Effects of Si Substitution on the Ei Reaction of Alkyl Sulfoxides

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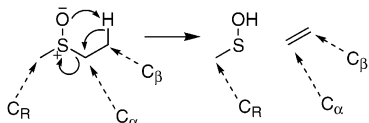
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A computational study has been carried out on the effects of SiH_3 substitution on the Ei reaction of alkyl sulfoxides. SiH_3 substitution in the β-position (relative to the sulfur atom) is found to lower the barrier to elimination about 5 kcal mol^{-1}, in line with qualitative experimental observations. However, SiH_3 substitution at the α-position has a similar, if smaller, effect. It is argued that the barrier-lowering in the latter case is mainly correlated with changes in the overall ΔH of the elimination reaction. In contrast, electronic effects in the transition state overcome an unfavorable $\Delta(\Delta H)$ when SiH_3 is in the β-position. On the basis of estimated magnitudes of the various energy changes and the fractional change in bond orders in the transition state, it is argued that both hyperconjugative stabilization and inductive effects of Si substitution contribute. Finally, it is shown that the elimination reaction by SiH_3 transfer from C_β to O has a surprisingly high enthalpic barrier, given its modest endothermicity, and it is suggested that this is due to a forced unfavorable geometry at the Si center in the transition state.
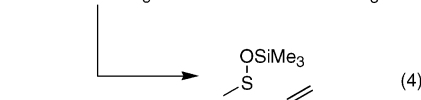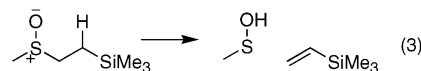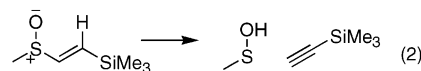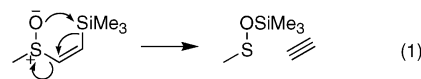
Introduction

The internal elimination reaction of alkyl sulfoxides to form a sulfenic acid and an olefin is a reaction that has found substantial utility in organic synthesis.[1−3] Though the analogous reaction of selenoxides has partially supplanted the sulfur-based reaction, the sulfinyl elimination remains important and is finding new applications. (See, for example, ref 4.) Reactions of related functional groups, including sulfinates, thiosulfinates, sulfilimines, and sulfones, are also known.[5−14]

Although the analogous elimination of vinyl sulfoxides to form acetylenes is known,[15] it is rarely observed exper-
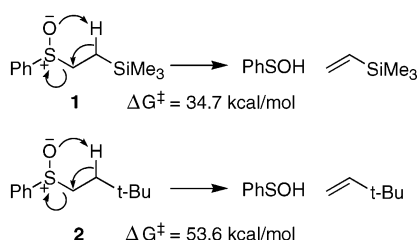
imentally, presumably because its activation enthalpy (ca. 42 kcal mol^{-1}) is too high for the reaction to be practical. One approach to circumvent this difficulty is to replace the abstracted proton with a silicon functionality, so an O−Si bond is formed, rather than an O−H bond (reaction 1).[16,17] Such reactions are presumed to be accelerated because the reaction is less endothermic, i.e., ΔH_{elim} is less positive. Another approach is to use the TMS group in the trans β-position (reaction 2). This has also been done in reactions that produce olefins (reactions 3 and 4).[16−19] In the olefin-forming reaction, though two different elimination pathways may be followed, both are accelerated relative to the parent reaction without the silyl group.

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The sulfoxide Ei elimination has been explored computationally by a variety of methods.[4,15,20] All authors agree on a planar, 5-centered transition state and a concerted, relatively synchronous reaction. We demonstrated that experimentally evaluated substituent effects at C_α, C_β, and C_R can be well modeled by MP2 calculations with a sufficiently large basis set.[15] Recently, Toru examined the effect of trimethylsilyl substitution at C_β on the elimination reaction of sulfoxide **1**, using compound **2** as a control.[19] Using HF/3-21+G(d) to do calculations on these two large (for computational chemistry, at any rate) molecules, the barrier was 18.9 kcal/mol lower for the silicon-substituted molecule **1** than for the *tert*-butyl analogue, and the effect was attributed to silicon's well-demonstrated[21−28] ability to stabilize β-carbocations (i.e., at C_α). Other authors attributed analogous effects to anticipated charge separation at C_α and C_β in the transition state.[29]

Toru's reported $\Delta(\Delta G^{\ddagger}_{elim})$ piqued our interest, partly because we knew of no other simple substituent that had such a dramatic effect. Hartree−Fock calculations are known to overestimate barriers in reactions such as these but might reproduce trends well. However, large basis sets, particularly those containing tight d-polarization functions, are necessary to correctly estimate the relative energies of oxidized sulfur compounds (e.g., sulfoxide, sulfones, SO_2).[30−37]

In this paper, we report a computational chemical study on the Ei elimination reactions of several SiH_3-substituted sulfoxides and their methyl analogues. The SiH_3 substituent was chosen in favor of the larger TMS group in order to make more rigorous calculations plausible while maintaining the essential electronic effects. We find that contributions to the change of activation barrier come from the stabilization of potential charge build-up at C_β and C_α and also from changes in the endothermicity of the reaction being reflected in the transition state.

