

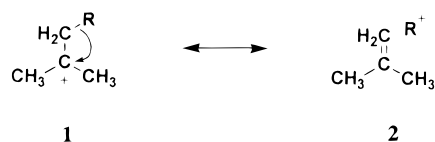
# The $\beta$ Effect of Silicon and Related Manifestations of $\sigma$ Conjugation

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Stabilization of carbocations through donation of  $\pi$  electrons from adjacent carbon orbitals results in well-known species such as the allyl and benzyl cations. Adjacent nonbonding (n) electrons on heteroatoms also can provide considerable stabilization, as in oxonium ions such as  $\text{CH}_2=\text{O}^+\text{CH}_3$  and iminium ions such as  $\text{CH}_2=\text{N}^+(\text{CH}_3)_2$ . Less well known is stabilization of carbocations by  $\sigma$  orbitals. In its most common example this interaction provides stabilization of tertiary over secondary over primary carbocations. According to the valence bond representation of this interaction, a filled  $\sigma$  orbital donates electrons to an empty  $\pi$  orbital, as in **1** and **2** ( $\text{R} = \text{H}$ ).



Positive charge moves from carbon in **1** to hydrogen in **2**. The canonical form **2** has suggested the term *double-bond–no-bond resonance* for the phenomenon. *Hyperconjugation* and  $\sigma\pi$  conjugation, however, are more common terms. The latter term indicates either that a  $\sigma$  bond is donating electrons to an empty  $\pi$  orbital in **1** or that a  $\sigma$  orbital in **1** is replaced by a  $\pi$  orbital in **2**.

The weakness of  $\sigma$  donation compared with the  $\pi$  and n effects has several causes. In particular, a  $\sigma$  orbital is higher in energy than the empty p orbital to which it donates electrons, whereas a  $\pi$  or n orbital offers a better energy fit. Thus, lowering the energy of the  $\sigma$  orbital

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should enhance the effect. Moreover, the C–H bond in the example of **1** and **2** ( $\text{R} = \text{H}$ ) is poorly polarizable. It might then be thought that a C–C bond in the same context (as in **1** and **2** with  $\text{R} = \text{CH}_3$ ) might be more polarizable and hence provide better hyperconjugation. The higher electronegativity of carbon than hydrogen, however, renders it a poorer acceptor of positive charge and offsets such considerations.

The ideal  $\sigma$  donor C–R bond is highly polarizable and has sufficiently low energy to match that of the empty p orbital, and the atom R is electropositive in order to receive the positive charge better. It was recognized over 60 years ago<sup>1</sup> that the carbon–silicon bond admirably provides these characteristics. Thus, when placed  $\beta$  to positive charge on carbon, silicon is well suited to provide stabilization through what has come to be known as the  *$\beta$  effect of silicon* (**1** and **2**,  $\text{R} = \text{SiR}'_3$ ).

In 1990, we reviewed this field comprehensively.<sup>2</sup> The ensuing several years have seen remarkable progress in the study of this and related phenomena. This Account focuses on the contributions from our research group since the 1990 Tetrahedron Report. During this period, the field saw excellent contributions from numerous other research groups.<sup>3–8</sup> Some of this work is mentioned herein briefly. This Account is divided into four sections: (1) progress on understanding the mechanism of formation of saturated  $\beta$ -silyl carbocations through kinetic and stereochemical studies; (2) longer range effects analogous to the  $\beta$  effect, in which the number of bonds between silicon (or germanium or tin) and the cationic carbon is increased; (3)  $\beta$  effects from outside group 14; (4) stable, isolable cations with  $\sigma$  conjugation.

## Stereochemistry and Mechanism

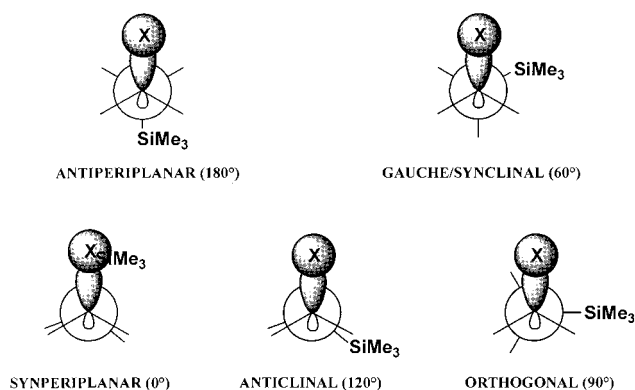
Possibly the major structural and mechanistic question concerning the  $\beta$ -silyl cation has been whether it prefers the open form **3**, stabilized by hyperconjugation, or the bridged form **4**. The respective mechanistic pathways have



