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The Question of Vertical or Nonvertical Participation of Silicon β to a Cation in the Antiperiplanar Stereochemistry

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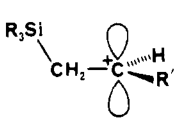
Abstract: The mechanism of stabilization of a β positive charge by silicon in the antiperiplanar stereochemistry has been clarified by the α secondary deuterium kinetic isotope effect. A k_H/k_D of 1.17 ± 0.01 has been observed for the trifluoroethanolysis of *r*-5-*tert*-butyl-*c*-2-(trimethylsilyl)cyclohex-*t*-yl-1,3,3-d_3 3,5-dinitrobenzoate (**3**) at 25 °C. This value is consistent with vertical (hyperconjugative) stabilization (**1**) probably with rate-determining conversion of an intimate ion pair to a solvent-separated ion pair. The isotope effect is inconsistent with nonvertical participation to form a bridged intermediate (**2**).

The ability of silicon to stabilize positive charge two carbons away, $R_3Si-CH_2-CH_2^+$, has been termed the β effect and may be the most important electronic interaction of silicon in organic chemistry.[2] It has been exploited, for example, to direct electrophilic additions to double or triple bonds. Although the ability of silicon to stabilize β positive charge is ultimately related to its high polarizability and low electronegativity, the β effect has been discussed in terms of two possible mechanisms.[3] (1) Vertical stabilization or hyperconjugation involves donation of C–Si σ electrons to the empty carbon p orbital without significant movement of atomic positions, as in **1**. (2) Nonvertical stabilization is analogous to neighboring group participation of lone-pair-bearing atoms (internal S_N2) and involves closure of a three-membered ring to form a siliconium ion, **2**, in the rate-determining step. In addition, silicon may stabilize positive charge by through-bond σ induction. Jorgensen and co-workers[4] found that the nonvertical or bridged form **2** is more stable by about 2.4 kcal mol^{-1} than the vertical or open form when the carbocation is primary (R, R′ = H). When it is secondary (R′ = CH_3), however, the vertical form is more stable by about 4 kcal mol^{-1}, and the bridged form moreover is not an energy minimum.



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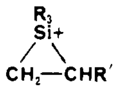

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In principle these two mechanisms may be distinguished by their dependences on the stereochemical relationship between silicon and the leaving group (X) in the ground state antecedent to the carbocation, $R_3Si-CH_2-CH_2-X$. The vertical mechanism should vary as a cosine-squared function of the Si–C–C–X dihedral angle, in order to have maximum overlap when the C–Si and p orbitals are parallel and minimum overlap when they are orthogonal. Thus a plot of the dihedral angle vs β stabilization as measured, for example, by a rate acceleration of the Si system compared with a structurally analogous Si-free system (k_{Si}/k_H) should resemble a Karplus curve, with maxima at 0° and 180° and a minimum at 90°. On the other hand, the nonvertical mechanism should have a maximum only at 180°, corresponding to the best geometry for backside displacement of X by Si, and a monotonically and rapidly decreasing effect as the dihedral angle decreases.

In order to assess the relative importance of the two mechanisms, we previously prepared systems with ground-state dihedral angles of 0°, 60°, 120°, and 180°.[6,7] The antiperiplanar system (180°) exhibited an extremely large β effect, as indicated by a k_{Si}/k_H of 10^{12}. The clinal geometries (60°, 120°) exhibited much smaller accelerations, circa 10^4, as expected. A symmetrical cosine-squared plot would predict a synperiplanar (0°) acceleration of magnitude similar to that of the antiperiplanar geometry, but we observed[7] an acceleration of only about 10^5. Thus the β effect is extremely strong at 180° and significant but essentially constant at the other angles examined to date.

