α-Silyl Effects on the Acidities of Carbon Acids and the Homolytic Bond Dissociation Enthalpies of Their Acidic C−H Bonds

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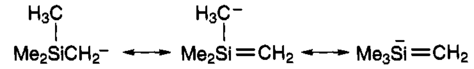
Abstract: Deprotonation of 9-(trimethylsilyl)fluorene (**2**) by $CH_3SOCH_2^-K^+$ in dimethyl sulfoxide (DMSO) is accompanied by desilylation, whereas the more sterically hindered 9-(triethylsilyl)- and 9-(triphenylsilyl)fluorenes (**3** and **4**) undergo only deprotonation. Compounds of **2** and **3** are each 2.2 kcal/mol more acidic than fluorene in DMSO, and **4** is 5.9 kcal/mol more acidic. The homolytic bond dissociation enthalpies (BDEs) of the acidic C−H bonds in **2**, **3**, and **4** are stronger by an average of 1.9 kcal/mol than that of fluorene (BDE = 79.5). The carbon acids $PhSO_2CH_2SiMe_3$ and $PhSO_2CH_2SiPh_3$ are 4.2 and 10.5 kcal/mol more acidic, respectively, in DMSO than is $PhSO_2CH_3$, and the BDEs of their acidic C−H bonds are estimated to be 0.5 kcal/mol stronger and 1.6 kcal/mol weaker, respectively. $PhSO_2CH(SiMe_3)_2$ is a 12.5 kcal/mol stronger acid than $PhSO_2CH_3$, and the BDE of its acidic C−H bond is estimated to be 2.5 kcal/mol weaker. The carbon acid $PhS(O)({=}NSO_2C_7H_7)CH(SiMe_3)_2$ is 8.1 kcal/mol stronger than $PhS(O)({=}NSO_2C_7H_7)CH_3$, and the BDE of its acidic C−H bond is 3.3 kcal/mol weaker. Here there is a sizable increase in acidity but a relatively small effect on BDE despite the introduction of *two* $SiMe_3$ groups at the acidic site. These large acidifying effects accompanied by little or no effect on the BDE are characteristic of a polarizability effect.

Introduction

Organic silicon compounds have found wide application in organic synthesis,[1] and studies on silyl reaction intermediates have provided information concerning reactions and mechanisms that had led to discoveries of new synthetic methods.[2] Silicon is an intriguing atom since it can (a) exert strong polarizability effects, (b) display a wide range of field inductive effects depending on the ligands attached, *e.g.*, $\sigma_F = 0.01$ for Me_3Si,[3a] −0.04 for Ph_3Si,[3b] 0.47 for F_3Si,[3c] (c) act as a (p−d) π acceptor toward adjacent R_2N, RO, or X groups, and (d) undergo bonding that involves higher coordination numbers.

Ab initio calculations indicate that the $H_3SiCH_2^+$ cation is stabilized by about 16 kcal/mol, relative to the CH_3^+ cation, but the H_3Si group in $H_3SiCH_2^+$ is predicted to be less stabilizing than the Me group in $MeCH_2^+$ by 13 kcal/mol.[4] (Henceforth, kcal/mol will be abbreviated as kcal.) Attempts to generate the $Me_3SiCH_2^+$ cation in solution have been unsuccessful.[5] Theoretical calculations predict a hyperconjugative stabilization by silicon of the β-silyl cation, $H_3SiCH_2CH_2^+$, of 29 kcal,[6] and here, supporting experimental evidence for strong stabilization of silicon to its β-carbocation has been found.[7]

Although the α- and β-silyl carbocations have been studied extensively in the past two decades, much less information has been forthcoming concerning silyl effects on carbanions or carbon-centered radicals. *Ab initio* calculations indicate that the $H_3SiCH_2^-$ anion is stabilized by 29 kcal by the H_3Si group.[8] This stabilization can be rationalized in terms of polarization of the Si atom (**1c**), in order to stabilize the negative charge, by a hyperconjugative effect (**1a** ↔ **1b**). The weak π bonding in contributor **1b** is offset by the placement of the negative charge on carbon, rather than on silicon, which is favorable because of the substantially higher electronegativity of carbon (2.5) when compared to silicon (1.8).



