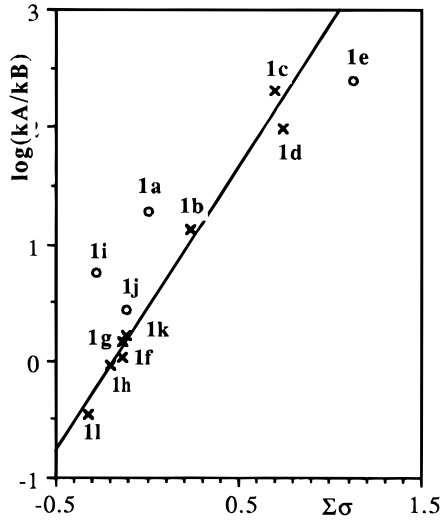


Figure 1. Hammett correlation of the regioselectivity of cleavage of disilanes **1** (line drawn with "X" points).

mentioned, **1i** and **1j** bearing *ortho* substituents, as well as the peculiar **1e**, which also has *ortho* substituents. Obviously, taking $\sigma_{ortho} = \sigma_{para}$ for the latter three compounds is a very crude approximation since by doing so no account is taken of the steric effects of the *ortho* substituents. Neglecting the points corresponding to these three compounds, we obtain the correlation equation (eq 1) represented by the line drawn on Figure 1.

$$\log(k_A/k_B) = 0.4334 + 2.421(\Sigma\sigma) \qquad (R = 0.983) \quad (1)$$

This correlation line with its slope of 2.42 indicates a relatively strong dependence of the rate ratio on electronic effects and nicely corroborates the prevalence of kinetic control in the disilane cleavage reactions reported here. It suggests that the slow step of these reactions is the nucleophilic attack on silicon,[19] which is favored by the latter's electrophilic character. Quite reasonably, the electrophilicity of silicon atom A increases more with electron-withdrawing substituents on the phenyl ring than that of silicon atom B, hence the positive slope in Figure 1. In this context, the deviation of **1a** from the correlation line might be accommodated at least in part by considering that the electrophilicity of silicon atom A is in fact more strongly increased by the unsubstituted phenyl ring than the ordinary hydrogen Hammett σ of 0.0 allows. Some sort of inductive σ (σ_I or σ^*, or a combination thereof) would probably be better suited.

In conclusion, the present investigation shows that the earlier belief that nucleophilic cleavage of unsymmetrical disilanes always produces the more stable silyl anionic species (thermodynamic control) should be abandoned, or at least strongly amended. Kinetic factors appear indeed to exert a primary influence on the outcome of such reactions: as long as nucleophilic attack at a given silicon atom is not completely suppressed by unfavorable steric effects, for example, the electrophilic character of that silicon atom (as determined by electronic effects) always seems to play a predominant role. Of course, the nature of the nucleophile, its size, nucleophilicity, and solvation properties should also be taken into account. Therefore, we consider the results reported here as the first stage of a more complete work that should include the investigation of the nucleophile and the reaction conditions used.

Experimental Section

All reactions were carried out in septum-fitted glassware under an argon atmosphere. Solvents diethyl ether and THF were freshly distilled from sodium benzophenone ketyl, and

(19) A reviewer has proposed single-electron transfer (SET) as a possible alternative mechanism for the cleavage of disilanes **1**. The compulsory first formed intermediate would be the radical anion of **1**, the extra electron residing either on one of the silicon atoms or on the aryl moiety. This radical anion could decompose into a silyl radical and a silyl anion that, on coupling with methyl radicals or by hydrogen abstraction, could lead to the observed products. Therefore, such a mechanism cannot be ruled out entirely. It seems to us, however, that in our case SET can not be more than a minor side reaction since otherwise considerable amounts of symmetrical 1,2-diaryltetramethyl disilanes should also be formed. We have not observed these products. It is also interesting to note that SET has often been observed in reactions of silyl anions with various electrophiles[4,6,7] and only under particular circumstances in reactions of nucleophiles with silicon substrates.[11a,17a,20]

(20) Corriu, R. J. P.; Ould-Kada, S.; Lanneau, G. F. *J. Organomet. Chem.* **1983**, *248*, 39).