This asymmetric plot may be explained in at least two different ways, and it was the objective of the present study to distinguish these two possibilities. (1) If the mechanism of stabilization is entirely vertical, then the reduced 0° arm must be caused by a nonelectronic phenomenon. We suggested[7] that the syn leaving group prevents the C–Si bond from overlapping optimally with the developing p orbital, whereas in the anti geometry the leaving group is not in the way and optimal overlap may be achieved. By this scenario, the stereochemical dependence has a highly asymmetric cosine-squared form. (2) Alternatively, the observations could be the result of the superposition of both vertical and nonvertical effects. Vertical stabilization then provides nearly symmetrical, cosine-squared stabilization with a maximum of about 10^5 at both 0° and 180°. In addition, nonvertical stabilization enhances the 180° stabilization by another factor of 10^7. This scenario means that both mechanisms contribute at the antiperiplanar geometry, with nonvertical stabilization dominant, and below about 150° only vertical stabilization contributes.

These two mechanistic explanations agree that hyperconjugation is the key element in providing stabilization from 0° up to about 150° (induction may contribute as well). It is at the antiperiplanar geometry, then, that there are conflicting explanations. One scenario attributes all of the acceleration at this geometry to vertical interactions, and the other attributes the acceleration to a combination of vertical and nonvertical, but with a preponderance of the latter. After numerous studies, no clear experimental distinction to date has emerged between the vertical and nonvertical contributions at the antiperiplanar geometries.[2] Moreover, theory has found the energies of the respective intermediates (**1** and **2**) to be of similar energy, but with a small preference for vertical in secondary systems.[4,5]

In the present study, we have endeavored to provide a mechanistic resolution by means of the α secondary hydrogen/deuterium kinetic isotope effect. In the vertical mechanism, the hybridization of the carbon atom changes from sp^3 to sp^2, as in the S_N1 reaction, for which the α hydrogen/deuterium kinetic isotope effect is normally in the range 1.15–1.25.[8] The nonvertical

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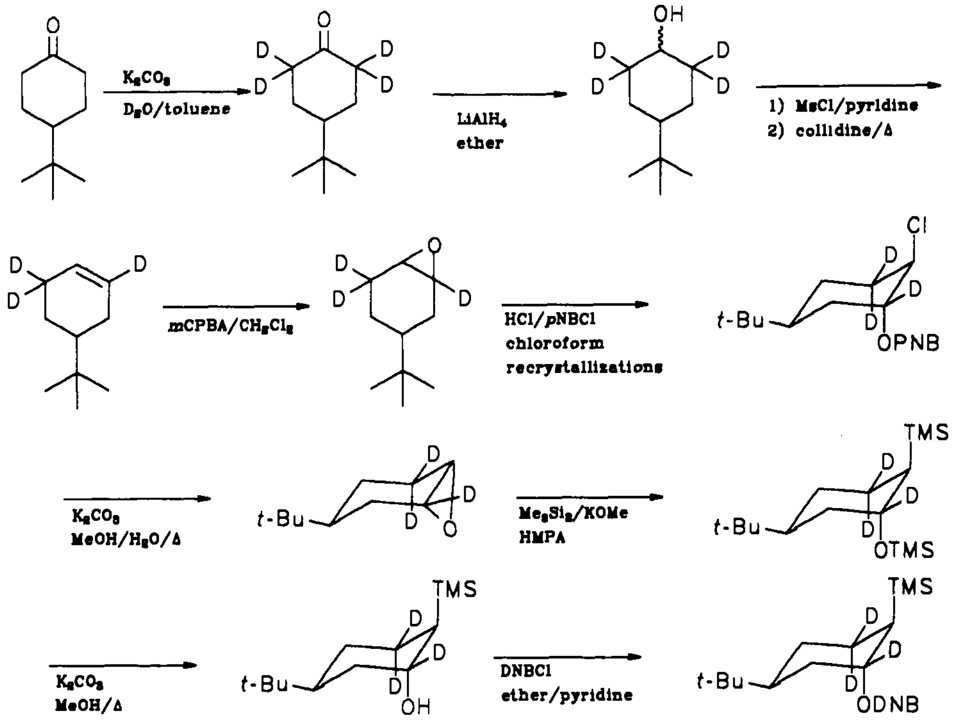
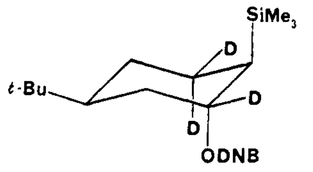
Scheme I