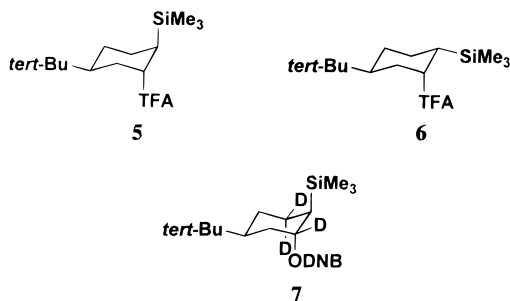
been termed *vertical* for **3**, since there is minimal movement of the C–Si bond between the ground and transition states, and *nonvertical* for **4**, since the silicon atom moves appreciably to permit bonding with the  $\beta$  carbon.<sup>9</sup> Theory was not definitive here, as the work of Jorgensen and co-workers found that both modes of interaction provide considerable stabilization, when a silicon system is compared with a hydrogen system, e.g.,  $\text{R} = \text{SiH}_3$  and  $\text{H}$  in **1** and **2**.<sup>10</sup>

In our earlier work,<sup>2</sup> we compared the rates of reaction for systems containing the  $\text{SiMe}_3$  group with structural analogues containing  $\text{H}$ , to obtain the ratio  $k_{\text{Si}}/k_{\text{H}}$ . This ratio is a measure of the ability of silicon to accelerate

Chart 1



carbocation formation. Solvent studies demonstrated that the reaction occurred via carbocation intermediates, leading to substitution and elimination, and the pathway was optimized in trifluoroethanol. We used biased *tert*-butyl-substituted cyclohexanes to provide conformationally pure species with dihedral angles of about  $180^\circ$  (antiperiplanar, **5**) and  $60^\circ$  (synclinal or gauche, **6**).<sup>11</sup> The stereochemical relationships within the Si–C–C–X groups of **5** and **6** are illustrated as the first two structures in Chart 1. The respective values of  $k_{\text{Si}}/k_{\text{H}}$  were  $2.4 \times 10^{12}$  for **5** and  $4.0 \times 10^4$  for **6** in 97% trifluoroethanol.



These figures established the  $\beta$  effect as one of the kinetically strongest in organic chemistry, but they did not provide a distinction between open and bridged intermediates. The antiperiplanar arrangement offers not only the optimal arrangement for hyperconjugation in the open form **3** but also the only stereochemical arrangement for backside displacement that leads to the bridged form **4**. The relatively large acceleration in the gauche form **6** is more in agreement with hyperconjugation, which varies with the square of the cosine of the dihedral angle between the C–Si bond and the empty p orbital, whereas bridging should not be possible from the gauche arrangement. If the trimethylsilyl group, however, could provide an acceleration of  $10^4$  strictly through induction, because of the higher electropositivity of silicon than hydrogen, the gauche acceleration is explicable by either the open or the bridging model.

To distinguish these two pathways, we measured the  $\alpha$  secondary deuterium kinetic isotope effect.<sup>12</sup> We prepared *r*-5-*tert*-butyl-*c*-2-(trimethylsilyl)cyclohex-*t*-yl-1,3,3-*d*<sub>3</sub> 3,5-dinitrobenzoate (**7**) and measured  $k_{\text{H}}/k_{\text{D}}$  by comparison with the dinitrobenzoate analogue of **5**. The value

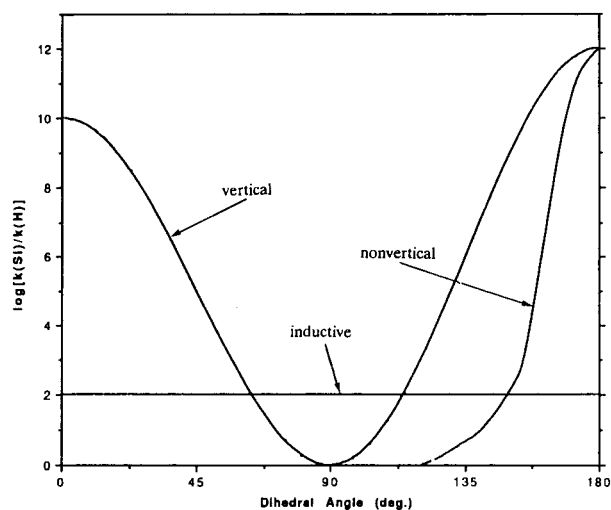
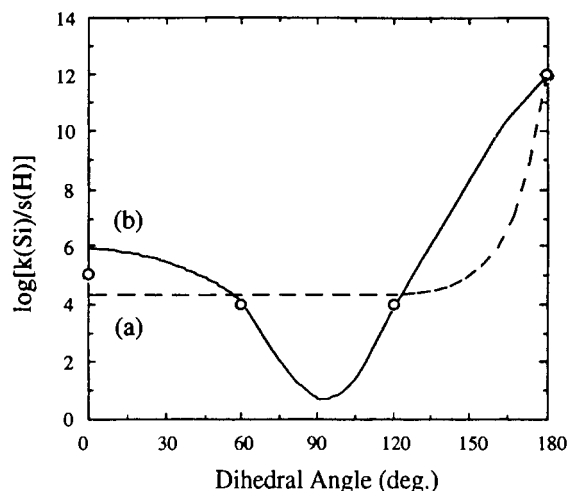


FIGURE 1. Qualitative dihedral dependences for the inductive, vertical, and nonvertical modes of  $\beta$  stabilization.

of  $1.17 \pm 0.01$  in 97% trifluoroethanol compares favorably with the value of 1.18 for 2-adamantyl tosylate in the same solvent. The value for **7** indicates a transition state containing an  $\text{sp}^2$  carbon in agreement with **3** rather than **4**. Formation of a bridged ion would have resulted in a much smaller isotope effect characteristic of nucleophilic displacement in the transition state. Models indicate that such a pathway should have a value of  $k_{\text{H}}/k_{\text{D}}$  in the range 1.00–1.08. The most critical interpretation, however, would point out that these models included only open chain and six-membered bridged systems. None contained the three-membered bridge of **4**, so some residual doubt remained.