$$\underset{\textbf{1a}}{\overset{H_3C}{\overset{|}{Me_2SiCH_2^-}}} \longleftrightarrow \underset{\textbf{1b}}{\overset{H_3C^-}{\overset{|}{Me_2Si{=}CH_2}}} \longleftrightarrow \underset{\textbf{1c}}{Me_3\bar{Si}{=}CH_2}$$

1a **1b** **1c**

In the computational studies, it was found that the inclusion of d orbitals did not cause significant changes. Therefore, (p−d) π overlap appears to be unimportant. Measurement of the electron photodetachment spectrum of the $Me_3SiCH_2^-$ anion in the gas phase revealed its proton affinity to be 25.7 kcal, relative to that of the methide ion.[9] This result provided the first experimental evidence for the striking α-silyl stabilizing effect on anions predicted by the calculations.

The data available concerning the effect of silyl groups on radical stabilities are limited and appear to be controversial. The homolytic bond dissociation enthalpy (BDE) of the C−H bond in tetramethylsilane, $Me_3SiCH_2{-}H$, has been determined to be

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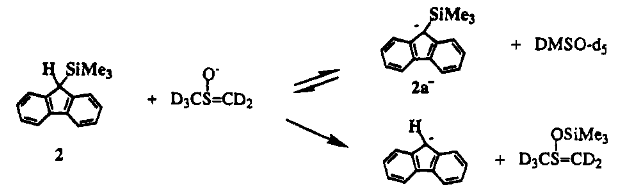
Table 1. NMR Data of Silyl-Substituted Acids and Their Conjugate Bases

compounds	^{1}H NMR (DMSO-d_6), ppm	^{13}C NMR (DMSO-d_6), ppm
9-(triethylsilyl)fluorene (**3**)	0.45 (6H, q, CH_2), 0.78 (9H, t, CH_3), 4.16 (1H, s, CH), 7.36, 7.52, 7.99 (8H, m, aromatic)	2.02, 7.40, 38.95, 120.30, 124.18, 125.47, 126.33, 140.20, 145.57
9-(triethylsilyl)fluorenide ion	1.00 (15H, m), 6.54 (2H, t), 6.87 (2H, t), 7.53 (2H, d), 7.92 (2H, d)	6.25, 8.67, 109.24, 117.66, 118.45, 119.56, 125.90, 144.06
9-(triphenylsilyl)fluorene (**4**)	5.21 (1H, s, CH), 6.90, 7.09, 7.30, 7.90 (8H, m, aromatic H's of fluorene), 7.37−7.45 (15 H, m, Ph)	38.72, 120.14, 124.82, 125.84, 126.05, 128.00, 129.95, 133.07, 135.79, 140.81, 144.26
9-(triphenylsilyl)fluorenide ion	6.54 (2H, t), 6.59 (2H, t), 6.76 (2H, d), 7.95 (2H, d) (the 8 H's of fluorene), 7.35−7.65 (15H, m, Ph)	76.32, 110.24, 118.25, 118.40, 119.66, 126.72, 128.45, 128.33, 136.39, 140.35, 144.70
$PhSO_2CH_2SiMe_3$ (**5**)[a]	0.22 (Me_3Si), 3.17 (CH_2)	−0.54 (Me_3Si), 46.82 (CH_2)
$PhSO_2CH^-SiMe_3$[a]	−0.03 (Me_3Si)	3.31 (Me_3Si), 38.09 (CH)
$PhSO_2CH_2SiPh_3$ (**6**)[a]	4.20 (CH_2)	44.60 (CH_2)
$PhSO_2CH^-SiPh_3$[a]	CH^- is not observed[b]	CH^- is not observed[b]
$PhSO_2CH(SiMe_3)_2$ (**7**)[a]	0.16 (Me_3Si), 3.51 (CH)	1.26 (Me_3Si), 46.50 (CH)
$PhSO_2C^-(SiMe_3)_2$[a]	−0.03 (Me_3Si)	5.21 (Me_3Si)

[a] Peaks of the phenyl groups are not listed. [b] The intensity of this CH peak may be significantly reduced by H−D exchange, but after the conjugate base was quenched by D_2O, the NMR peaks of $PhSO_2CH_2SiPh_3$ were observed.