transition state is analogous to the S_N2 reaction, for which the α isotope effect is negligible or inverse, 0.95–1.05. The difference between these predictions provides the basis for a mechanistic distinction. Therefore, we have prepared the substrate 3 (ODNB is dinitrobenzoate), in which the Si–C–C–X geometry is antiperiplanar, and there is a deuterium atom α to the leaving group (the spectator geminal deuterium atoms were an artifact of the synthesis). We report herein the synthesis of this material, its kinetic comparison with the corresponding undeuterated material, and an experimental resolution of this mechanistic problem.



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Results and Discussion

Substrate 3 was chosen because it represents a fully biased antiperiplanar geometry and because its synthesis could be adapted from the synthesis of the analogous undeuterated material (Scheme I).[6] The readily available 4-*tert*-butylcyclohexanone was subjected to basic exchange of the four α hydrogen atoms for deuterium. Two of these ultimately become the spectator geminal deuteriums in 3. Reduction to the alcohol and elimination gave the alkene, in which the single alkenic deuterium atom will become the source of the α secondary isotope effect. Epoxidation yielded a mixture of diastereoisomers that were separated by the method of Rickborn and Quartucci,[9] which involves opening to the chloro benzoate, separation by recrystallization, and reclosure. The purified epoxide then was opened with the trimethylsilyl anion equivalent to give the protected alcohol (to avoid elimination under reaction conditions). Removal of the protection group and esterification gave 3.

The solvolysis reaction was carried out at 25.0 °C in 97% trifluoroethanol, conditions that are known to form a cation from 3.[6] Kinetics were followed by changes in conductivity. The rate of the undeuterated substrate was measured in six runs, with a mean of 6.50×10^{-3} s^{-1} (SD 0.06×10^{-3}), which is within 10% of the previously measured rate based on fewer runs.[6] The rate of the deuterated substrate was measured in four runs, with a mean of 5.55×10^{-3} s^{-1} (SD 0.04×10^{-3}). From these values, k_H/k_D is 1.17 ± 0.01.

The textbook analysis of α secondary deuterium isotope effects generally characterizes the S_N1 transition state as having a value near 1.20 and the S_N2 transition state as having a value near 1.00. The out-of-plane C–D bending force constant changes by a factor of about 1.4 more than does the same C–H force constant between the sp^3 ground state and the sp^2 transition state, so that the hydrogen system reacts more rapidly. In the S_N2 transition state the leaving group compensates for the incoming nucleophile, resulting in effects close to unity. At first glance, therefore, our observed value of 1.17 is strong evidence that the transition state resembles an sp^2 carbocation and does not contain either an external or an internal nucleophile. Our previous solvent effect studies[6] had indicated no participation by an external nucleophile. The present evidence therefore supports the hyperconjugative or vertical transition state.

The situation, however, is more complicated for several reasons. Great care must be taken in selecting appropriate models. The Winstein mechanism of solvolysis reactions includes a sequence of steps, starting with C–X bond breaking to form an intimate ion pair (k_1), followed by conversion of the intimate ion pair to a solvent-separated ion pair (k_2), and finally conversion of the solvent-separated ion pair to entirely free ions (k_3). Each of these species (covalent starting material, two ion pair species, and the free ions) may react with solvent as nucleophile to form the product. The large secondary α deuterium isotope effect that we observe indicates that one of the steps along the ion pair coordinate is rate determining, rather than reaction of any of these species with a nucleophile. The exact value of the isotope effect, however, is determined both by the nature of the leaving group[10] and by the specific step (k_1, k_2, k_3) that is rate determining. With sulfonate groups, for which k_2 (conversion of the intimate ion pair to the solvent-separated ion pair) is rate determining, the max-

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(8) For reviews of α secondary deuterium isotope effects, see: Isaacs, N. *Physical Organic Chemistry*; Longman: Essex, UK, 1987; pp 265, 394–395, 599–600. Shiner, V. J., Jr. In *Isotope Effects in Chemical Reactions*; Collins, C. J., Bowman, N. S., Eds.; Van Nostrand Reinhold: New York, 1970; pp 104–137. Harris, J. M. *Prog. Phys. Org. Chem.* **1974**, *11*, 103–108.