HMPA was distilled from barium oxide and stored on molecular sieves; other reagents were purchased from Aldrich, Fluka (Bornem, Belgium), and Acros Chimica (Geel, Belgium). Unless otherwise noted, IR spectra were recorded on liquid films between sodium chloride plates; ^{1}H NMR spectra were obtained at 90 MHz or at 400 MHz in $CDCl_3$ solution with TMS reference. ^{13}C and ^{29}Si NMR spectra were recorded under the same conditions at 100.4 and 79.3 MHz, respectively. Gas chromatographic analyses were effected on an SE-30HL column using dodecane as internal standard.

Chloropentamethyldisilane was prepared from hexamethyldisilane and acetyl chloride in the presence of aluminum trichloride by a modified literature procedure.[21] The modification consisted in using a dichloromethane solution[22] of $CH_3COCl/AlCl_3$ instead of letting the mixture react without solvent;[21b] a typical experiment follows.

Acetyl chloride (7.9 g, 100 mM) was added dropwise from a pressure-equalizing funnel to a stirred suspension of aluminum trichloride (13.3 g, 100 mM) in 20 mL of dichloromethane cooled to 0 °C under argon. The so-obtained orange-yellow homogeneous solution was transferred into another pressure-equalizing funnel from which it was slowly added (over 20 min) to a solution of hexamethyldisilane (14.6 g, 100 mM) in 20 mL of dry dichloromethane stirred at 0 °C under argon. After the addition was complete, the mixture was stirred for 1 h and then extracted three times with 20 mL of dry pentane. Fractionation of the pentane solution led to 12.5 g (65%) of chloropentamethyldisilane, bp 128−132 °C (lit.[21c] bp 133−135 °C) >95% pure. Since the only detectable (NMR) impurity was hexamethyldisilane, the sample was used without further purification: ^{1}H NMR (ref CH_2Cl_2) δ 0.16 (s, 9H), 0.47 (s, 6H).

1,2-Dichlorotetramethyldisilane[21c] can be prepared by the same procedure but using twice the amount of acetyl chloride−aluminum chloride complex.

Synthesis of Disilanes 1. All the unsymmetrical disilanes have been prepared from the corresponding aryl bromides and chloropentamethyldisilane.

General Procedure. *tert*-Butyllithium (20 mM, 1.7 M solution in pentane) was added by a syringe to an ethereal (15 mL) solution of the aryl bromide (10 mM) cooled to −78 °C under argon. After the solution was stirred at this temperature for 1−2 h, chloropentamethyldisilane (1.7 g, 10 mM) dissolved in 5 mL of dry ether was added, and the mixture was stirred for a further 2 h; during this time, the temperature was allowed to reach 20 °C (in the case of **1i** the mixture was stirred for 24 h at room temperature and for 24 h at reflux). Conventional aqueous ammonium chloride workup followed by purification (vacuum distillation or column chromatography (SiO_2, eluent pentane/cyclohexane, 9/1 v/v)) led to pure **1** in 65−75% yields.

Phenylpentamethyldisilane (1a) (65% yield after column chromatography of crude **1a**): ^{1}H NMR(ref CH_2Cl_2) δ 0.10 (s, 9H), 0.38 (s, 6H), 7.35 (m, 3H), 7.50 (m, 2H); ^{13}C NMR δ −3.7, −2.0, 128.0, 128.6, 134.0, 139.9; ^{29}Si NMR δ −19.4, −21.7; IR 3050, 3020, 2950, 1486, 1400, 1245, 1105, 833, 760, 698 cm^{-1}.