Scheme 1



99.2 kcal,[10] *i.e.*, only about 0.4 kcal less than that of Me_3CCH_2-H. In contrast, Davidson and co-workers[11] found that the activation energy for generation of the $Me_3SiCH_2^•$ radical by pyrolysis of $Me_3SiCH_2CH_2CH=CH_2$ or Me_3SiCH_2-*t*-Bu was about 2−3 kcal lower than that for the formation of the $CH_3CH_2^•$ radical by pyrolysis of CH_3CH_2-*t*-Bu, suggesting appreciable stabilization of the $Me_3SiCH_2^•$ radical by Me_3Si.

Results and Discussion

Reactions of $CH_3SOCH_2^-K^+$ with 9−(Trimethylsilyl)fluorene and (Trimethylsilyl)methyl Phenyl Sulfones. In the reaction of 9-(trimethylsilyl)fluorene (**2**) with $CH_3SOCH_2^-K^+$, both NMR and cyclic voltammetry (CV) showed that considerable desilylation accompanied the deprotonation. (See the Experimental Section for details.) The reactions occurring are summarized in Scheme 1.

The conjugate base of dimethyl sulfoxide (DMSO) is about 13 pK_{HA} units stronger than anion **2a**$^-$, so the deprotonation of **2** to **2a**$^-$ in Scheme **1** is very fast. The desilylation of **2** to give 9-FlH$^-$ anions is much slower but is irreversible under the reaction conditions. In time, the initial acid−base reaction is completely reversed and the fluorenide ion is formed. The *O*-silyl derivative is pictured as being formed because oxygen bases are good desilylation reagents due to the formation of a strong silicon−oxygen bond (129 kcal), and it has been shown by X-ray crystallography that the conjugate base of PhS(O)-CH_3 is an oxygen base, *i.e.*, $PhS(=CH_2)O^-$.[14]

Reactions of $PhCOCH_2SiMe_3$ or $CH_3CONHSiMe_3$ with $CD_3SOCD_2^-K^+$ in DMSO-d_6 resulted only in desilylation to form $PhCOCH_2^-$ or CH_3CONH^- ions, respectively. This is expected since these anions are relatively weakly basic, having pK_{HA} values of 24.7 and 25.5, respectively. Desilylation also occurs, however, even when $CD_3SOCD_2^-K^+$ is quenched prior to titration with a sulfone acid with a pK_{HA} value near that of the liberated anions. In the reactions of **3**, **4**, **5**, **6**, and **7** with $CH_3SOCH_2^-K^+$, however, only deprotonation was observed by the NMR studies (Table 1). After the deprotonation, each conjugate base was protonated by a stronger acid, *e.g.*, $(t\text{-}BuSO_2)_2CH_2$(pK_{HA} = 13.7), and the starting acid was recovered. NMR data for the acids and their conjugate bases are listed in Table 1.

Equilibrium Acidities of 9-(Trimethylsilyl)fluorene (2), 9-(Triethylsilyl)fluorene (3), and 9-(triphenylsilyl)fluorene (4). Our objective was to obtain information concerning the effects of α-silyl groups on carbanion stabilities by measuring the acidities of carbon acids containing Me_3Si, Et_3Si, and Ph_3Si groups (pK_{HA} values in DMSO) and to obtain information on the effects of these α-silyl groups on BDEs by combining the pK_{HA} values with the oxidation potentials of the conjugate anions, $E_{ox}(A^-)$ by eq 1.[12]

$$\mathrm{BDE\ (kcal)} = 1.37\mathrm{p}K_{HA} + 23.1E_{ox}(A^-) + 73.3 \qquad (1)$$

The pK_{HA} values of **2**−**4** were measured in DMSO by the overlapping indicator method previously developed.[13] For acids having colored conjugate bases, such as fluorenes, this involves generating the anion A^- by adding increments of the acid HA in DMSO to $CH_3SOCH_2^-K^+$ ("potassium dimsyl") in DMSO, followed by titration with a DMSO solution of a standard acid. This procedure proved to be unsuitable for **2**, however, because of the desilylation. The conjugate base of 9-Me_3SiFlH (**2**) was generated by using the conjugate base derived from benzyl methyl sulfone (pK_{HA} = 25.4). Titration using **2a**$^-$ as its own indicator was then carried out with the standard acid *m*-fluorobenzyl phenyl sulfone (pK_{HA} = 21.7). The average of three titrations gave pK_{HA} = 21.5 ± 1 for **2**, which agrees reasonably well with the value of 21.6 obtained earlier by Vanier.[15] The conjugate bases of 9-Et_3SiFlH (**3**) and 9-Ph_3-SiFlH (**4**) were generated using $[CH_3SOCH_2]^-K^+$ without any evidence of desilylation. The results of pK_{HA} measurements and BDE estimates are summarized in Table 2.