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imum value seems to be about 1.22.[8,11,12] Higher values may be observed if k_3 becomes rate determining, and lower values if k_1 becomes rate determining.

Thus the choice of model must involve careful matching of solvent, substrate, and leaving group. We have not found comparison values for carboxylate leaving groups, but they should not be appreciably different from those for sulfonate leaving groups, which abound. 2-Adamantyl tosylate is the standard model for the limiting or S_N1 transition state, because backside displacement is sterically prohibited. The values of the α isotope effect for this system vary from 1.15 in ethanol to 1.26 in trifluoroacetic acid, as the transition state moves along the ion pair coordinate. The value in our solvent, 97% trifluoroethanol, is 1.18, which is experimentally indistinguishable from the value 1.17 that we observe for **3**. Thus we can conclude that, in this solvent, the transition state for β silicon stabilization lacks internal or external nucleophilic involvement to the same extent that 2-adamantyl tosylate does.

We also have sought models for the reduced isotope effect when there is nucleophilic involvement. The case is clear for external nucleophiles. Again in 97% trifluoroethanol, *p*-nitrobenzyl brosylate reacts primarily by attack by external nucleophile, as k_H/k_D is 1.03.[13] The electron-withdrawing nitro group destabilizes the carbocation transition state, permitting solvent attack to become rate determining. Removal of the nitro group results in a change in mechanism to carbocation formation, as benzyl brosylate under the same conditions exhibits an α deuterium isotope effect of 1.17.[13] This value again is the same as that observed by us for **3**.

Finally, we sought models for internal nucleophilic involvement. Sunko and co-workers examined methoxy participation in $MeO(CH_2)_3CHMeOBs$[14] and found an α isotope effect of 1.08 for formation of the five-membered oxonium ion. This value compares with 1.16 for 2-propyl tosylate in 97% trifluoroethanol,[11] which is appropriate for unassisted carbocation formation. The value of 1.08 may indicate that the transition state to oxygen participation has some mixture of carbocation formation, but it does confirm that internal nucleophilic participation decreases the isotope effect significantly from the 1.17–1.20 region observed in 97% trifluoroethanol for carbocation formation.

The work of Maskill[15] provides a second precedent that internal nucleophilic involvement reduces the α secondary deuterium isotope effect. Maskill observed that the α deuterium isotope effect for ethanolysis of *exo*-2-norbornyl-2-*d* brosylate is 1.12, whereas that for *endo*-2-norbornyl-2-*d* brosylate is 1.19. The latter value is typical for carbocation formation without internal participation, whereas the reduced former value supported the emerging picture of σ participation. Thus the work of Sunko et al. indicates that internal displacement by n electrons reduces the α deuterium isotope effect, and the work of Maskill indicates that internal displacement by σ electrons does the same. We conclude that the lack of such a reduction in the present case indicates that the mode of interaction by silicon is vertical.

Saunders and co-workers studied α deuterium isotope effects in phenyl participation.[16,17] They found in systems such as $ArCH_2CH_2OTs$ that deuterium at the position β to tosylate brings about no isotope effect (circa 1.00), whereas deuterium at the α position brings about a full isotope effect (circa 1.20). They interpreted these observations to indicate a very early transition state with regard to Ar–C bond migration, in which the aryl group is bonded almost entirely to the carbon to which it was originally attached and is only very weakly bonded to the carbon bearing tosylate. Such a transition state, with little movement of the aryl ring, is very close to what we have referred to as vertical participation. Actual movement of the phenyl or silicon to the phenonium or siliconium ion then would take place at a later stage. In both cases the kinetic acceleration from the neighboring group occurs before the group migrates.