(4-Chlorophenyl)pentamethyldisilane (1b) (67% yield after column chromatography): ^{1}H NMR(ref CH_2Cl_2) δ 0.06 (s, 9H), 0.33 (s, 6H), 7.32 (m, 2H), 7.37 (m, 2H); ^{13}C NMR δ −3.7, −2.0, 128.0, 128.3, 134.4, 135.0, 138.4; ^{29}Si NMR δ −19.4, −21.1; IR 3070, 2892, 1574, 1482, 1400, 1246, 1086, 833, 796, 761 cm^{-1}; MS *m*/*e* 242 (M), 227 (M − CH_3), 207 (M − Cl), 169 (M − $SiMe_3$), 134 (M − $SiMe_3$ − Cl), 73 ($SiMe_3^+$). Anal. Calcd for $C_{11}H_{19}ClSi_2$: C, 54.40; H, 7.88. Found: C, 54.47; H, 8.02.

[4-Chloro-3-(trifluoromethyl)phenyl]pentamethyldisilane (1c) (68% yield after column chromatography): ^{1}H NMR (ref CH_2Cl_2) δ 0.07 (s, 9H), 0.36 (s, 6H), 7.47 (d, J = 8 Hz, 1H), 7.52 (d, J = 8 Hz, 1H), 7.72 (s, 1H); ^{13}C NMR δ −4.9, −2.5, 130.0, 132.1, 132.2, 132.3, 138.1, 139.5; ^{29}Si NMR δ −19.3, −20.1; IR 3048, 2951, 1567, 1474, 1248, 1098, 838, 794, 761 cm^{-1}.

(3,5-Dichlorophenyl)pentamethyldisilane (1d) (58% yield after column chromatography): ^{1}H NMR δ 0.07 (s, 9H), 0.33 (s, 6H), 7.25 (d, J = 1.7 Hz, 2H), 7.28 (t, J = 1.7 Hz, 1H); ^{13}C NMR δ −3.9, −2.1, 128.6, 131.8, 135.1, 145.0; ^{29}Si NMR δ −19.1, −19.5; IR 3065, 2951, 2893, 1567, 1542, 1390, 1247, 1099, 836, 807, 761 cm^{-1}. Anal. Calcd for $C_{11}H_{18}Cl_2Si_2$: C, 47.64; H, 6.54. Found: C, 47.66; H, 6.59.

(Pentafluorophenyl)pentamethyldisilane (1e) (67% yield after column chromatography): ^{1}H NMR(ref CH_2Cl_2) δ 0.11 (s, 9H), 0.44 (s, 6H); ^{13}C NMR δ −2.7, −2.2, 136.3, 138.9, 140.8, 143.0, 148.0, 150.4; ^{29}Si NMR δ −17.6, −19.6; IR 2955, 2897, 1511, 1458, 1400, 1250, 1050, 798 cm^{-1}; MS (m/e) 298 (M), 283 (M − CH_3), 73 ($SiMe_3^+$). Anal. Calcd for $C_{11}H_{15}F_5Si_2$: C, 44.28; H, 5.07. Found: C, 44.35; H, 5.13.

(2-Methylphenyl)pentamethyldisilane (1f) (62% yield after distillation; $bp_{0.2Torr}$ 60−65 °C): ^{1}H NMR (ref CH_2Cl_2) δ 0.08 (s, 9H), 0.39 (s, 6H), 2.41 (s, 3H), 7.15 (t, J = 7.2 Hz, 2H), 7.24 (d, J = 7.2 Hz, 1H), 7.41 (d, J = 7.2 Hz, 1H); IR 3055, 3001, 2950, 2892, 1586, 1443, 1400, 1245, 1125, 836, 805, 762 cm^{-1}; MS (m/e) 222 (M), 207 (M − CH_3), 149 (M − $SiMe_3$), 91 (M − Si_2Me_5), 73 ($SiMe_3^+$). Anal. Calcd for $C_{12}H_{22}Si_2$: C, 64.78; H, 9.97. Found: C, 64.88; H, 10.07.