Examination of Table 2 shows that 9-Me_3Si and 9-Et_3Si groups each increase the acidity of fluorene in DMSO by about 2.2 kcal (statistically corrected for the number of acidic hydrogen atoms). In contrast, the 9-Me_3C group *decreases* the acidity of fluorene by 2.9 kcal, presumably because of steric inhibition of solvation. The steric effect of the Me_3Si group should be considerably less than that of the Me_3C group because the Si−C

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Table 2. Acidity and Homolytic Bond Dissociation Enthalpies (BDEs) of the Acidic C−H Bonds in 9-Substituted Fluorenes, 9-R-FlH

R	pK_{HA}[a]	$E_{ox}(A^-)$[e]	BDE[f]
H	22.6	−1.07	79.5[g]
Me_3C	24.4	−1.18	79.4[g]
Ph_3C	20.3	−1.03	77.2[g]
Me_3Si (**2**)	21.5[b]	−0.90	82.5
Et_3Si (**3**)	21.4[c]	−0.93	81.2
Ph_3Si (**4**)	18.6[d]	−0.78	80.6

[a] Measured in DMSO against standard acids. [b] For details, see the Experimental Section. [c] Titrated with standard acid, *m*-fluorobenzyl phenyl sulfone ($pK_{HA} = 21.7$). [d] Titrated with standard acid, *p*-cyanobenzyl phenyl sulfone ($pK_{HA} = 18.5$). [e] Irreversible oxidation potentials measured by cyclic voltammetry in DMSO by the method described in the earlier paper[12] and referenced to the ferrocene−ferrocenium couple; the $E_{1/2}$ for the Fc/Fc^+ couple is 0.875 *vs* Ag/AgI in DMSO when the electrolyte is $Et_4N^+BF_4^-$ and is 0.930 when the electrolyte is $Bu_4N^+PF_6^-$. [f] Calculated by eq 1. [g] Bordwell, F. G.; Zhang, X.-M. *J. Am. Chem. Soc.* **1994**, *116*, 973−976.

Table 3. Acidity and Homolytic Bond Dissociation Enthalpies (BDEs) of the Acidic C−H Bonds in Sulfones and Related Compounds

R	pK_{HA}[a]	$E_{ox}(A^-)$[b]	BDE[d]
$PhSO_2CH_3$	29.0	−0.605	99.0[e]
$PhSO_2CH_2SiMe_3$ (**5**)	26.1	−0.416	99.4
$PhSO_2CH_2SiPh_3$ (**6**)	21.3	−0.222	97.4
$PhSO_2CH(SiMe_3)_2$ (**7**)	20.4	−0.205[c]	96.5
$PhS(O)(=NSO_2Tol)CH_3$ (**8**)	24.5	−0.164	103.1
$PhS(O)(=NSO_2Tol)CH(SiMe_3)_2$ (**9**)	19.05	0.018	99.8
$PhSO_2CH_2Ph$ (**10**)	23.4	−0.652	90.2[e]
$PhSO_2CH(CH=CH_2)(SiMe_3)$ (**11**)	24.1	−0.657	91.1

[a] Measured in DMSO against two indicators. [b] Irreversible oxidation potentials measured by cyclic voltammetry in DMSO by the method described in an earlier paper[12] and referenced to the ferrocene−ferrocenium couple; the $E_{1/2}$ for the Fc/Fc^+ couple is 0.925 *vs* Ag/AgI in DMSO when the electrolyte is ${}^tBu_4N^+PF_6^-$. [c] The oxidation potential is reversible. [d] Calculated by eq 1. [e] Bordwell, F. G.; Harrelson, J. A., Jr.; Zhang, X.-M. *J. Org. Chem.* **1991**, *56*, 4448.

bond is longer than the C−C bond (1.85 vs 1.55 Å). Indeed, steric inhibition of solvation does not appear to be a factor for R_3Si groups since the acidifying effect of the (larger) Et_3Si group on fluorene is essentially identical to that of the Me_3Si group. An ion pair (IP) pK_{HA} for $9\text{-}Me_3SiFl^-Cs^+$ in tetrahydrofuran (THF) has been reported recently[16] to be almost identical with the pK_{HA} in DMSO, and some desilylation by a carbon base was observed.