As an alternative approach to distinguish open and bridged pathways, we sought to define the entire stereochemical map for the dihedral dependence of the rate acceleration from the  $\beta$  effect as a function of the Si–C–C–X dihedral angle  $\theta$ . Our expectation for hyperconjugation is a cosine-squared function, whereas for bridging there should be a large acceleration at  $\theta = 180^\circ$  and a rapid falloff to a low constant value characteristic of the through-bond, angle-independent inductive effect. Figure 1 illustrates the dependences for the two mechanisms in the absence of an inductive contribution. Any acceleration from induction would raise the vertical and nonvertical curves by a similar amount.

A key point on the map is the synperiplanar, or  $\theta = 0^\circ$ , point (Chart 1). The C–Si and empty p orbitals are parallel, as for  $180^\circ$ , and can overlap in the hyperconjugative model, but backside displacement from  $0^\circ$  is out of the question. We used the norbornyl framework to obtain this dihedral angle.<sup>13</sup> The rate acceleration  $k_{\text{Si}}/k_{\text{H}}$  for **8**, with a dihedral angle of  $0^\circ$ , with mesylate as leaving group, and with 97% trifluoroethanol as solvent, proved to be only  $9.4 \times 10^4$  by comparison with **9**, only slightly more than the acceleration for the gauche form **6**. If the contribution from induction is negligible, this value indicates a significant but small acceleration for the synperiplanar geometry. The calculations of Green, Kuan, and White<sup>8</sup> supported these observations, as they found that  $\sigma\pi$  overlap



**FIGURE 2.** Dihedral angle dependence of the  $\beta$  effect of silicon based on rate accelerations,  $k_{\text{Si}}/k_{\text{H}}$ , measured for 0, 60, 120, and 180°. The dashed line is the expectation for the nonvertical mechanism and the solid line for the vertical mechanism.

is much weaker in the synperiplanar than in the anti-periplanar geometry, despite the identical values of  $\cos^2(0)$  and  $\cos^2(180)$ . Thus, the cosine-squared model does not apply directly, although it can be fixed up in the manner of the Karplus equation with separate multiplicative factors for the ranges 0–90° and 90–180° ( $A \cos^2(0)$  and  $A' \cos^2(180)$  with  $A < A'$ ), or by the use of a  $\cos 2\theta$  term. The value of  $k_{\text{Si}}/k_{\text{H}}$  was estimated<sup>13</sup> for the 120° (anticlinal) system **10** (compared with **9**) to be  $10^5$ .

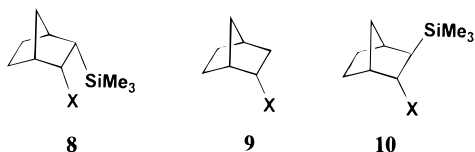


Figure 2 contains points for the 0, 60, 120, and 180° systems, with the expected dihedral angle dependences drawn in for the two mechanisms. Hyperconjugation explains the data (solid curve) if synperiplanar overlap is much less favorable than anti-periplanar overlap, as supported by the calculations of White and co-workers.<sup>8</sup> The dip at 90° would require the inductive effect to be essentially zero. Backside displacement to form the bridged ion in the rate-determining step also can explain the data, with a sharp rise at 180° and a level inductive dependence of  $10^4$  elsewhere (dashed line). Such a model requires that the inductive contribution also be about  $10^4$  at 90°, when the C–Si and empty p orbitals are orthogonal. This angle thus provides another opportunity to distinguish the mechanisms. There should be no acceleration to form the open cation at 90°, but a strong, inductively based acceleration of about  $10^4$  to form the bridged cation. Thus, we sought a system with orthogonal orbitals.

Near orthogonality (Chart 1) may be achieved in the bicyclo[2.2.2]octane system **11**. As positive charge develops, the 3-fold symmetry of the molecule allows the C–Si orbital to become fully orthogonal to the empty p orbital. The rate ratio  $k_{\text{Si}}/k_{\text{H}}$  was measured by comparison with

**12** in 97% trifluoroethanol and found to be 1.2–1.3.<sup>14</sup> Thus



at 90°, the  $\beta$  effect of silicon has essentially disappeared. Neither hyperconjugation nor backside displacement is allowed in the orthogonal geometry, so the only remaining electronic effect is induction. The observation of essentially no acceleration in this system means that the inductive effect is very low and that the horizontal line in Figure 1 should be drawn close to the 0 ( $\log 10^0$ ) line. In the absence of an inductive effect, the interpretation of the data in Figure 2 in terms of bridging fails, and the only remaining option is hyperconjugation with weak overlap in the synperiplanar geometry.