(4-Methylphenyl)pentamethyldisilane (1g) (67% yield after distillation; $bp_{0.1Torr}$ 60−63 °C): ^{1}H NMR (ref CH_2Cl_2) δ 0.06 (s, 9H), 0.31 (s, 6H), 2.35 (s, 3H), 7.16 (m, 2H), 7.36 (m, 2H); IR 3063, 3009, 2949, 2892, 1600, 1437, 1391, 1244, 1100, 836, 808, 759; cm^{-1}; MS (m/e) 222 (M), 207 (M − CH_3), 149 (M − $SiMe_3$), 91 (M − Si_2Me_5), 73 ($SiMe_3^+$). Anal. Calcd for $C_{12}H_{22}Si_2$: C, 64.78; H, 9.97. Found: C, 64.80; H, 9.97.

(2,5-Dimethylphenyl)pentamethyldisilane (1h) (72% yield after distillation; $bp_{0.25Torr}$ 68−72 °C): ^{1}H NMR (ref CH_2Cl_2) δ 0.08 (s, 9H), 0.38 (s, 6H), 2.31 (s, 3H), 2.37 (s, 3H), 7.05 (s, 2H), 7.20 (s, 1H); IR 3083, 3026, 3002, 294, 2892, 1481, 1448, 1399, 1381, 1245, 1144, 1076, 836, 797, 765 cm^{-1}; MS (m/e) 236 (M), 221 (M − CH_3), 163 (M − $SiMe_3$), 105 (M − Si_2Me_5), 73 ($SiMe_3^+$). Anal. Calcd for $C_{13}H_{24}Si_2$: C, 66.02; H, 10.23. Found: C, 66.05; H, 10.31.

(2,6-Dimethylphenyl)pentamethyldisilane (1i) (37% yield after column chromatography and distillation; $bp_{0.1Torr}$ 63−65 °C): ^{1}H NMR (ref CH_2Cl_2) δ 0.09 (s, 9H), 0.48 (s, 6H), 2.40 (s, 6H), 6.96 (d, J = 8 Hz, 2H), 7.11 (t, J = 8 Hz, 1H); IR 3049, 2949, 2892, 1585, 1559, 1448, 1399, 1375, 1245, 1144, 1076, 834, 801, 768; MS (m/e) 236 (M), 221 (M − CH_3), 163 (M − $SiMe_3$), 105 (M − Si_2Me_5), 73 ($SiMe_3^+$). Anal. Calcd for $C_{13}H_{24}Si_2$: C, 66.02; H, 10.23. Found: C, 66.03; H, 10.29.

(2-Methoxyphenyl)pentamethyldisilane (1j) (68% yield after distillation; $bp_{0.1Torr}$ 54−57 °C): ^{1}H NMR (ref CH_2Cl_2) δ 0.03 (s, 9H), 0.30 (s, 6H), 3.78 (s, 3H), 6.80 (d, J = 7.8 Hz, 1H), 6.96 (t, J = 7.3 Hz, 1H), 7.33 (m, 2H); IR 306, 2950, 2892, 1586, 1570, 1440, 1400, 1234, 1127, 1045, 833, 802 cm^{-1}; MS (m/e) 238 (M), 223 (M − CH_3), 165 (M − $SiMe_3$), 135 (M − 2Me − $SiMe_3$), 107 (M − Si_2Me_5), 73 ($SiMe_3^+$). Anal. Calcd for $C_{12}H_{22}OSi_2$: C, 60.44; H, 9.30. Found: C, 60.51; H, 9.27.