The 5.9 kcal acidifying effect of the 9-Ph_3Si group in 9-Ph_3SiFlH (**4**), relative to the hydrogen atom fluorene, is 2.3 kcal greater than that of the Ph_3C group in 9-Ph_3CFlH. Both of these effects are believed to be due in part to stabilization of the anion conjugate bases by polarizability effects and in part to increases in ground state energies that are relieved by deprotonation to form the carbanion. The 5.9 kcal acidifying effect of the 9-Ph_3Si group in 9-Ph_3SiFlH may be compared with the 16 kcal acidifying effect of the Ph_3P^+ group in 9-Ph_3P^+FlH,[17] which also has a 3rd-row element as the binding ligand. For Ph_3P^+, however, the polarizability effect is augmented by a large field/inductive effect due to the positive charge, which is absent in the Ph_3Si function in **4**.

Equilibrium Acidities of Silyl Derivatives of Sulfones and Oxosulfoximines. Data on the equilibrium acidities and BDEs of silylated derivatives of sulfones and oxosulfoximines are shown in Table 3.

Examination of Table 3 shows that an α-Me_3Si group in $PhSO_2CH_2SiMe_3$ (**5**) increases the acidity of phenyl methyl sulfone by 4.2 kcal and that an α-Ph_3Si group in $PhSO_2CH_2SiPh_3$ (**6**) increases the acidity by 10.8 kcal. These acidifying effects provide support for the theoretical calculations that predict large stabilizing effects of α-silyl groups on carbanions. Although these effects are sizable, they are much smaller than the calculated gas-phase stabilities. This is expected since the solution effects are strongly attenuated by solvation effects. For example, the gas phase pK_{HA} of fluorene of 344 kcal is attenuated to 31 kcal in DMSO solution. As brought out in the previous section, the much larger acidifying effect of Ph_3Si compared to that of Me_3Si is believed to be due, at least in part, to its larger polarizability effect, perhaps aided by an inductive effect of Ph. Although σ_I for Ph is only 0.1 toward carbon, it may be enhanced toward Si, as pointed out by a referee.

The effect of introducing a second α-Me_3Si group into the methyl group of $PhSO_2CH_3$ to give $PhSO_2CH(SiMe_3)_2$ (**7**) is to increase the acidity by 8.2 kcal, compared to a 4.2 kcal increase caused by the introduction of the first α-Me_3Si group. The larger increase for the second substituent is most unusual since saturation (leveling) and increased steric effects usually cause the effect of the second substituent to be *smaller* than that of the first. We believe that this surprisingly large effect of the second Me_3Si substituent is caused by a substantial increase in the ground state energy of **7** due to a large increase in steric interactions resulting from the presence of three large groups on the acidic methine carbon in the $PhSO_2CH(SiMe_3)_2$ molecule. The effect of substituting two α-Me_3Si groups into methyl *N*-(*p*-tolylsulfonyl)phenyloxosulfoxime (**8**) causes an increase in the acidity of 8.15 kcal compared to 12.5 kcal for the effect of substituting two Me_3Si groups into methyl phenyl sulfone, a less acidic substrate. It is interesting to note that the presence of an α-Me_3Si group in $PhCH_2SiMe_3$ has been found to increase the ion pair (IP) acidity of toluene in THF by 3 IP pK_a units, and incorporation of a second α-Me_3Si group has a like effect, for a total effect of 8.2 kcal.[16]