Computational Methods

To find the lowest energy conformations of the starting materials and products, conformational searches were performed using the PM3 semiempirical method as implemented in Spartan.[38] These were used as the initial geometries for subsequent optimizations. Initial guess transition states were also found at this level of theory. All other calculations were performed using the GAMESS suite of programs,[39] and the results were visualized using MacMolPlt.[40]

Geometries were optimized at HF/6-31G(d,p) and then refined at MP2(fc)/6-31G(d,p). Previous studies revealed that use of MP2(fc)/6-31G(d,p) produces geometries with S−O bond lengths that are somewhat too long.[4,15,41−44] However, calculated energy barriers for parent systems (e.g., reaction 5) using single-point calculations at these geometries are very similar to those calculated from fully optimized geometries with MP2 and large basis sets. Moreover, they reproduced experimental data quite nicely.[11,15]

Geometries and absolute energies of all species are given in the Supporting Information. Results in Table 1 are from calculations at the MP2(fc)/6-311+G(3df,2p)//MP2(fc)/6-31G-(d,p) level. MP2(full)/G3Large single-point energies were done using mixed basis sets. G3Large basis functions were used on Si, S, and O, while the remaining atoms were represented using the 6-311++G(3df,2p) basis set. Coefficients and exponents for G3Large[35,36] were obtained from chemistry.anl. gov/compmat/g3theory.htm and 6-311++G(3df,2p) from www.emsl.pnl.gov:2080/forms/basisform.html. The widely popular B3LYP method was avoided because it is known[15] to perform poorly for this reaction.

Hessians were obtained at the MP2(fc)/6-31G(d,p) level to confirm the nature of the stationary points and to determine zero-point energy corrections. The Gonzales−Schlegel second-order method[45] was used for determining intrinsic reaction coordinate paths, which invariably connected transition states to starting materials or products as expected. The reported ΔH and $\Delta H^{\ddagger}$ values are obtained from the absolute energies of the substrates at 0 K and the unscaled ZPEs. Products were calculated as isolated molecules.

Results

A series of elimination reactions of sulfoxides with appended SiH_3 or CH_3 groups are illustrated in Table 1. The methyl compounds were viewed as the controls, so that the substituent effect of the silyl group could be probed. Compounds **4** and **5** form acetylenes and test the

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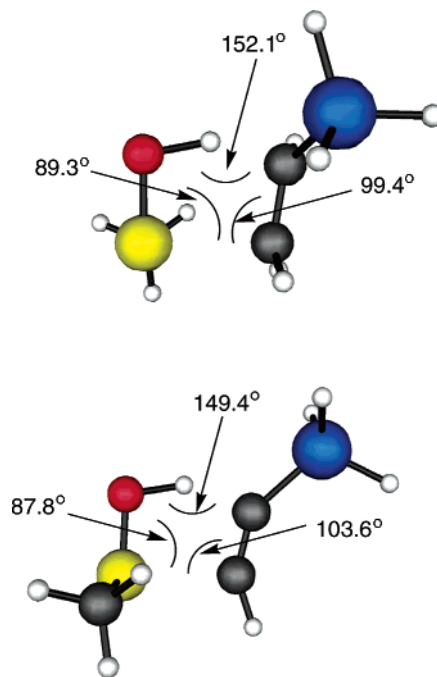
TABLE 1. Calculated Heats of Reaction and Activation Enthalpies (kcal mol^{-1})

Reaction		$\Delta H^{\ddagger}_{elim}$	ΔH	$\Delta H^{\ddagger}_{addn}$	Z^a
5	**3**	32.3	22.6	9.7	
6	**4**	30.7	22.3	8.4	-7.8
7	**5**	34.1	23.3	10.8	-1.8
8	**6**	26.9	21.3	5.6	-5.3
9	**7**	28.9	21.4	7.5	-1.8
10	**6**	29.8	5.2	24.6	
11	**8**	40.3	28.7	11.6	
12	**9**	41.1	27.3	13.8	
13	**10**	38.8	28.8	10.0	
14	**11**	31.1	19.2	11.9	
15	**12**	31.2	22.5	8.7	
16	**13**	34.3	6.0	28.3	

^{a} See text for definition.

FIGURE 1. Calculated transition states for reactions 8 and 6. Bonds are shown that correspond to the configuration of the products. In the top figure, the yellow sulfur atom obscures a methyl group behind it.

TABLE 2. Calculated Enthalpies and Activation Enthalpies Comparing Basis Sets

	$\Delta H_{elim}/\Delta H^{\ddagger}_{elim}$ (kcal mol^{-1})	
reaction	MP2/6-311+G(3df,2p)	MP2/6-311+G(3df,2p) G3Large on S, O
6	22.3/30.7	23.2/30.9
8	21.3/26.9	22.5/27.0
9	21.4/28.9	22.9/28.9
15	22.5/31.2	23.6/31.3

"directionality" of the effects of silyl substitution. The analogues of these compounds for olefin formation are represented by **6** and **7**. The (S_S, R_C) configuration of **7** allows the methyl and silyl groups to be on opposite sides of the key transition state plane of 5 atoms, analogous to the illustration of the transition state for compound **6**, illustrated in Figure 1. It was decided that CH$_3$ would be used as the control model for SiH$_3$, so compounds **9**–**12** were added. Compound **13** allows for acetylene formation by attack at Si, rather than H.