(4-Methoxyphenyl)pentamethyldisilane (1k) (52% yield after distillation; $bp_{0.1Torr}$ 68−72 °C):^{1}H NMR (ref CH_2Cl_2) δ 0.06 (s, 9H), 0.31 (s, 6H), 3.81 (s, 3H), 6.91 (m, 2H), 7.38 (m, 2H); ^{13}C NMR δ −3.8, −2.3, 54.7, 113.6, 130.0, 135.0, 160.0; IR 3078, 2949, 2892, 1593, 1563, 1500, 1440, 1395, 1276, 1246, 1106, 1034, 833, 800, 760; MS (m/e) 238 (M), 223 (M − CH_3), 165 (M − $SiMe_3$), 135 (M − 2Me − $SiMe_3$), 107 (M − Si_2Me_5), 73 ($SiMe_3^+$). Anal. Calcd for $C_{12}H_{22}OSi_2$: C, 60.44; H, 9.30. Found: C, 60.00; H, 9.12.

[4-(*N*,*N*-Dimethylamino)phenyl]pentamethyldisilane (1l) (50% yield after recrystallization from ethanol/water 3.5/1 v/v, mp 45 °C): ^{1}H NMR (ref CH_2Cl_2) δ 0.05 (s, 9H), 0.28 (s, 6H), 2.95 (s, 6H), 6.73 (m, 2H), 7.32 (m, 2H); IR (KBr pellet) 3078, 3020, 2948, 2889, 1601, 1515, 1442, 1400, 1364, 1243, 1108, 828, 794 cm^{-1}; MS (m/e) 251 (M), 236 (M − CH_3), 178 (M − $SiMe_3$), 134 (M − NMe_2 − $SiMe_3$), 120 (M − Si_2Me_5), 73 ($SiMe_3^+$). Anal. Calcd for $C_{13}H_{25}NSi_2$: C, 62.08; H, 10.02; N, 5.57. Found C, 62.60; H, 9.93; N, 5.31.

Synthesis of Silanes 2 and 5. These reference compounds have been prepared by the same general procedure using trimethylchlorosilane and dimethylchlorosilane, respectively,

(21) (a) Frainnet, E.; Calas, R.; Gerval, P.; Dentone, Y.; Bonastre, J. *Bull. Soc. Chim. Fr.* **1965**, 1259. (b) Sakurai, H.; Tominaga, K.; Watanabe, T.; Kumada, M. *Tetrahedron Lett.* **1966**, 5493. (c) Ishikawa, M.; Kumada, M.; Sakurai, H. *J. Organomet. Chem.* **1970**, *23*, 63.

(22) Calas, R.; Gerval, J. *C. R. Acad. Sci., Ser. II: Mec., Phys., Chim., Astron.* **1985**, *301*, 1289.

instead of chloropentamethyldisilane. The yields in **2** and **5** were generally good (70−90%); silanes **2a** and **5a** are commercially available.

(4-Chlorophenyl)trimethylsilane (2b): ^{1}H NMR δ 0.26 (s, 9H), 7.33 (m, 2H), 7.43 (m, 2H); ^{13}C NMR δ −0.7, 128.4, 135.1, 135.6, 139.1; IR 3050, 2954, 1576, 1483, 1406, 1250, 1080, 840, 755 cm^{-1}.

(2-Methylphenyl)trimethylsilane (2f): ^{1}H NMR 0.37 (s, 9H), 2.51 (s, 3H), 7.21 (overlapping t + d, J = 8 Hz, 2H), 7.32 (td, J = 8 Hz, J' = 1.6 Hz, 1H), 7.52 (d, J = 8 Hz, 1H); IR 3055, 3001, 2955, 2897, 1588, 1564, 1447, 1407, 1263, 1248, 1128, 837, 741 cm^{-1}.

(4-Methylphenyl)trimethylsilane (2g): ^{1}H NMR (ref CH_2Cl_2) δ 0.26 (s, 9H), 2.36 (s, 3H), 7.19 (m, 2H), 7.44 (m, 2H); IR 3065, 3031, 3010, 2953, 2895, 1604, 1448, 1404, 1258, 1247, 1107, 838, 754 cm^{-1}.