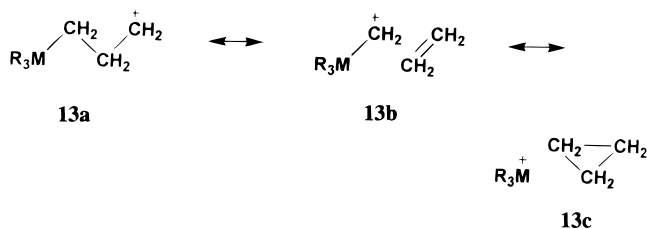
The  $\beta$  effect also has been studied quantitatively for the group 14 congeners of silicon.<sup>15</sup> Using systems analogous to **5** and **6** but without the biasing *tert*-butyl groups, we found that anti-periplanar germanium gives rise to an acceleration of about  $10^{13}$  (after conformational adjustment) and synclinal (*gauche*) germanium to an acceleration of  $4.6 \times 10^5$  in 97% trifluoroethanol. Thus, the  $\beta$  effect of germanium is qualitatively similar to but slightly stronger than that of silicon. The higher polarizability of germanium enhances the ability of the C–Ge bond to hyperconjugate. As expected, the effect continues with tin.<sup>15</sup> The effect in fact is so strong that making measurements has proved difficult. Even nitrobenzoates in the *gauche* geometry had rates exceeding the measurable range. The poor leaving group ability of acetate permitted measurement of  $k_{\text{Sn}}/k_{\text{H}}$  for the *gauche* (like **6**) but not the anti geometry. Mathematical conversion to trifluoroacetate as the leaving group led to a calculated acceleration of  $10^{11}$ , a very remarkable value for the nonoptimal *gauche* geometry. No measurements have been reported to date for any tin anti-periplanar system, but the acceleration must be at least  $10^{14}$  and may be  $10^{20}$  or larger.<sup>15</sup>

Gordon and co-workers<sup>16</sup> corroborated these results theoretically. Using an isodesmic reaction, they compared the acceleration of the metal in  $\text{H}_3\text{MCH}_2\text{CH}_2^+$  with  $\text{CH}_3^+$  and found an increasing stabilization for C, Si, Ge, and Sn of 48, 69, 77, and 89 kcal mol<sup>-1</sup>, respectively. Alternatively, they compared the stabilization in the anti-periplanar geometry with that in the synclinal geometry and found for the same series that the anti-periplanar form is more stable by 8, 29, 39, and 48 kcal mol<sup>-1</sup>. Thus, both experiment and theory agree that germanium has a stronger  $\beta$  effect than silicon, and tin has a stronger effect than germanium.

## Effects beyond the $\beta$ Position

Shiner's group<sup>2,5</sup> first provided a quantitative assessment of the  $\gamma$  effect of silicon in solvolysis reactions analogous to that of **5**. They found a modest acceleration ( $k_{\text{Si}}/k_{\text{H}}$ ) on replacement of R = H by SiMe<sub>3</sub> in R–C–C–X. The

interaction, sometimes called *percaudal*, is not explicable in terms of simple hyperconjugation (**13b**), which does not involve silicon directly, but requires the valence bond structure **13c**. The phenomenon has been called *homohyperconjugation* or  $\sigma\sigma$  conjugation. The latter term<sup>17</sup> was intended to highlight that a  $\sigma$  bond in **13a** is replaced by another  $\sigma$  bond in **13c**. The interaction also was examined in the 1,3-dioxo geometry of norbornane by Kirmse and co-workers.<sup>6</sup>

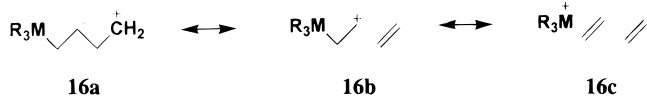


The  $\gamma$  effect of tin has been examined by Shiner, Adcock, and others.<sup>5</sup> We found that the acceleration ( $k_{\text{Sn}}/k_{\text{H}}$ ) in the cyclohexyl system **14**, in which the electrofuge and nucleofuge are both cis, is at least  $2.0 \times 10^3$  in 97% trifluoroethanol, whereas the trans system **15** had es-

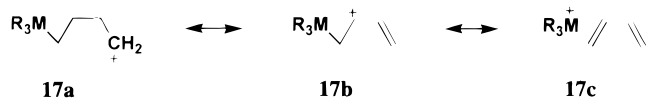


sentially no acceleration (a factor of 8).<sup>18</sup> Thus, the W geometry of **14** is clearly better than the sickle geometry of **15**. The acceleration ( $k_{\text{Si}}/k_{\text{H}}$ ) for the silicon analogue of **14** is only 460,<sup>5</sup> so that tin homohyperconjugates better than silicon.