Due to previous success with calculations at the MP2-(fc)/6-311+G(3df,2p)//MP2(fc)/6-31G(d,p) level, and to be consistent with our previous published data, our impulse was to use this same protocol. It is well understood that "tight" d-polarization functions (i.e., those with large negative radial exponents) are required to get good energies for sulfoxides, sulfones, and related compounds.[30–34,36] The 6-311+G(3df,2p) basis set has such a d-function, with a polarization exponent of 2.3. However, recent workers
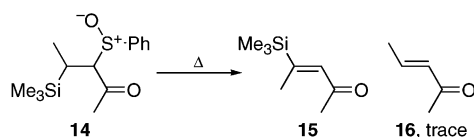
have emphasized the addition of even tighter d-polarization functions to effect core-polarization. Among the available basis sets that include these is the "G3Large" basis set of Curtiss,[35,36] which includes both a tight valence d (exponent = 3.4) and a core polarization d (exponent = 15).

To see if MP2(full) calculations with basis sets including core polarization functions produced significantly different results than the established method, direct comparisons were made and are shown in Table 2. When G3Large basis functions are used for silicon, sulfur, and oxygen and 6-311++G(3df,2p) basis functions for carbon and hydrogen, $\Delta H^{\ddagger}_{elim}$ is essentially the same while ΔH_{elim} increases by roughly 1 kcal/mol. Since the deviations are small, we stayed with the earlier method for consistency with our previous reports.[11,15,46] However, these results may indicate a systematic overestimate of ΔH_{addn} and $\Delta H^{\ddagger}_{addn}$ by ~1 kcal mol^{-1}.

Ideally, data from Table 1 would be compared to experimental values. However, the number of silyl-substituted sulfoxide elimination reactions whose kinetics have been studied is quite limited and they all also

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contain a carbonyl functionality. Nonetheless, some qualitative comparisons to experiment can be made. Fleming studied the thermolysis of **14** and found that elimination proceeded almost entirely through oxygen attack at the proton to give **15**, rather than at the silicon atom to give **16**. Note that compound **6** is a model for **14** in which the phenyl and carbonyl have been stripped off. It can undergo analogous reactions 8 and 10. Reaction 8, representing the elimination by way of attacking H, has an activation enthalpy 3 kcal mol^{-1} lower than reaction 10 (Si attack), despite having a ΔH_{elim} that is 16 kcal mol^{-1} more unfavorable. Similarly, acetylene-forming reaction 16 of sulfoxide **13** is about 16 kcal mol^{-1} less endothermic than that of its stereoisomer **6** but has a $\Delta H^{\ddagger}_{elim}$ that is 3.6 kcal mol^{-1} higher.
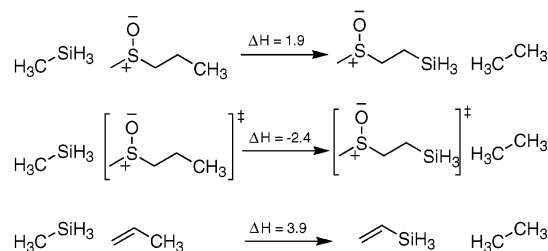

Representative transition-state geometries are illustrated in Figure 1. As usual, all transition states had approximately planar arrangements of the five key atoms. Substituting SiH$_3$ for CH$_3$ at either C$_\alpha$ or C$_\beta$ universally lowers the barrier to olefin formation by 2−4 kcal mol^{-1}. This point is important; Si catenation lowers the activation barrier at C$_\beta$ (as experimentally observed), but it also lowers the barrier at C$_\alpha$. For formation of acetylenes, the effects of silicon substitution on the activation barrier are larger: $\Delta(\Delta H^{\ddagger}_{elim}) = -4.2$ and -10.4 kcal mol^{-1} at C$_\alpha$ and C$_\beta$.

It is difficult to understand the origins of $\Delta(\Delta H^{\ddagger}_{elim})$ induced by silicon substitution solely by examining its magnitude. We suggest that substituent-induced differences in reaction barrier should be considered in two parts. One contribution to $\Delta(\Delta H^{\ddagger})$ will derive from the change in overall reaction enthalpy. In more familiar terms, this is "the transition state partially reflecting the stability of the product". For example, $\Delta(\Delta H^{\ddagger})$ will be almost $\Delta(\Delta H)$ for the substitutive perturbation of a very endothermic reaction with a late transition state, assuming the transition state is very product-like. By microscopic reversibility, $\Delta(\Delta H^{\ddagger})$ will be near 0 for a modest perturbation of a very exothermic reaction. In intermediate cases, there will always be some contribution from this effect.

Another way a substituent can contribute to $\Delta(\Delta H^{\ddagger})$ is that it may interact with the active portion of the transition state (henceforth called simply "the transition state" for sake of brevity) in a manner distinct from the way it interacts with the functional groups in the starting material or product. For example, a reaction might have a transition state with considerable localized charge build-up that might be additionally stabilized or destabilized by a particular substituent. A substituent might also cause a particular steric interaction unique to the transition state because of geometry changes. No obvious correlation between $\Delta(\Delta H)$ and this contribution to $\Delta(\Delta H^{\ddagger})$ can be expected.