Conclusions

The α secondary deuterium isotope effect for β participation of silicon in the antiperiplanar stereochemistry, as exemplified by system **3**, is 1.17 ± 0.01 in 97% trifluoroethanol at 25 °C. This value compares very favorably with 1.18 for 2-adamantyl tosylate in the same solvent and indicates a vertically stabilized carbocation transition state (similar to **1**), probably with a rate-determining conversion of the intimate ion pair to the solvent-separated ion pair. Direct participation of silicon in a nonvertical transition state illustrated by **2** would have resulted in a much smaller isotope effect, certainly no larger than 1.08 as observed for internal oxygen participation[14] or 1.12 as observed for σ participation[15] and possibly as low as 1.00–1.02 as observed for participation by an external nucleophile (solvent displacement). The highly unsymmetrical observed dihedral dependence of silicon participation therefore may be attributed almost entirely to the hyperconjugation model without special (nonvertical) involvement of the internal silicon nucleophile at the 180° point. These conclusions are in agreement with the recent structural conclusions of White et al.[18]

These observations are not sufficiently refined to eliminate entirely small contributions from internal nucleophilic (nonvertical) participation. Moreover, they do not eliminate the possibility that siliconium ion **2** is formed as an intermediate or transition state further along the reaction coordinate. The solvent and isotope effects, however, do provide compelling evidence that the preponderance of the kinetic acceleration at the 180° dihedral angle (the "β effect") is caused by vertical participation with little movement of the C–Si bond, corresponding to a transition state resembling the open carbocation **1**.

Experimental Section

4-*tert*-Butylcyclohexanone-2,2,6,6-d_4 was prepared by treatment of 35.0 g (0.227 mol) of 4-*tert*-butylcyclohexanone with D_2O in the presence of K_2CO_3 and toluene. Toluene was used to prevent the reactant from crystallizing in the condenser during refluxing. Three such treatments were carried out to give 31.21 g (87%) of the product, which was >98.6% deuterated in the desired positions according to ^1H NMR and mass spectra, which were in agreement with expectations from comparisons with spectra of the commercially available undeuterated material.

4-*tert*-Butylcyclohexanol-2,2,6,6-d_4 was prepared by treatment of the ketone with $LiAlH_4$ in 92% yield (28.94 g) (mp 64–67 °C). Satisfactory NMR and mass spectra were obtained.

4-*tert*-Butylcyclohexene-2,6,6-d_3 was prepared by treating the alcohol with methanesulfonyl chloride in pyridine followed by elimination in collidine: 15.14 g (59%) after distillation.[19] Satisfactory NMR and mass spectra were obtained.

4-*tert*-Butylcyclohexene-2,6,6-d_3 oxide was prepared as a mixture of diastereoisomers by treatment of the alkene with *m*-chloroperbenzoic acid in 92% yield (15.41 g).[6] Satisfactory NMR and mass spectra were obtained.

***r*-2-Chloro-*c*-5-*tert*-butylcyclohex-*t*-yl-1,3,3-d_3 *p*-Nitrobenzoate.** An oven-dried, nitrogen-flushed, 1-L, three-necked flask was fitted with a gas inlet adapter, an addition funnel, a nitrogen outlet, and a magnetic stirring bar and was charged with 15.41 g (97.98 mmol) of the epoxide and 325 mL of dry $CHCl_3$. Anhydrous HCl was bubbled for 40 min rapidly through the stirred solution as it was generated by the dropwise addition of H_2SO_4 to NaCl in a separate flask connected to the reaction vessel by the gas inlet adapter. The system was purged for 90 min with N_2 through the HCl generator and the reaction flask. To the pink solution was added 22.18 g (117.6 mmol) of *p*-nitrobenzoyl chloride in 170 mL of dry $CHCl_3$ over 15 min. The combined solution was stirred for 30 min and then was transferred to a single-necked flask for removal of the solvent and excess HCl by rotary evaporation. The light brown