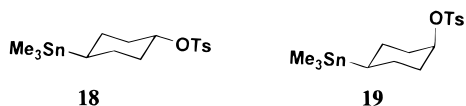
When the metal moves to the  $\delta$  position, there are several possible carbocation geometries. In the anti-anti geometry (**16**), the interaction may be represented by



simple hyperconjugation (**16b**) or by *double hyperconjugation* (**16c**, also called second sphere hyperconjugation or  $\sigma\pi/\sigma\pi$  conjugation<sup>17</sup>). Alternatively, the anti-syn geometry provides similar resonance structures (**17**) but a



different relationship between the double bonds in the valence form **17c**. An initial attempt to measure the  $\delta$  effect of silicon resulted in the observation of no acceleration.<sup>19</sup> We prepared the cyclohexyl systems **18** and **19**,

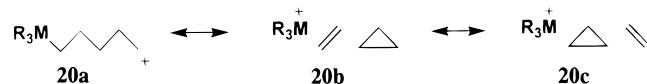


which would lead to the anti-anti geometry **16** for the carbocation.<sup>18,20</sup> We found that the trans form **18**, com-

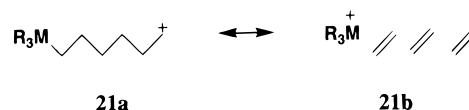
pared with cyclohexyl ( $k_{\text{Sn}}/k_{\text{H}}$ ), exhibited an acceleration of 42 and the cis form **19** an acceleration of 6. The latter is within the range of simple nucleophilic displacements by solvent, whereas the former indicates a small rate acceleration. Solvent variation confirmed that **18** passed through a carbocation intermediate whereas **19** experienced nucleophilic displacement by solvent. The  $\alpha$  secondary deuterium isotope effect ( $k_{\text{H}}/k_{\text{D}}$ ) for **18** of 1.19 confirmed an  $\text{sp}^2$  geometry in the transition state, as expected for a carbocation mechanism.<sup>18,20</sup>

Working with rigid bicyclic systems, the groups of Adcock and Shiner<sup>5</sup> found much larger rate accelerations for the  $\delta$  effect of tin, and even found significant accelerations for the  $\delta$  effects of silicon and germanium. Either the rigidity of the bicyclic framework favors a better interaction geometry, or the anti-gauche geometry (**17**) present in these systems offers better double hyperconjugation than the anti-anti geometry (**16**) of the cyclohexyl systems. To date there have been no theoretical studies of the  $\delta$  effect, which might clarify the relative merits of the various geometries.

Continued enumeration of the Greek alphabet would next lead to the  $\epsilon$  effect, of which no studies have been reported. Any effect of an  $\epsilon$  atom (**20a**) would have to involve both a percaudal and a hyperconjugative interaction (**20b** or **20c**, which, respectively, could be said to represent  $\sigma\pi/\sigma\sigma$  and  $\sigma\sigma/\sigma\pi$  conjugation according to our notation<sup>17</sup> or hyperconjugation/homohyperconjugation).



Triple or third-sphere hyperconjugation (**21b**,  $\sigma\pi/\sigma\pi/\sigma\pi$  conjugation<sup>17</sup>) could be observed when the heteroatom is  $\zeta$  to the leaving group. We sought to uncover such a



phenomenon by examination of the rigid decalin systems **22** and **23**.<sup>21</sup> The trans system **22** can lead to successful



orbital overlap and triple hyperconjugation, whereas the cis system **23** does not permit such overlap. Both systems, however, exhibited negligible rate accelerations ( $k_{\text{Sn}}/k_{\text{H}}$ ), and the solvent dependences of the rates were characteristic of a solvent displacement mechanism rather than carbocation formation. Thus, triple hyperconjugation or the  $\zeta$  effect has not been observed.

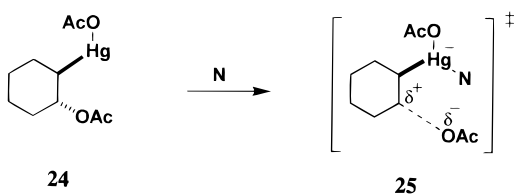
It is reasonable that the atom lead should carry the group 14 trends observed for silicon, germanium, and tin to a further extreme. Early studies by Eaborn,<sup>22</sup> Davis,<sup>23</sup> and Traylor<sup>24</sup> confirmed this expectation, but no further studies have been reported in over 25 years on  $\beta$  or longer

range effects of lead. It is possible that its more metallic properties could lead to behavior that does not follow the trends from its lower group 14 congeners, for example, in the role of solvent nucleophilicity.

Various forms of  $\sigma$  conjugation, of which the  $\beta$  effect may be thought of as the parent, give rise to observable but diminishing rate accelerations as the donor atom moves further from the cationic carbon. The magnitude of the interaction depends on the donor ability of the atom (H, C, Si, Ge, Sn) and on the conformational arrangement of the intervening bonds, in addition to the number of intervening bonds. When the number of intervening bonds is even, the effects may be termed  $\sigma\pi$  conjugation (and higher order variants such as double hyperconjugation), whereas when the number is odd there is  $\sigma\sigma$  conjugation (homohyperconjugation and higher order variants).