Homolytic Bond Dissociation Enthalpies (BDEs) of Silylated Fluorenes, Sulfones, and Oxosulfoximes. Turning to the effects on enthalpies of replacing the acidic hydrogen atoms in fluorenes, sulfones, and oxosulfoximes by silyl groups, we find that the BDEs of the acidic C−H bonds in 9-(trimethylsilyl)-, 9-(triethylsilyl)-, and 9-(triphenylsilyl)fluorenes average 81.4 ± 1 kcal, *i.e.*, the BDEs are all increased slightly, relative to that of fluorene (Table 2). Also, the effect of the α-Me_3Si group in $PhSO_2CH_2SiMe_3$ (**5**) is to *increase* the BDE of the acidic hydrogen atom, relative to that of methyl phenyl sulfone, by about 0.5 kcal, whereas the α-Ph_3Si group in $PhSO_2CH_2SiPh_3$ (**6**) *decreases* the BDE of the acidic C−H bond by about 1.6 kcal (Table 3). Also, the BDE of the acidic C−H bond in $PhSO_2CH(SiMe_3)CH=CH_2$ (**11**) is slightly higher than that in $PhSO_2CH_2Ph$ (**10**), an analogue without a Me_3Si group where $CH=CH_2$ is replaced by Ph. The BDE results with **2, 3, 4, 5,** and **11** indicate, therefore, that a single α-Me_3Si group causes a small *increase* in the BDE. Our results support those of Doncaster and Walsh, who found that Me_3SiCH_3 and Me_3CCH_3 have nearly the same C−H BDEs.[10] On the other hand, the presence of a single Ph_3Si group in $Ph_3SiCH_2SO_2Ph$ (**6**) or *two* Me_3Si groups in $(Me_3Si)_2CHSO_2Ph$ (**7**) or $PhS(O)=NSO_2C_7H_7)\text{-}CH(SiMe_3)_2$ (**9**) weakens the acidic C−H bonds by 1.6, 2.5, and 3.2 kcal, respectively. As brought out earlier, the presence of large groups in these substrates is believed to cause increases in their ground state energies leading to sizable increases in acidity. Since we have also often observed, empirically, that increases in ground state energies are often accompanied by

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decreases in BDEs (and *vice versa*),[18] the prevent results appear to be consistent with this pattern of behavior.

The reversibility of the oxidation potential of $PhSO_2\bar{C}(SiMe_3)_2$ anion at a scan rate of 100 mV/s and of the $PhS(O){=}NSO_2(C_7H_7)\bar{C}(SiMe_3)_2$ anion at a faster scan rate (25 V/s) is no doubt associated with the strong steric shielding of the radicals by the large phenyl sulfonyl, $PhS(O){=}NSO_2(C_7H_7)$, and trimethylsilyl groups. The radicals formed are persistent for steric reasons, but the relatively high BDEs of the C−H bonds of the parents (96.5 and 103 kcal, respectively) show that they are not *inherently* highly stabilized.

In an earlier paper we have suggested that, in general, the ΔBDEs of $GCH_2{-}H$ bonds, relative to that of methane ($CH_3{-}H$, BDE 105 kcal), provide good estimates of the radical stabilization energies (RSEs) of the corresponding radicals, $GCH_2^{\bullet}$.[19] On this basis an RSE of 6 kcal was assigned to the $Me_3SiCH_2^{\bullet}$ radical based on the BDE of $Me_3SiCH_2{-}H$ (99 kcal) measured by Doncaster and Walsh. The bulk of the evidence now available indicates, however, that the presence of the Me_3Si group in the $Me_3SiCH_2^{\bullet}$ radical is slightly destabilizing and that the RSE is slightly negative rather than positive by 6 kcal.

Summary and Conclusions. The increases in acidity of 2 and 4.2 kcal for introducing a Me_3Si group into the 9-position of fluorene and into the methyl group of $PhSO_2CH_3$, respectively, and for the similar acidity increases in these substrates of 5.9 and 10.5 kcal, respectively, for introducing Ph_3Si groups are attributed to a combination of (a) polarizability effects of these silyl groups in stabilizing the anion and (b) relief of steric strains in the neutral substrates on deprotonation to form the carbanions. The small *increases* in BDEs caused by introducing Me_3Si, Et_3Si, or Ph_3Si groups into the 9-position of fluorene or the introduction of an α-Me_3Si group into the methyl group of $PhSO_2CH_3$ indicate that Me_3Si, Et_3Si, or Ph_3Si groups have small *destabilizing* effects on adjacent radicals. The sizable increases in acidity caused by introducing *two* Me_3Si groups into the acidic sites of $PhSO_2CH_3$ and $PhS(O){=}N(C_7H_7)CH_3$ (12.5 and 8.15 kcal, respectively) are believed to be caused primarily by increased ground state effects due to steric crowding in these two substrates, which are relieved by deprotonation to form the corresponding carbanions.