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crystalline solid was dissolved in 40 mL of pyridine. An exothermic reaction took place immediately, and a copious amount of pyridinium hydrochloride precipitated rapidly. The mixture was cooled in an ice bath to ensure complete reaction. The mixture was diluted with 1200 mL of diethyl ether and extracted with 2 N HCl (3 × 200 mL), 5% $NaHCO_3$ (2 × 200 mL), and H_2O (200 mL). The organic portion was dried (Na_2SO_4) and concentrated by rotary evaporation to give 40.99 g of crude material as a mixture of diastereoisomers. The desired isomer was isolated in pure form after five recrystallizations from CH_3OH (mp 120–122 °C, lit.[9] mp 122–124 °C): 4.63 g (13.8%); ^1H NMR ($CDCl_3$) δ 0.90 (s, 9 H), 1.45 (m, 1 H), 1.57 (m, 1 H), 1.65 (m, 1 H), 1.90 (d, 2 H), 4.28 (s, 1 H), 8.19 (d, 2 H), 8.31 (d, 2 H); ^{13}C NMR ($CDCl_3$) δ 19.8, 25.3, 27.3, 29.0, 32.2, 41.5, 55.5, 73.9, 123.5, 130.7, 135.4, 150.6, 163.3.

***trans*-4-*tert*-Butylcyclohexene-2,6,6-d_3 Oxide.** Preparation of the deuterated materials followed our earlier preparation of the analogous undeuterated materials.[6] A nitrogen-flushed, 250-mL, round-bottomed flask was fitted with a reflux condenser, a nitrogen outlet, and a magnetic stirring bar and was charged with 4.63 g (13.5 mmol) of the chloro benzoate, 65 mL of CH_3OH, 6.5 mL of H_2O, and 5.40 g of K_2CO_3. The heterogeneous mixture was heated to reflux for 2.5 h. Now homogeneous, the solution was diluted with 100 mL of H_2O and extracted with pentane (3 × 150 mL). The combined organics were dried (Na_2SO_4) and concentrated by rotary evaporation to a golden oil, 2.04 g (96%), which was >94.5% pure by gas chromatography: ^1H NMR ($CDCl_3$) δ 0.85 (s, 9 H), 1.23 (t of m, 1 H), 1.40 (t, 1 H), 1.51 (d, 1 H), 2.18 (d of q, 1 H), 3.12 (br s, 1 H); ^{13}C NMR ($CDCl_3$) δ 22.5, 24.0, 26.4, 27.1, 31.8, 39.3, 51.7, 53.9; MS (EI) *m/z* 157 (M^+, 1.3), 142 (16), 124 (20), 101 (21), 100 (69), 99 (33), 98 (10), 97 (9), 96 (20), 95 (10), 85 (11), 84 (30), 83 (53), 82 (25), 57 (100).

***r*-5-*tert*-Butyl-*t*-1-(trimethylsiloxy)-*c*-2-(trimethylsilyl)cyclohexane-1,3,3-d_3.**[6] The oxide was divided into three portions that were reacted separately. An oven-dried, nitrogen-flushed, 100-mL, three-necked flask was fitted with a reflux condenser, a nitrogen outlet, a rubber septum, and a magnetic stirring bar and was charged with 0.06 g of KOMe as catalyst and 25 mL of dry HMPA. To this was added 2.05 mL (10 mmol) of hexamethyldisilane.[18,20] The mixture was heated to about 65 °C, and the epoxide (0.63 g, 4.00 mmol) was added all at once. The solution turned blue, then green, and then a coppery orange. After stirring at 56–67 °C for 12 h, the solution was cooled to room temperature and poured into 125 mL of aqueous NaCl. This solution was extracted with pentane (3 × 75 mL). The combined organics were washed with saturated aqueous NaCl (2 × 75 mL), dried ($MgSO_4$), and concentrated by rotary evaporation to yield 1.21 g (100%) of a yellow oil. The combined crude products of the three runs were purified by flash chromatography (400 g of silica, pentane as eluent) to yield 2.63 g (8.66 mmol, 65%) of the siloxy silane, which was >98% pure by gas chromatography: ^1H NMR ($CDCl_3$) δ 0.04 (s, 9 H), 0.09 (s, 9 H), 0.82 (s, 9 H), 0.90 (br s, 1 H), 1.1–1.7 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ –0.8, 0.3, 20.5, 24.7, 27.4, 32.1, 32.6, 33.1, 40.3, 68.6; MS (EI) *m/z* 303 (M^+, 15), 288 (10), 246 (45), 216 (10), 212 (28), 206 (15), 205 (45), 204 (46), 149 (12), 148 (22), 147 (100).