We previously[15] tried to get at this transition-state-specific electronic contribution by examining the activation enthalpy for the reverse of the elimination reaction,

SCHEME 1. Isodesmic Reactions Associated with Substituting SiH$_3$ (Reaction 8) for CH$_3$ (Reaction 14)

the addition of RSOH to an olefin. It was argued that less of $\Delta(\Delta H^{\ddagger}_{addn})$ would be directly related to the change in reaction enthalpy because the addition is exothermic. This gave a satisfying rationalization of the substituent effects, which were not always straightforward to understand otherwise. For example, the values of $\Delta H^{\ddagger}_{addn}$ are within 2 kcal mol^{-1} for reactions 5 and 11, reflecting the apparently similar natures of the reactions, despite grossly different $\Delta H^{\ddagger}_{elim}$ values obtained from experiment.

Thus, we briefly use this analysis here. The data in Table 1 reveal that when Si is substituted at C$_\beta$, $\Delta H^{\ddagger}_{addn}$ is several kcal mol^{-1} smaller than that of the corresponding all-carbon case (e.g., reaction 6 vs reaction 12). However, it is not obvious that this is due entirely to hyperconjugation. In the vinylsilane product and transition states of reactions 8 and 9; for example, the Si substituent is not well aligned to participate in hyperconjugation that might stabilize the addition pathway. However, Mulliken and Lowden analysis of the charges on the carbon atoms show an extra negative charge of ∼0.1e on the C directly bonded to Si (data not shown), which is in line with expectations for the inductive effect of Si. These results hint that the polarizability of Si may be important in understanding the reduced barrier, as we shall argue again below. When the Si substituent is at C$_\alpha$, the addition barriers are closer to the corresponding all-carbon case.

Beyond this qualitative analysis, we hoped to develop a method to separate $\Delta(\Delta H^{\ddagger})$ into two explicit parts more quantitatively, as shown in in eq 1, where Y is the "$\Delta(\Delta H)$ contribution to $\Delta(\Delta H^{\ddagger})$", i.e., the partial reflection of product stability in the transition state. With Y in hand, the rest of $\Delta(\Delta H^{\ddagger})$, defined as Z, could be attributed to the interaction of the substituent with a unique feature of the transition state.

$$\Delta(\Delta H^{\ddagger})_{substituent} = Y(\Delta(\Delta H) \text{ contribution}) + Z$$
$$\text{(specific interaction with TS)} \quad (1)$$

Appropriate reference isodesmic reactions can be used to gauge the energetic effects of a substituent on starting materials, transition states, and products. This is shown in Scheme 1 and graphically in Figure 2 for reaction 8, using reaction 14 as the control. Since the isodesmic reactions for both the starting material and product are endothermic but that for the transition state is exothermic, it is obvious that there is a specific favorable interaction between the SiH$_3$ group and the transition state.

Of the three terms in eq 1, only $\Delta(\Delta H^{\ddagger}_{elim})$ is experimentally accessible. Thus, to approximate the magnitude of the specific interaction between the SiH$_3$ group and
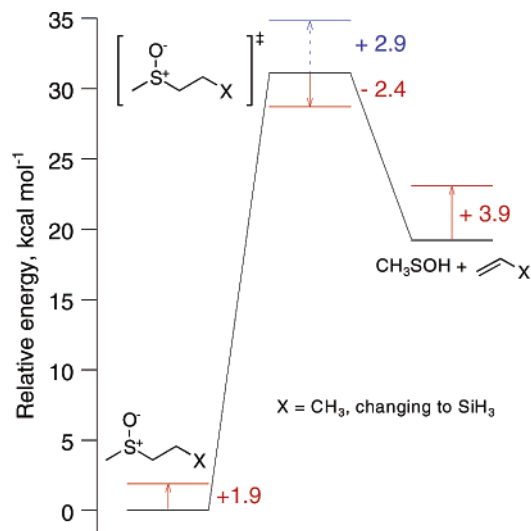
FIGURE 2. Energetic effects associated with changing from reaction 14 to reaction 8. In red are the actual energetic data going from CH$_3$ to SiH$_3$, and in blue is the projected change in the transition-state energy based on a linear interpolation between starting materials and products.

the transition state, we must guess what the expected energy of the transition state would be in its absence, allowing determination of *Y*. To do this, we crudely assume that the transition-state energy should move up or down by an amount that can be linearly interpolated from the isodesmic reactions on the starting materials and products and the degree of progress in the reaction at the transition state. The transition-state progress is, in turn, approximated by averaging the fractional progress of the bond order indices in the transition state (vide infra). Then *Y* is determined by subtracting the isodesmic exchange energy (shown in blue in Figure 2) for the starting material from the "projected" isodesmic exchange energy for the transition state, i.e.

$$Y = [C_{\mathrm{sm}}(\Delta H_{\mathrm{iso,sm}}) + C_{\mathrm{p}}(\Delta H_{\mathrm{iso,p}})] - \Delta H_{\mathrm{iso,sm}} \quad (2)$$

where C_i are the weighting factors for the starting material and product, respectively, and $\Delta H_{\mathrm{iso,i}}$ are for the respective isodesmic reactions.

In both reactions 8 and 14, the position of the transition state is almost halfway between the starting materials and the products, giving weighting coefficients very near 0.50. Thus, an energy change of +2.9 kcal mol^{-1} (halfway between +1.9 and +3.9) is projected and $Y = (2.9-1.9)$ kcal mol^{-1} = 1.0 kcal mol^{-1}. The magnitude of *Z* can then be obtained from Figure 2. It is the difference between the projected and actual energy changes of the transition state, -5.3 kcal mol^{-1} in this case. The *Z* values obtained in an identical fashion for other reactions are given in Table 1. For reaction 6, in which a β-silyl group assists formation of an acetylene, *Z* is -7.8 kcal mol^{-1}. For the two reactions in which the SiH$_3$ is attached at C$_\alpha$, the value of *Z* is -1.8 kcal mol^{-1}.