(2,5-Dimethylphenyl)trimethylsilane (2h): ^{1}H NMR δ 0.31 (s, 9H), 2.31 (s, 3H), 2.41 (s, 3H), 7.07 (m, 2H), 7.26 (bs, 1H); IR 3085, 3002, 2952, 2868, 1516, 1450, 1399, 1262, 1248, 1119, 837, 760 cm^{-1}.

(2,6-Dimethylphenyl)trimethylsilane (2i). ^{1}H NMR δ 0.43 (s, 9H), 2.50 (s, 6H), 7.01 (d, J = 7.3 Hz, 2H), 7.17 (t, J = 7.3 Hz, 1H).

(2-Methoxyphenyl)trimethylsilane (2j): ^{1}H NMR δ 0.26 (s, 9H), 3.80 (s, 3H), 6.83 (d, J = 8.2 Hz, 1H), 6.95 (t, J = 7.3 Hz, 1H), 7.3−7.4 (m, 2H); IR 3062, 2953, 2833, 1587, 1570, 1497, 1429, 1235, 1128, 1044, 839 cm^{-1}.

(4-Methoxyphenyl)trimethylsilane (2k): ^{1}H NMR δ 0.24 (s, 9H), 3.81 (s, 3H), 6.92 (m, 2H), 7.45 (m, 2H); IR 3081, 2953, 2835, 1595, 1564, 1502, 1441, 1396, 1276, 1246, 1111, 1033, 839.

[4-(*N*,*N*-dimethylamino)phenyl]trimethylsilane (2l): ^{1}H NMR δ 0.23 (s, 9H), 2.95 (s, 6H), 6.73 (m, 2H), 7.40 (m, 2H); IR 3080, 2951, 2893, 2803, 1598, 1508, 1443, 1404, 1353, 1245, 1112, 845.

(4-Chlorophenyl)dimethylsilane (5b): ^{1}H NMR (ref CH_2Cl_2) δ 0.35 (d, J = 4 Hz, 6H), 4.43 (heptet, J = 4 Hz, 1H), 7.32 (m, 2H), 7.48 (m, 2H); IR 3065, 2959, 2903, 2155, 1569, 1498, 1413, 1250, 1138, 886, 780 cm^{-1}.

(2-Methylphenyl)dimethylsilane (5f): ^{1}H NMR δ 0.35 (d, J = 4 Hz, 9H), 2.45 (s, 3H), 4.53 (heptet, J = 4 Hz, 1H), 7.17 (overlapping t + d, J = 7.2 Hz, 2H); 7.28 (td, J = 7.2 Hz, J' = 1.8 Hz, 1H), 7.47 (bd, J = 7.2 Hz, 1H); IR 3055, 3001, 2957, 2869, 2119, 1589, 1448, 1249, 1130, 836 cm^{-1}.

(4-Methylphenyl)dimethylsilane (5g): ^{1}H NMR δ 0.32 (d, J = 4 Hz, 6H), 2.35 (s, 3H), 4.41 (heptet, J = 4 Hz, 1H), 7.18 (m, 2H), 7.44 (m, 2H); IR 3065, 3031, 3010, 2957, 2867, 2117, 1601, 1458, 1248, 1109, 836 cm^{-1}.

(2,5-Dimethylphenyl)dimethylsilane (5h): ^{1}H NMR δ 0.35 (d, J = 4 Hz, 6H), 2.31 (s, 3H), 2.41 (s, 3H), 4.51 (heptet, J = 4 Hz, 1H), 7.08−7.12 (m, 2H), 7.27 (bs, 1H); IR 3084, 3000, 2956, 2865, 2119, 1481, 1448, 1248, 1145, 1079, 810 cm^{-1}.

(2,6-Dimethylphenyl)dimethylsilane (5i): ^{1}H NMR (ref CH_2Cl_2) 0.41 (d, J = 4 Hz, 6H), 2.48 (s, 6H), 4.76 (heptet, J = 4 Hz, 1H), 7.00 (d, J = 7.5 Hz, 2H), 7.17 (t, J = 7.5 Hz, 1H).