## Elements Outside Group 14

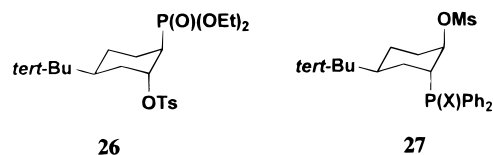
The preponderance of studies of the  $\beta$  effect and related  $\sigma\pi$  phenomena have been carried out on the group 14 elements. There is, however, nothing unique about this column in regard to the relevant electronic effects. That silicon has dominated the field speaks more to the importance of silicon in main group chemistry than to any central role of this element in the question of  $\sigma\pi$  conjugation. Traylor's early studies of the phenomenon in fact regularly included mercury along with the group 14 elements,<sup>24</sup> and even used the ferrocenyl group as a pseudoelement.<sup>25</sup> We found a strong acceleration in the mercury system **24**, although the solvent (N) was incorporated into the transition state (**25**).<sup>26</sup> It is at least feasible that many other main group elements and possibly some transition metals could exhibit  $\beta$  effect phenomena.



All  $\beta$  effect groups discussed up to now have been electron donating by reason of their high electropositivity. Our studies of the orthogonal silicon substrate **11**, however, demonstrated that the inductive effect was negligible (Figure 2). Thus, electron donation through  $\sigma$  bonds (induction) is much less important than the  $\sigma\pi$  or hyperconjugative effect, which depends largely on bond polarizability. The question then arises whether highly polarizable but electron-withdrawing bonds can exhibit a  $\beta$  effect. The effect of a bond dipole  $\mu$  on a charge  $q$  is given from electrostatic theory by the expression  $q\mu|\cos \theta|/\epsilon r^2$ , and the effect of bond polarizability  $\alpha$  on the charge is given by  $-\alpha q^2/2\epsilon r$ ,<sup>4</sup> in which  $\theta$  is the angle from the dipole to the charge,  $\epsilon$  is the dielectric constant of the medium, and  $r$  is the distance from the bond to the charge. If  $\alpha$  is sufficiently large, it can overcome the effect of  $\mu$  and of the stronger  $r$  dependence in the dipolar expression.

We sought to explore this possibility in the reactivity of group 15 substrates. Group 14 substrates lack lone pairs on the heteroatom, whereas those of groups 15–17 can possess lone pairs. Closure to the bridged intermediate analogous to **4** then involves the nucleophilicity of the lone pair rather than of the  $\sigma$  bond to the main group element. This widespread phenomenon has been called anchimeric assistance and has been found for halogen, oxygen, sulfur, phosphorus, and other atoms possessing lone pairs. To eliminate the problem of the lone pair, we used phosphorus(V) substrates: phosphonates, phosphine oxides, and phosphine sulfides.<sup>27,28</sup>

We made kinetic comparisons of the antiperiplanar (trans) substrates **26** and **27** (X = O, S) with cyclohexyl to obtain a measure of the acceleration or deceleration ( $k_p/k_H$ ). We also examined the analogous gauche (cis) sub-

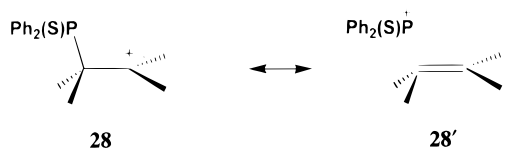


strates. We found in all cases that the cis substrates reacted very slowly and with nucleophilic solvent intervention, whereas the anti substrates reacted more rapidly and without nucleophilic solvent intervention. The trans/cis ratios were 12.7, 440, and 3 200 000, respectively, for the phosphonates, phosphine oxides, and phosphine sulfides.<sup>27,28</sup> In a comparison of the trans substrates with cyclohexyl, the ratios were 0.069, 0.63, and 220. Thus, the phosphine sulfide provides a large net acceleration. When compared with the huge  $\beta$  effects of the group 14 substrates, these values look quite small. They must, however, compensate for the dipolar (inductive) effect before they become observable. The cis substrates all typically react  $10^{-3}$ – $10^{-4}$  as fast as cyclohexyl and provide a measure of this inductive effect. Thus, the trans/cis ratios are a good measure of the  $\beta$  effect. Phosphonate is seen to be a weak  $\beta$  effect group, phosphine oxide a modest  $\beta$  effect group, and phosphine sulfide a strong  $\beta$  effect group.

The question of open vs bridged intermediates is not entirely settled for these systems. Bridging for **26** and **27**, in contrast to **4**, would involve closure to a four-membered ring by attack of X on C–O. The  $\alpha$  secondary deuterium isotope effect ( $k_H/k_D$ ) was measured to be 1.21 for the phosphine oxide and 1.26 for the phosphine sulfide, both values indicating a transition state leading to an open carbocation rather than to a bridged ion.<sup>28</sup>