There is another set of isodesmic reactions that is helpful in understanding these compounds, in which the position of the CH$_3$ or SiH$_3$ is moved from C$_\beta$ to C$_\alpha$. Enthalpies obtained for these reactions at the equilibrium geometry of the sulfoxides and the transition states are

TABLE 3. Isodesmic Reaction Enthalpies (Including ZPE) for the Low Energy Conformation and for the Transition State for Elimination

	ΔH (eqm geometry) kcal mol^{-1}	ΔH (transition state) kcal mol^{-1}
	-1.5	-3.8
	-1.0	2.4
	-3.2	-3.3
	-0.2	1.7

given in Table 3. At the equilibrium geometries, it is more favorable to have a methyl substituent at C$_\alpha$ than at C$_\beta$, but the difference is greater at the transition states.[47] This trend is in keeping with the classical notion of methyl being slightly electron donating, relative to hydrogen. In contrast, while the trend favoring C$_\alpha$ substitution is also seen for the SiH$_3$ compounds at the equilibrium geometries (though to a smaller degree), it is reversed in their transition states. This emphasizes the point that there is indeed a specific interaction between the SiH$_3$ group substituted at C$_\beta$ and the transition state for elimination.

Discussion

The enhancement of the rate of sulfoxide Ei elimination by C$_\beta$-trimethylsilyl substitution was first observed in 1981.[48] More recently, natural population analysis was used to suggest the rate enhancement was caused by the silyl group's ability to stabilize a β-carbocation (i.e., at C$_\alpha$) via hyperconjugation.[19] We point out here, however, that even a silyl substituent in the "wrong" position (C$_\alpha$) will lower the barrier the sulfoxide elimination. This suggests that factors aside from stabilization of positive charge β to the SiH$_3$ substituent in the transition state are important in this reaction. We argue that these include a simple reflection of product stability in the transition state and more general effects deriving from the polarizability of the silyl group.

A useful datum in illustrating that hyperconjugation cannot account for the full effect of silyl substitution is an estimate of its maximum possible effect on the transition state energy. This necessitates discussion of the stabilization of "β-carbocations" by silyl groups in other systems.[21−23] Early computational studies predicted β-silyl groups would stabilize carbocations by ∼25 kcal/mol, relative to the methyl analogue.[21] One-fourth of the
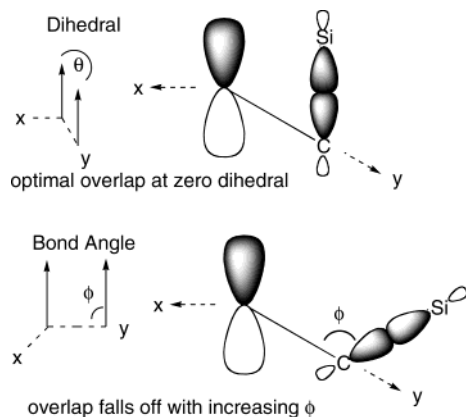
(47) The difference is 0 for the products, as they are identical.
(48) Fleming, I.; Perry, D. A. *Tetrahedron Lett.* **1981**, *22*, 5095−5096.

TABLE 4. Geometric Properties of Transition States

reaction	θ^a	ϕ^b	$\cos^2 \theta \cos^2(\phi - 90)$	max hyperconjugation energy (kcal mol^{-1})^c	Z^d (kcal mol^{-1})
6	178.3	145.2	0.33	−4.6	−7.8
8	112.7	119.1	0.11	−1.5	−5.3

^{a} Si−C−C−S dihedral angle. ^{b} C−C−Si bond angle. See Figure 3. ^{c} Based on 14 kcal mol^{-1} as a maximum in an ideal geometry. ^{d} From Table 1.

FIGURE 3. Illustrations of angular dependence of overlap between the C−Si bond and an adjacent empty p orbital.

β-silyl stabilization was attributed to inductive effects and the rest to hyperconjugative stabilization.

Experimentally, the angular dependence of the rate enhancement of solvolysis by a β-silyl group was determined by using *tert*-butylcyclohexane rings and bicyclic compounds to perform ionizations in fixed conformations.[22,23] The optimal rate enhancement is found when the dihedral angle ∠Si−C−C−LG is 180° (Figure 3).[22] At this geometry, the solvolysis rate enhancement by a β-trimethylsilyl is a factor of 10^{12}, when extrapolated to room temperature, which represents an activation barrier difference of about 17 kcal mol^{-1}. Further analysis assigned about 3 kcal mol^{-1} of this to inductive effects and 14 kcal mol^{-1} to hyperconjugation.

The angular dependence of the hyperconjugation is illustrated by the drop in the rate acceleration of solvolysis by a β-silyl group to 10^4 when the dihedral angle ∠Si−C−C−LG is 60°.[22] The usual form assumed for this dependence is $\cos^2 \theta$.[22,49-51] Using the experimental solvolysis data and the $\cos^2 \theta$ dependence, the 60° dihedral angle lowers the expected hyperconjugative contribution to 3.5 kcal mol^{-1}. If an assumption of constant (i.e., angle-independent) inductive effects is used, the observed hyperconjugative contribution is 2.8 kcal mol^{-1} for the 60°-constrained system, in reasonable agreement.