(2-Methoxyphenyl)dimethylsilane (5j): ^{1}H NMR (ref CH_2Cl_2) δ 0.34 (d, J = 4 Hz, 6H), 3.83 (s, 3H), 4.41 (heptet, J = 4 Hz, 1H), 6.85 (d, J = 8.3 Hz, 1H), 6.97 (t, J = 6.8 Hz, 1H), 7.38 (t, J = 7.1 Hz, 1H), 7.44 (d, J = 7.1 Hz, 1H); IR 3062, 3001, 2955, 2833, 2119, 1587, 1571, 1497, 1429, 1238, 1129, 1044, 838 cm^{-1}.

(4-Methoxyphenyl)dimethylsilane (5k): ^{1}H NMR δ 0.34 (d, J = 4 Hz, 6H), 3.82 (s, 3H), 4.41 (heptet, J = 4 Hz, 1H), 6.91 (m, 2H), 7.46 (m, 2H); IR 3081, 3015, 2955, 2834, 2115, 1593, 1564, 1502, 1441, 1396, 1276, 1246, 1113, 1033, 822 cm^{-1}.

[4-(*N*,*N*-Dimethylamino)phenyl]dimethylsilane (5l): ^{1}H NMR δ 0.30 (d, J = 4 Hz, 6H), 2.97 (s, 6H), 4.40 (heptet, J = 4 Hz, 1H), 6.74 (m, 2H), 7.42 (m, 2H); IR 3081, 2955, 2803, 2107, 1596, 1507, 1443, 1405, 1355, 1246, 1112, 834 cm^{-1}.

(2-Methylphenyl)dimethylsilanol (from alkaline hydrolysis of **5f**): colorless oily liquid: ^{1}H NMR (ref CH_2Cl_2) 0.45 (s, 6H), 2.13 (bs, 1H), 2.52 (s, 3H), 7.20 (t, J = 8 Hz, 2H), 7.30 (t, J = 7.3 Hz, 1H), 7.55 (d, J = 8 Hz, 1H); IR 3305, 3055, 3002, 2958, 1589, 1559, 1447, 1406, 1253, 1131, 862, 832 cm^{-1}; MS (m/e) 166 M), 151 (M − Me), 133 (M − Me − H_2O), 91 (M − $SiMe_2OH$), 75 ($SiMe_2OH$). Anal. Calcd for $C_9H_{14}SiO$: C, 65.00; H, 8.50. Found: C, 64.99; H, 8.48.

(4-Methylphenyl)dimethylsilanol (from alkaline hydrolysis of **5g**): ^{1}H NMR δ 0.38 (s, 6H), 2.03 (bs, 1H), 2.36 (s, 3H), 7.20 (m, 2H), 7.48 (m, 2H); IR 3340, 3065, 3031, 3010, 2953, 2895, 1604, 1448, 1404, 1258, 1130, 1083, 838, 786, 745 cm^{-1}.

(2,5-Dimethylphenyl)dimethylsilanol (from alkaline hydrolysis of **5h**): ^{1}H NMR δ 0.42 (s, 6H), 2.10 (bs, 1H), 2.31 (s, 3H), 2.45 (s, 3H), 7.04−7.14 (m, 2H), 7.35 (bs, 1H); IR 3347, 3027, 3005, 2957, 2868, 1481, 1448, 1405, 1382, 1252, 1145, 1083, 1053, 838, 786, 745; MS (m/e) 180 (M), 165 (M − Me), 147 (M − Me − H_2O), 105 (M − $SiMe_2OH$), 75 ($SiMe_2OH$).