Experimental Section

General. pK_{HA} measurements in Me_2SO were carried out as described in earlier publications.[13] Cyclic voltammetry was carried out in the manner previously described[12] with $t\text{-}Bu_4N^+PF_6^-$ as the electrolyte. The oxidation potential for $PhSO_2C^-(SiMe_3)_2$ was reversible even at the scan rate of 100 mV/s, $E_{1/2} = 0.720$ V. But, the $E_{ox}(A^-)$ value reported, 0.770 V, was taken from the oxidation peak position for consistency with other data. NMR experiments were carried out on the Varian 400 MHz spectrometer.

Compounds **2**, **3**, and **4** were prepared by the reaction of appropriate trialkyl or triarylsilyl chloride with fluorenide anion as reported in the literature.[20] Phenyl methyl sulfone silyl derivatives were prepared by the reaction of appropriate silyl chlorides with phenyl methyl sulfone anion.

NMR Study of the Reaction of 9-(Trimethylsilyl)fluorene (2) with $CD_3SOCD_2^-K^+$ (DIMSYL). $CD_3SOCD_2^-K^+$ was made from DMSO-d_6 with KH. DMSO-d_6 was purchased from Aldrich and dried by 4 Å molecular sieves before use.

In an NMR tube, 20 mg of **2** was dissolved in 0.6 mL of DMSO-d_6. Through a septum, 12 drops of DISYL-d_5 was added, and the NMR sample was quickly put into a 400 MHz NMR spectrometer. The ^1H spectrum revealed two new peaks at 0.132 and 0.423 ppm, indicating the formation of two trimethylsilyl-group-containing compounds. It was also noted that the major peak at 0.423 ppm decayed concurrently with the growth of the peak at 0.132 ppm. About 5 min after the addition of DIMSYL, the two peaks were about equal in size, and after 40 min, the peak at 0.423 ppm disappeared.

The peak at 0.423 ppm was assigned to anion **2a**, and the peak at 0.132 ppm to $D_3CS(OSiMe_3){=}CD_2$. The reactions occurring are sumarized in Scheme 1. The ^{13}C NMR spectrum of the final reaction solution showed only peaks identical with the ones observed in a solution of the fluorenide anion prepared by the reaction of fluorene with DIMSYL-d_5 in DMSO-d_6. Addition of the $(t\text{-}BuSO_2)_2CH_2$ ($pK_{HA} = 13.7$) to the final reaction solution resulted in the formation of fluorene identified by the NMR. The ^1H NMR peak of the trimethylsilyl group at 0.132 ppm remained unchanged.

The pK_{HA} Measurement of 9-(Trimethylsilyl)fluorene (2). To avoid desilylation during the titration, the strongly basic $CH_3SOCH_2^-K^+$ was quenched with a more acidic sulfone.

The pK_{HA} of **2** was first narrowed down to 21.7 ± 1 by the following experiments. A solution of *m*-cyanobenzyl phenyl sulfone ($pK_{HA} = 20.7$) anion was prepared by the reaction of excess sulfone with DIMSYL in DMSO. Then, a DMSO solution of **2** was added into the cuvette containing the sulfone anion, and the absorption at 530 nm [(trimethylsilyl)fluorenide anion] was monitored by a UV−vis spectrometer. No absorption was detected, but a change of absorption at 530 nm was observed when the solution of *m*-fluorobenzyl phenyl sulfone ($pK_{HA} = 21.7$) anion was mixed with **2**.

In the titration experiments, a DMSO solution of DIMSYL was quenched by benzyl methyl sulfone ($pK_{HA} = 25.4$); then a DMSO solution of **2** was added to the solution of benzyl methyl sulfone anion, a milder base, to generate 9-(trimethylsilyl)fluorenide. Titrations with the standard acid *m*-fluorobenzyl phenyl sulfone ($pK_{HA} = 21.7$) followed immediately and were completed within 3 min to minimize the error caused by the desilylation. The pK_{HA} of **2** was obtained from the average of three titrations as 21.5 ± 1.