We supported these experimental results with calculations at the MP2/6-31G(d) level.<sup>28</sup> The vertical contribution to the  $\beta$  effect could be measured by comparing the energy of M–CH<sub>2</sub>–CH<sup>+</sup>CH<sub>3</sub> when the M–C bond is parallel (as in **3**) and perpendicular (unable to engage in  $\sigma\pi$  conjugation). We found the difference between these two energies to be 8.0 kcal mol<sup>-1</sup> for P(O)(OH)<sub>2</sub>, 8.8 kcal mol<sup>-1</sup> for P(O)H<sub>2</sub>, and 10.5 kcal mol<sup>-1</sup> for P(S)H<sub>2</sub>. Thus, all of the substituents clearly exhibit net vertical stabilization (the inductive contribution should be the same in

the two forms and cancel out). Ibrahim and Jorgensen<sup>10</sup> calculated an analogous value of 22.2 kcal mol<sup>-1</sup> for the SiH<sub>3</sub> group. The valence forms **28** and **28'** illustrate



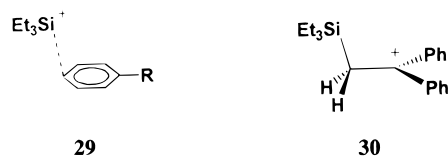
hyperconjugation for a phosphine sulfide. We could not make experimental measurements on phosphines, because of their instability under reaction conditions, and moreover they possess lone pairs. The pure vertical stabilization of PH<sub>2</sub>, however, can be measured calculationally by the same comparison. We found the value to be 22.9 kcal mol<sup>-1</sup>. By this one measure, phosphino is seen to be as strong a  $\beta$  effect group as silyl. Phosphines have not had the experimental impact as have silanes because of their instability and possibly because of their noxious properties not shared by the P(V) substrates we studied.

There appears to be a rich  $\beta$  effect field outside of group 14. It is obscured by the effects of transition state nucleophilicity, substituent electronegativity, and bridging. Nonetheless, vertical stabilization probably is viable throughout a wide variety of other elemental families.

## Stable Ions

Since many stable carbocations have been prepared at low temperatures in solvents such as magic acid, it was natural to consider whether  $\beta$ -silyl carbocations could be observed directly. The early results, however, were not promising. Olah et al.<sup>29</sup> attempted to generate Me<sub>3</sub>Si-CH<sub>2</sub>CPh<sub>2</sub><sup>+</sup> in FSO<sub>3</sub>H/SO<sub>2</sub>ClF from the analogous alcohol but instead obtained CH<sub>3</sub>CPh<sub>2</sub><sup>+</sup>, presumably by attack of an adventitious nucleophile on silicon, followed by desilylation to the alkene CH<sub>2</sub>=CPh<sub>2</sub>, which was protonated to form the product. Other attempts to obtain stable  $\beta$ -silyl carbocations sought to circumvent this problem by looking at alternative structures. Siehl and Kaufmann<sup>30</sup> prepared a vinyl cation in which the C-Si bond and the empty orbital are coplanar, although the carbon orbitals, respectively, are sp<sup>2</sup> and sp rather than sp<sup>3</sup> and sp<sup>2</sup> as in what we call the saturated structure (**3**). Lew et al.<sup>7</sup> reported complexes of silyl groups complexed with arenes that decomposed with rate constants on the order of 10<sup>4</sup>-10<sup>5</sup> s<sup>-1</sup>. We reported the ion **29** (R = H, Me), in which the charge is shared between silicon and the arene ring.<sup>31</sup> The resonance structures of **29** on one hand constitute a silyl cation and on the other a  $\beta$ -silyl carbocation. None of these approaches, however, resulted in a stable species with the classic, saturated  $\beta$ -silyl carbocation structure, in which a  $\beta$  sp<sup>3</sup>-sp<sup>3</sup> C-Si bond overlaps with an empty p orbital on an sp<sup>2</sup> carbon, as in **3**.

In 1996, we reported the preparation of such an ion that had long-term stability at room temperature.<sup>32</sup> We reasoned that the arene in ion **29** could be displaced by a more nucleophilic alkene, CH<sub>2</sub>=CPh<sub>2</sub>, and that the



resulting species, **30**, might prove to be stable. Critical to the argument was the observation in the context of **29** that such ions were stable in arene solvents (benzene, toluene) and with the anion (C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>B<sup>-</sup> (tetrakis(pentafluorophenyl)borate).<sup>31</sup> Indeed, ion **30** proved to be stable at room temperature for months. Although to date we have not succeeded in obtaining crystals for X-ray analysis, various NMR parameters were definitive in proving its structure. The cationic carbon resonated at  $\delta$  225.4, a position expected for a species with the positive charge primarily on carbon. The adjacent methylene carbon resonated at  $\delta$  56.2, indicative of the trigonal character expected from resonance contributions of the type **2**. The silicon atom resonated at  $\delta$  46.2, a value indicating only a minor amount of charge actually on silicon (in contrast to **29**, in which the silicon resonated at  $\delta$  92.3 in benzene). This stable, saturated  $\beta$ -silyl carbocation **30** must have the open structure analogous to **3** rather than the bridged structure analogous to **4** to produce these NMR chemical shifts. The presence of the two phenyl groups undoubtedly biases the result, so that there is only modest C-Si hyperconjugation. In a major accomplishment, the group of Siehl has succeeded in obtaining stable, saturated  $\beta$ -silyl carbocations at very low temperatures under magic acid conditions that rigidly excluded water and other nucleophiles.<sup>33</sup>