(2,6-Dimethylphenyl)dimethylsilanol (from alkaline hydrolysis of **5i**): ^{1}H NMR δ 0.48 (s, 6H), 2.04 (bs, 1H), 2.48 (s, 6H), 6.97 (d, J = 7.8 Hz, 2H), 7.15 (t, J = 7.8 Hz, 1H); IR 3347, 3050, 2956, 1586, 1559, 1443, 1400, 1254, 1131, 836 cm^{-1}.

[(3-Methylphenyl)methyl]trimethylsilane (6) (isolated as an inseparable mixture of **2i**, **5i**, and **6** from the cleavage reaction of **1i**) has been synthesized independently as follows.

A potassium ([K^+/K^-]) solution was prepared from 227 mg (5.8 mM) of potassium and 768 mg (2.9 mM) of 18-crown-6 in 10 mL of THF under argon at −20 °C, according to our recently described procedure.[23] (3-Methylphenyl)methyl bromide, 430 mg (2.33 mM) dissolved in 2 mL of THF, was slowly added by a syringe. During this addition the deep blue color of the potassium solution progressively turned into deep yellow-brown, characteristic of the formation of benzylic potassium derivatives. After 0.5 h of stirring, 315 mg (2.9 mM) of trimethylsilyl chloride, dissolved in 2 mL of THF, was added, and the so-formed white mixture was allowed to reach room temperature. Stirring was continued for another 0.5 h during which time the mixture turned brown again. Quenching with aqueous $NaHCO_3$ followed by conventional workup led to 185 mg of colorless crude product that was shown by gas chromatography to be a 57/43 mixture of *m*-xylene and **6**. Bulb-to-bulb distillation (50 °C/0.02 Torr) gave 80 mg (19%) of almost pure silane **6**. This synthesis has not been optimized, but the large amount of *m*-xylene formed suggests that much better yields of **6** should be feasible: ^{1}H NMR (ref CH_2Cl_2) δ −0.01 (s, 9H), 2.04 (s, 2H), 2.30 (s, 3H), 6.80 (d, J = 7.3 Hz, 1H), 6.83 (s, 1H), 6.88 (d, J = 7.3 Hz, 1H), 7.10 (t, J = 7.3 Hz, 1H); MS (m/e) 178 (M), 163 (M − Me), 105 (M − $SiMe_3$), 73 ($SiMe_3$).

2-(Trimethylsilyl)phenol (7): ^{1}H NMR δ 0.31 (s, 9H), 4.80 (bs, 1H), 6.68 (d, J = 7.7 Hz, 1H), 6.93 (t, J = 7.7Hz, 1H), 7.22 (dd, J = 7.7 Hz, 2.6 Hz, 1H), 7.37 (dd, J = 7.7, 2.6 Hz, 1H); IR 3353, 3065, 3015, 2953, 2896, 1593, 1571, 1484, 1437, 1275, 1244, 1123, 839, 755 cm^{-1}.

4-(Trimethylsilyl)phenol (8): ^{1}H NMR (ref CH_2Cl_2) δ 0.28 (s, 9H), 5.95 (bs, 1H), 6.90 (m, 2H), 7.45 (m, 2H); IR 3365, 3020, 2954, 2924, 2853, 1598, 1580, 1465, 1419, 1262, 1247, 1179, 1110, 860, 838, 756 cm^{-1}.

Acknowledgment. The authors thank Dow Corning Ltd., Barry (South Glamorgan, U.K.) for the gift of a significant batch of hexamethyldisilane, an important starting material in this work.

Supporting Information Available: Copies of ^{1}H NMR spectra of compounds **1a**,**d**,**l**, **2b**−**l**, **5b**−**l**, **6**−**8**, and three aryldimethylsilanols mentioned in the text as well as ^{13}C NMR spectra of **1a** and **1d** and ^{29}Si NMR spectrum of **1a** (28 pages). This material is contained in libraries on microfiche, immediately follows this article in microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

JO961131E

(23) Hevesi, L.; Lacave-Goffin, B. *Synlett* **1995**, 1047.