NMR Study of the Reaction of 9-(Triethylsilyl)fluorene (3) and 9-(Triphenylsilyl)fluorene (4) with $CD_3SOCD_2^-K^+$ (DIMSYL). In an NMR tube, 20 mg of **3** was dissolved in 0.6 mL of DMSO-d_6, a slight excess of DIMSYL-d_5 was added immediately through a septum, and the sample was put into a 400 MHz NMR spectrometer. Both ^1H and ^{13}C spectra revealed a single product, which can be assigned as 9-(triethylsilyl)fluorenide ion. The NMR data are listed in Table 1.

After the NMR spectra of 9-(triethylsilyl)fluorenide ion solution were recorded, excess $(t\text{-}BuSO_2)_2CH_2$ ($pK_{HA} = 13.7$) was added to neutralize the base, and NMR spectra were taken again. Complete recovery of the starting 9-(triethylsilyl)fluorene was shown in the NMR spectra taken before the addition of DIMSYL-d_5.

In the same fashion, the reaction of 9-(triphenylsilyl)fluorene (**4**) with DIMSYL-d_5 was examined. Again, clean deprotonation was observed in the reaction. The NMR data are listed in Table 3, and complete recovery of the starting material was observed by NMR after the 9-(triphenylsilyl)fluorenide ion solution was quenched by $(t\text{-}BuSO_2)_2CH_2$.

NMR Study of the Reactions of $CD_3SOCD_2^-K^+$ with $PhSO_2CH_2SiMe_3$, $PhSO_2CH(SiMe_3)_2$, and $PhSO_2CH_2SiPh_3$. A 50 mg sample of (trimethylsilyl)methyl phenyl sulfone and 0.5 mL of DMSO-d_6 were placed in an NMR tube. After the ^1H and ^{13}C NMR spectra were recorded, 20 drops of DIMSYL-d_5 was added. The well-mixed solution was then quickly put into the NMR spectrometer, where the ^1H and ^{13}C NMR spectra were taken. Excess $(t\text{-}BuSO_2)_2CH_2$ ($pK_{HA} = 13.7$) was added to the solution containing the sulfone anion and some unreacted DIMSYL-d_5. The NMR spectra were taken again to see if the (trimethylsilyl)methyl phenyl sulfone was recovered from its conjugate base. All three of the sulfones, $PhSO_2CH_2SiMe_3$, $PhSO_2CH(SiMe_3)_2$, and $PhSO_2CH_2SiPh_3$, underwent clean deprotonation in the reaction with DIMSYL-d_5 and were recovered after the addition of a stronger proton donor, $(t\text{-}BuSO_2)_2CH_2$ ($pK_{HA} = 13.7$).

The NMR data of typical H and C nuclei for sulfones and their conjugate bases are summarized in Table 1.

Reactions of $PhCOCH_2SiMe_3$ or $CH_3CONHSiMe_3$ with $CD_3SOCD_2^-K^+$. The NMR spectra of the reaction solution of $PhCOCH_2SiMe_3$ with $CD_3SOCD_2^-K^+$ in DMSO-d_6 were identical with the NMR

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[18] Bordwell, F. G.; Zhang, S.; Zhang, X.-M. *J. Am. Chem. Soc.* submitted for publication, **1994**.

[19] Bordwell, F. G.; Zhang, X.-M.; Alnajjar, M. S. *J. Am. Chem. Soc.* **1992**, *114*, 7623.

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spectra of the product of the reaction of $PhCOCH_3$ with $CD_3SOCD_2^-K^+$ under similar conditions. The ^{13}C spectra of the two reaction solutions had the following identical peaks: δ 70.64, 125.45, 125.80, 126.97, 146.99, and 168.17. Neutralization of the reaction solution of $PhCOCH_2SiMe_3$ with $CD_3SOCD_2^-K^+$ by D_2O produced $PhCOCH_2D$ instead of $PhCOCHDSiMe_3$. Titration of $PhCOCH_2SiMe_3$ gave the pK_{HA} characteristic of $PhCOCH_3$, *i.e.*, 25.0.

The desilylation reaction was also observed in the reaction of $PhCONHSiMe_3$ with $CD_3SOCD_2^-K^+$, and the titration of $PhCONHSiMe_3$ gave a pK_{HA} similar to that of $PhCONH_2$, *i.e.*, 25.5.

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