We prepared the  $\beta$ -germyl carbocation analogous to **30** (with Bu<sub>3</sub>Ge in place of Et<sub>3</sub>Si).<sup>34</sup> Its cationic carbon resonated at  $\delta$  213.4, indicating less positive charge on carbon and presumably more on germanium than was the case for the silicon ion **30**. The resonances of the adjacent methylene carbon and of the para carbon in the phenyl rings confirmed this conclusion, that the C-Ge bond engaged in slightly stronger hyperconjugation than did the C-Si bond in **30**. The same strategy with tin led to no change in the alkene resonances of the starting material, CH<sub>2</sub>=CPh<sub>2</sub>, or of the <sup>119</sup>Sn resonance position of the starting tin electrophile at  $\delta$  263. Thus, either the tin electrophile, Bu<sub>3</sub>Sn(benzene)<sup>+</sup>, had not reacted with the alkene or the resulting  $\beta$ -stannyl carbocation is essentially fully hyperconjugated. Plots for the series R<sub>3</sub>M-CH<sub>2</sub>-CPh<sub>2</sub><sup>+</sup> (R<sub>3</sub>M = H, Et<sub>3</sub>Si, Bu<sub>3</sub>Ge) and the alkene CH<sub>2</sub>=CPh<sub>2</sub> between any two of (1) the <sup>13</sup>C resonance of the cationic carbon, (2) the <sup>13</sup>C resonance of the adjacent methylene carbon, (3) the <sup>13</sup>C resonance of the *p*-phenyl carbons, or (4) the one-bond coupling constant between <sup>13</sup>C and <sup>1</sup>H of the methylene group were linear, indicating that all these NMR parameters reflected the same structural considerations.

The structure of these stable ions could be compared with the transition states studied in solvolysis reactions.<sup>34</sup> Only for the synclinal systems (**6** and the germanium and tin analogues) is the full solvolytic series available, with

relative rates for H/Si/Ge/Sn of  $1.0/3.3 \times 10^4/4.6 \times 10^5/1.3 \times 10^{11}$ . The plot of these rates, converted to  $\text{kcal mol}^{-1}$ , vs the chemical shift of the methylene carbon in **30** for the hydrogen, silicon, and germanium systems was linear with a correlation coefficient of 0.996, indicating that the solvolytic transition states in the cyclohexyl systems electronically parallel the stable ions. The tin system was left off the plot, because it was not clear whether the observations were of unreacted alkene or a lightly complexed  $\beta$ -stannyl carbocation.

We suggested the term *hyperconjugativity* to represent the relative contribution of valence form **2** compared with **1** (with phenyl replacing methyl for the stable ions).<sup>34</sup> If there is no hyperconjugation in the hydrogen system  $\text{H}-\text{CH}_2-\text{CPh}_2^+$  (hyperconjugativity of 0.00) and complete hyperconjugation in the alkene (1.00), one can interpolate hyperconjugativities of 0.31 for silicon and 0.43 for germanium from a plot of hyperconjugativity vs any of the NMR parameters. By taking advantage of the linearity between the NMR parameters and the solvolytic rates, tin can be included in the interpolation, to give a hyperconjugativity of 0.82. These calculations involve a number of assumptions, but they give at least a qualitative indication of the relative abilities of C–H, C–Si, C–Ge, and C–Sn bonds to hyperconjugate.

## Conclusions

The phenomenon of  $\sigma$  conjugation had its genesis in Mulliken's theory of hyperconjugation.<sup>35</sup> The concept was criticized in structural contexts because of its small size for neutral systems containing only C, H, O, and N.<sup>36</sup> Its utility to explain relative stabilities of saturated carbocations, however, was well supported. The subject was considerably enlarged by Hoffmann and co-workers.<sup>37</sup> Because of the large effects of highly polarizable and electron-donating atoms such as Si, Ge, Sn, Pb, and Hg, the phenomenon has been found to have very wide applications. In this Account we have reviewed our results in this area from the last eight years. The mechanism of the  $\beta$  effect of silicon (a  $\sigma\pi$  effect) has been demonstrated to involve the open, unbridged intermediate **3**, according to the secondary deuterium isotope effect and a detailed examination of the stereochemical relationship between silicon and the nucleofugal leaving group X (Si–C–C–X). More distant effects have been demonstrated for silicon but more significantly for tin, including the  $\gamma$  effect involving  $\sigma\sigma$  conjugation (**13c**) and the  $\delta$  effect involving  $\sigma\pi/\sigma\pi$  conjugation (**16c** and **17c**). Investigations have expanded the subject outside group 14 to include not only previously studied atoms such as mercury but also electron-withdrawing  $\beta$  organophosphorus groups. When the effects of bond polarizability exceed those of induction, even inductively withdrawing substituents such as phosphonate, phosphine oxide, and phosphine sulfide can exhibit  $\beta$  effect activity. Finally, use of conditions of lower nucleophilicity for solvent and anion has led to the observation of stable, saturated  $\beta$ -silyl and  $\beta$ -germyl carbocations.

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