Similar arguments suggest an attenuation of hyperconjugation based on the ∠C−C−Si bond angle ϕ should occur (Figure 3).[27] We take that relationship to go as $\cos^2$-

$(90 - \phi)$.[27,52] The geometric parameters of the transition states for reactions 6 and 8 (Table 4) yield $\cos^2 \theta \cos^2$-$(\phi-90)$ values of 0.33 and 0.11, respectively. Using 14 kcal mol^{-1} as the maximum value for hyperconjugation in an ideal geometry, these attenuated maximum values of hyperconjugative stabilization are compared to Z in Table 4. Though qualitatively in the right order, the values clearly suggest that there is at least another contribution to Z. Furthermore, these maxima for hyperconjugative stabilization correspond to full cation formation, implying a completely E1-like mechanism. There is no evidence for such a mechanism here. As a result, we must conclude that the maximum hyperconjugative stabilizations cited in Table 4 are overestimates of the real situation.

We can probe the type of transition state in these reactions by examining the calculated bond orders.[53-55] The absolute calculated BOI values, which range from 0 to slightly less that the classic bond order of 1, 2, or 3, are given in the Supporting Information. In Table 5, the fractional progress for each of the five key bonds, in sulfoxide, transition state, and products, is presented.[56] If stabilization of β-carbocationic charge were the dominant interaction specific to the transition state, the transition-state bond orders for reactions 6 and 8 should shift toward the E1 limit (e.g., very low C_α−S bond order), relative to reactions 12 and 14. Another possibility is that the carbanionic stabilization effected by a silyl group is the most important factor in the electronic stabilization. α-Silyl carbanions are stabilized by the increased polarizability of the C−Si bond and hyperconjugation between the carbanion p-orbital and the Si−R σ^* orbital.[57-64] This stabilization has been estimated to be 20 kcal mol^{-1} in the gas phase[57-59,63,64] and about 5 kcal mol^{-1} in solu-

(49) Sunko, D. E.; Szele, I.; Hehre, W. J. *J. Am. Chem. Soc.* **1977**, *99*, 5000−5005.

(50) Kelly, D. P.; Underwood, G. R.; Barron, P. F. *J. Am. Chem. Soc.* **1976**, *98*, 3106−3111.

(51) This relationship draws from evidence that the angular dependence of the deuterium kinetic isotop effect and C−H NMR coupling constants follow the same dependence and is similar to arguments made about the strength of twisted π-bonds.

(52) This is based on the rate enhancement of the protonation of silylacetylenes.

(53) Giambiagi, M.; Giambiagi, M.; Grempel, D. R.; Heymann, C. D. *J. Chim. Phys. Phys.-Chim. Biol.* **1975**, *72*, 15−22.

(54) Mayer, I. *Chem. Phys. Lett.* **1983**, *97*, 270−4.

(55) Mayer, I. *Chem. Phys. Lett.* **1985**, *117*, 396.

(56) In other words, if the bond order in the starting material is 0.90, that in the transition state is 0.60, and that of the products is 0, the fractional progress is 0.33 in that the bond is one-third broken. If a bond is made as a result of the reaction, the fractional progress represents the progress towards forming the bond instead.

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(58) Brinkman, E. A.; Berger, S.; Brauman, J. I. *J. Am. Chem. Soc.* **1994**, *116*, 8304−8310.

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(64) Giordan, J. C. *J. Am. Chem. Soc.* **1983**, *105*, 6544−6546.

TABLE 5. Fractional Progress in Bond Making and Breaking for Elimination Reactions

reaction	substrate	S$-$C$_\alpha$ breaking σ	S$-$O ylide to σ	O$-$H making σ	C$_\beta$$-$H breaking σ	C$_\alpha$$-C_\beta$ making π
6	**4**	0.45	0.60	0.54	0.57	0.46
7	**5**	0.51	0.56	0.49	0.53	0.49
8	**6**	0.42	0.58	0.49	0.52	0.39
9	**7**	0.49	0.48	0.47	0.51	0.40
10[a]	**6**	0.47	0.75	0.44	0.59	0.47
12	**9**	0.50	0.59	0.54	0.57	0.47
13	**10**	0.50	0.59	0.55	0.59	0.48
14	**11**	0.47	0.55	0.48	0.52	0.40
15	**12**	0.45	0.55	0.51	0.54	0.39
16[a]	**13**	0.54	0.82	0.77	0.70	0.59

[a] In this case, O$-$Si making, rather than O$-$H making, and C$_\beta$$-$Si breaking, rather than C$_\beta$$-$H breaking.
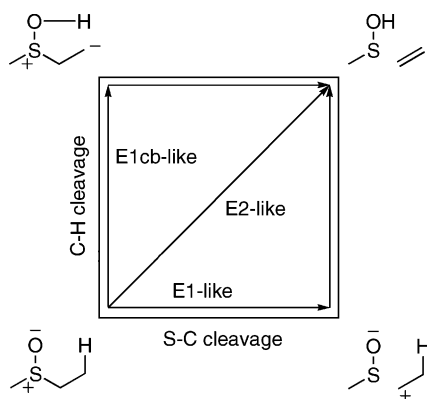

FIGURE 4. Reaction coordinate diagram for the syn-elimination of sulfoxides, indicating E1-, E1$_{cb}$-, and E2-like reaction pathways.

tion.[61,62,65] If this effect were dominant in the sulfoxide Ei elimination with Si substituted at C$_\beta$, the transition state would be expected to become more E1$_{cb}$-like (Figure 4).