***r*-5-*tert*-Butyl-*c*-2-(trimethylsilyl)cyclohexan-*t*-ol-1,3,3-d_3.**[6] An oven-dried, nitrogen-flushed, 250-mL, round-bottomed flask was fitted with a reflux condenser, a nitrogen outlet, and a magnetic stirring bar and was charged with 2.63 g (8.66 mmol) of the siloxy silane, 2.89 g of K_2CO_3, and 70 mL of CH_3OH. The solution was heated to reflux for 4 h. The solution was poured into 280 mL of saturated aqueous NaCl and was extracted with 3 × 150 mL of ether. The combined organics were washed with aqueous NaCl (150 mL), dried ($MgSO_4$), and concentrated by rotary evaporation to 1.97 g (99%) of a pale oil that solidified in the freezer but remelted outside the freezer: ^1H NMR ($CDCl_3$) δ 0.03 (s, 9 H), 0.82 (s, 9 H), 1.02 (br s, 1 H), 1.22 (m, 2 H), 1.44 (d of t, 1 H), 1.62 (d of t, 1 H), 1.70 (br s, 1 H), 1.78 (d of q, 1 H); ^{13}C NMR ($CDCl_3$) δ –0.9, 20.8, 24.6, 27.3, 29.7, 31.9, 32.3, 40.6, 68.4; MS (EI) *m/z* 231 (M^+, <1), 230 (3), 216 (10), 214 (10), 212 (10), 198 (13), 147 (30), 141 (35), 98 (47), 85 (93), 83 (82), 76 (65), 57 (100).

***r*-5-*tert*-Butyl-*c*-2-(trimethylsilyl)cyclohex-*t*-yl-1,3,3-d_3 3,5-Dinitrobenzoate.**[6] An oven-dried, nitrogen-flushed, 10-mL, round-bottomed flask was fitted with a nitrogen outlet, a rubber septum, and a magnetic stirring bar and was charged with 0.28 g (1.2 mmol) of 3,5-dinitrobenzoyl chloride and 5.0 mL of pyridine. The solution was cooled to 0 °C, and 0.23 g (1.0 mmol) of the silyl alcohol in 1.0 mL of pyridine was added dropwise. The resulting solution was stirred at 0 °C for 4.5 h and poured into a mixture of 10 mL of H_2O and 15 mL of ether. The organic portion was isolated, and the aqueous portion was extracted with ether (2 × 15 mL). The combined organics were dried ($MgSO_4$) and concentrated by rotary evaporation to give an oil. The oil was subjected to overnight pumping at about 0.2 mmHg, and 0.41 g (95%) of crude product was isolated. Recrystallization from absolute ethanol (8 mL, dissolution at about 45 °C, cooling to –20 °C) yielded 0.25 g (54%) of pale needles (mp 96–98 °C): ^1H NMR ($CDCl_3$) δ 0.14 (s, 9 H), 0.87 (s, 9 H), 1.12 (t, 1 H), 1.37–1.55 (m, 3 H), 1.77 (d, 1 H), 2.08 (d of d, 1 H), 9.14 (d, 2 H), 9.22 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ –1.0, 22.6, 24.3, 27.3, 29.2, 29.8, 32.3, 41.9, 77.2, 122.1, 129.3, 135.1, 148.6, 161.9.

Kinetics were measured according to previously described procedures.[6]

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