The parent reactions for olefin and acetylene formation, respectively, are 14 and 12. In general, the transition state for reaction 12 is somewhat later than that for reaction 14, in keeping with the fact that it is more endothermic. Overall, there may be a slight E1$_{cb}$-cast to what is best described as an E2-like transition state in both cases. In principle, a Si substituent at C$_\beta$ is in the correct position to favorably affect both an E1 and E1$_{cb}$ pathway by interacting with a cationic C$_\alpha$ and/or an anionic C$_\beta$. To see the effect of the C$_\beta$ substitution on the position of the transition states, we compare reaction 8 to 14 for the olefin-forming reaction. There is only one significant change, a lessening in the progress of the S$-$C breaking with the SiH$_3$ group present. If anything, the reaction is slightly *less* E1-like. The same trend is observed when comparing acetylene-forming reaction 6 to its control, reaction 12.

Thus, while our calculations do not sample large portions of the energy surface represented in Figure 4, we can reasonably arrive at the following: (1) Due to the change in relative product stabilities of the elimination reactions when substituting a silyl group for a methyl group at C$_\beta$, $\Delta(\Delta H^{\ddagger}_{elim})$[66] should be <0 for reaction 6 and >0 for reaction 8. (2) There is a stabilizing electronic interaction (Z) between the silyl group and the active centers of the transition state that causes $\Delta H^{\ddagger}_{elim}$ for reaction 6 to be about 8 kcal mol^{-1} less than would be predicted on the basis of product stability alone. (3) The magnitude of Z exceeds any reasonable maximum that can be attributed to hyperconjugation alone, and the bond orders do not support approaching the maximum in any case. Therefore, we may conclude that the stabilization of the transition state in reactions 6 and 8 includes other significant electronic contributions from the silyl group, in addition to the expected stabilization of β-cationic charge by hyperconjugation and a contribution due to the relative stability of the product.

Next, we consider reactions 7 and 9, in which the silyl group is at C$_\alpha$, and the control reactions are 13 and 15, respectively. As seen in Table 1, Z has been estimated at -1.8 kcal mol^{-1} for both reactions, but it should be emphasized that the exact values of Z depend on our computational estimate of Y. It is not surprising that Z for the C$_\alpha$ cases is smaller in that the Si is in the "wrong" position to assist with either the E1 or E1$_{cb}$ mechanism. Any developing positive charge on C$_\alpha$ would be destabilized by the C$_\alpha$-silyl group, as has been shown in previous solvolysis experiments.[67-69] The E1$_{cb}$ mechanism is not helped either in that existing evidence on the effects of silicon substitution on the stability of β-carbanions indicates a small, possibly destabilizing interaction.[61,64,70,71]

There are a few significant differences in the positions of the transition states for reactions 7 and 9 and their respective controls. However, the factor that ties them all together is that each significant change brings the transition state *closer* to 0.50 fractional progress, i.e., the synchronous E2-like limit. Reaction 7 illustrates spectacularly the point we have made earlier: although the barrier to reaction 7 is fully 5.5 kcal mol^{-1} lower than that of reaction 13, we estimate that the contribution to the Si substituent effect by a specific interaction with the transition state (i.e., Z) is no more than a third of that amount, with the rest being due to the transition state simply reflecting an intermediate value of the relative (de-)stabilization of the starting materials and the products (i.e., Y).

Finally, we address reactions 10 and 16, in which the

(65) Streitwieser, A.; Linfeng, X.; Wang, P.; Bachrach, S. M. *J. Org. Chem.* **1993**, *58*, 1778−1784.

(66) That is, the difference in activation enthalpy between the silyl- and methyl-substituted compounds.

(67) Apeloig, Y.; Biton, R.; Abu-Freih, A. *J. Am. Chem. Soc.* **1993**, *115*, 2522−2523.

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(69) Nadler, E. B.; Rappoport, Z.; Arad, D.; Apeloig, Y. *J. Am. Chem. Soc.* **1987**, *109*, 7873−7875.

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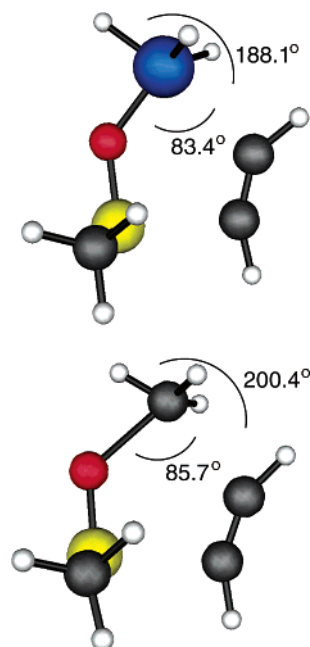(71) Engel, W.; Fleming, I.; Smithers, R. H. *J. Chem. Soc., Perkin Trans. 1* **1986**, 1637.

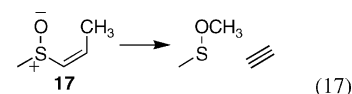**FIGURE 5.** Transition state for reactions 16 and 17. "Bonds" are drawn as found in the products.

oxygen atom attacks at Si, rather than H. While the ΔH_{elim} for these reactions is considerably smaller than for the parent reactions, the activation enthalpy is not affected nearly as much. It is self-evident that the SiH_3 transfer is kinetically disfavored because of an unfavorable interaction in the transition state. However, we cannot define Y and Z in the same fashion as previously, since we cannot write the same isodesmic exchange reaction for the starting materials and products.[72]

From Table 5, it can be seen that the transition states for reactions 10 and 16 are considerably later than the others in some aspects and are more $E1_{cb}$-like if we take the Si transfer as equivalent to proton removal. The transition-state geometry for reaction 16 is illustrated in Figure 5.[73] (That for reaction 10 is closely analogous.) The large size and long C–Si bond of the SiH_3 group (compared to H) precludes the nearly linear O–H(Si)–C_β arrangement found in the other transition states. Essentially, by replacing H with SiH_3, this becomes a 5-endo-tet reaction, classically disfavored by Baldwin's rules.[74]

Furthermore, the transfer of the Si atom from C_β to O can be thought of as a nucleophilic substitution. As would be expected for an Sn2-type event, the geometry about Si is approximately trigonal bipyramidal, except that the nucleophile has attacked *side on* and is equatorial, rather than axial. In unconstrained Si systems (e.g., SiH_4), such side-on nucleophilic attacks are deflected to a standard

backside attack, despite the availability of stable isoenergetic pentavalent structures.[75] Presumably, the distortion of the SiH_3 center in reactions 10 and 16 is of higher energetic cost than it would be if the attack were from behind because it must be side-on.

To examine this hypothesis at least qualitatively, one last reaction was studied. Reaction 17, like reactions 12 and 16, violates standard Baldwin's rule type constraints, but a methyl group has been used instead of the silyl.

The distortion required for a methyl group in the transition state for reaction 17 should be more energetically costly than the analogous SiH_3 distortion in reaction 16. The calculated ΔH_{elim} for reaction 17 is 39.1 kcal mol^{-1}. However, the $\Delta H^{\ddagger}_{elim}$ is an astonishing 98.4 kcal mol^{-1}.[76] Note that the geometry of the transferring methyl group (Figure 5) is less like a trigonal bipyramid than in the SiH_3 transfer case, presumably because of the lower tolerance of C for this type of structure. The hydrogens maintain more of a quasi-tetrahedral arrangement, as if the methyl is being shifted from C_β to O "with retention" rather than with inversion through any kind of trigonal bipyramidal transition state.

Summary

Silyl groups attached at either the C_α or C_β position of an alkyl sulfoxide lower the activation enthalpy of the sulfoxide syn elimination reaction by a few kcal mol^{-1}, the exact figure depending on what reaction is taken as the reference. When the silyl substituent is at the C_α position, the barrier-lowering effect is mostly due to the transition state partially reflecting the fact that silyl substitution on the resulting olefin is more favorable than is the substitution on the sulfoxide, particularly for reaction 7. However, for reaction 8, substituting SiH_3 for CH_3 raises ΔH_{elim}, yet $\Delta(\Delta H^{\ddagger}_{elim})$ is negative. Thus, there is clearly a favorable interaction between the silyl group and the transition state center, whose energy we have labeled Z. We calculate Z to be -5.3 kcal mol^{-1} for reaction 8. The combination of the relative product destabilization and Z still results in an experimentally relevant negative $\Delta(\Delta H^{\ddagger}_{elim})$, but not the tens of kcal mol^{-1} implied by earlier accounts for related molecules.

For reactions with the silyl substituent at C_β, several factors point to the conclusion that stabilization of potential positive charge build-up at C_α in the transition state is not the sole predominating effect, but is comparable to the stabilization negative charge build-up at C_β. These include analyses of the transition state geometries, the magnitudes of Z, and the fractional progress of bond making and breaking.

In contrast, a C_α-silyl group is in an unfavorable position to interact favorably with any charge build-up in the transition state. Given the uncertainties of computational data, it is less certain whether the small

(72) Hypothetically, one could apply the formula for Y by assigning a fractional progress in the transition state and applying it to $\Delta(\Delta H)$ rather than weighting the isodesmic exchange reactions. However this would violate the principle of microscopic reversibility in that different Y values would be predicted depending on which reaction direction was being considered. This is the case in general when the substituent in question is an "active participant" that changes its bonding dramatically in the reaction rather than a "spectator".

(73) It should be pointed out that although at least transiently stable trigonal bipyramidal anionic Si structures are known, we find no evidence for an intermediate in this reaction.

(74) Baldwin, J. E. *J. Chem. Soc., Chem. Commun.* **1976**, 734–736.

(75) Taketsugu, T.; Gordon, M. S. *J. Phys. Chem.* **1995**, *99*, 14597–14604.

(76) This reaction would obviously never happen because this barrier is much higher than the C–S homolytic bond dissociation energies.

negative Z in reactions 7 and 9 represent a modest but real transition state stabilization, perhaps due to a general polarizability effect of Si, or an artifact of the approximations made in arriving at Z.

The formation of olefins or acetylenes by SiH_3 transfer reactions such as 10 and 16 has a barrier that is much higher than might be anticipated from ΔH_{elim}. We hypothesize that this is due to an additional unfavorable interaction that must occur, namely a nonideal side-on nucleophilic substitution reaction at the Si center that also violates Baldwin's rules.