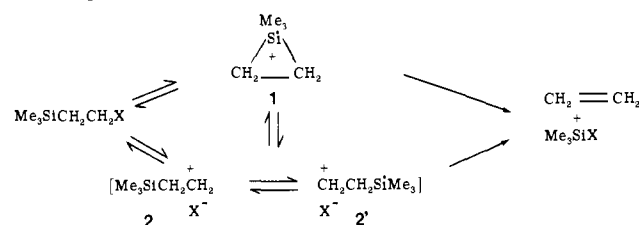




Scheme I

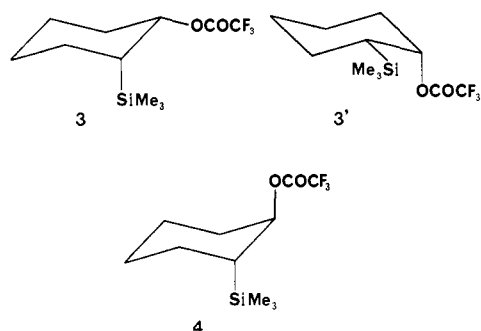


mechanism in which silicon-assisted cleavage of the C-X bond is rate determining,<sup>6,7</sup> because the reaction is sensitive to ionizing power rather than nucleophilicity of the solvent, because it exhibits a strong stereoselectivity for anti elimination of the elements of Me<sub>3</sub>SiX, and because deuterium is partially scrambled between the  $\alpha$  and  $\beta$  positions of recovered starting material. Solvent dependence of the rate and of the stereoselectivity has been interpreted as evidence that both a siliconium ion (1) and a carbenium ion (2) are intermediates (Scheme I).

Silicon involvement can be viewed in terms of induction (silicon is electropositive with respect to carbon), vertical stabilization<sup>8</sup> ( $\sigma$ - $\pi$  participation without nuclear motion, as in the formation of the carbenium ion in Scheme I), or direct nucleophilic attack (participation with nuclear motion to form the bridged siliconium ion in Scheme I). Mechanistic partition of these modes of involvement has not been carried out previously.<sup>9</sup> Our interest in  $\beta$ -silicon activation developed from our studies of the instability of silylenium ions<sup>10</sup> and of the influence of  $\beta$  electron-withdrawing groups on solvolytic rates.<sup>11</sup>

Previous mechanistic studies of  $\beta$ -silyl systems focused on open-chain systems, in which trans and gauche conformers are in rapid equilibrium. The inductive and participative modes of involvement can be distinguished in principle by the use of conformationally constrained systems. Participation, either vertical or nucleophilic, requires the antiperiplanar relationship between Si and X that is present in anti conformations, whereas the through-bond inductive effect can be operative in all forms.<sup>12</sup>

We selected the cyclohexyl systems 3 and 4 for our studies.



They were prepared by standard, stereospecific reactions.<sup>13</sup> Each

(5) Bott, R. W.; Eaborn, C.; Rushton, B. M. *J. Organomet. Chem.* **1965**, *3*, 455-463.

(6) Cook, M. A.; Eaborn, C.; Walton, D. R. M. *J. Organomet. Chem.* **1970**, *24*, 301-306. Jarvie, A. W. P.; Holt, A.; Thompson, J. *J. Chem. Soc. B* **1969**, 852-855. *Ibid.* **1970**, 746-748.

(7) Vencl, J.; Hetflejš, J.; Čermák, J.; Chvalovský, V. *Collect. Czech. Chem. Commun.* **1973**, *38*, 1256-1262.

(8) Traylor, T. G.; Hanstein, W.; Berwin, H. J.; Clinton, N. A.; Brown, R. S. *J. Am. Chem. Soc.* **1971**, *93*, 5715-5725.

(9) Whereas mechanistic study of  $\beta$ -silyl participation has been relatively quiescent for a decade, its synthetic uses have been thoroughly scrutinized. Reactions of the type given in eq 1 offer an alternative to the Wittig reaction, with mild conditions and high stereoselectivity. See: Chan, T.-H. *Acc. Chem. Res.* **1977**, *10*, 442-448.

(10) Lambert, J. B.; Sun, H.-n. *J. Am. Chem. Soc.* **1976**, *98*, 5611-5615.

(11) Lambert, J. B.; Mark, H. W.; Holcomb, A. G.; Magyar, E. S. *Acc. Chem. Res.* **1979**, *12*, 317-324.

(12) The inductive effect is maximal in the antiperiplanar arrangement but still significant in gauche conformers: Lambert, J. B.; Greifenstein, L. G. *J. Am. Chem. Soc.* **1974**, *96*, 5120-5124.

is a conformational mixture of two forms. The cis molecule has a gauche relationship between silicon and the leaving group in both forms (3 and 3'), so that neither vertical nor nucleophilic participation is possible.<sup>15</sup> The trans molecule exists as an equilibrium between the gauche diequatorial form and the anti diaxial form 4. The latter is not destabilized by the intersubstituent gauche interaction in the diequatorial form. Furthermore, the diaxial form contains substituents of relatively low  $A$  value.<sup>16</sup> If vertical or nucleophilic participation is important, it should be able to occur easily in the diaxial form shown for 4, even if it is the minor conformer.

Rates were measured in 97% trifluoroethanol in order to minimize the effect of external nucleophiles ( $N = -2.59$ ).<sup>19</sup> Both 3/3' and 4 gave cyclohexene as the only product. The trans isomer 4 solvolyzed rapidly at 25 °C and the cis isomer at 50 °C, but cyclohexyl<sup>20</sup> trifluoroacetate failed to solvolyze beneath the boiling point of the solvent. Its rate at 25 °C was obtained by linear extrapolation of the rates in 60%, 70%, and 80% trifluoroethanol. In this fashion, the following rates were found at 25 °C: cyclohexyl,  $7.05 \times 10^{-10} \text{ s}^{-1}$  (relative rate 1.0);<sup>20</sup> cis-2-(trimethylsilyl)cyclohexyl  $2.36 \times 10^{-5} \text{ s}^{-1}$  (relative rate  $3.35 \times 10^4$ ); trans-2-(trimethylsilyl)cyclohexyl,  $1.74 \times 10^{-3} \text{ s}^{-1}$  (relative rate  $2.47 \times 10^6$ ).

The cis material 3/3' cannot provide the antiperiplanar relationship needed for neighboring-group participation, yet it solvolyzes up to 4 orders of magnitude faster than the material lacking silicon. The only mode of solvolytic involvement available to the cis isomer is induction, probably through the  $\sigma$  bonds. The trans isomer can attain the antiperiplanar relationship, and indeed it solvolyzes 75 times more rapidly than the cis isomer. This additional acceleration can be attributed to participation by silicon. Comparison of the trans isomer directly with cyclohexyl trifluoroacetate shows a misleading rate enhancement of over 6 orders of magnitude. As shown by the rapid rate of the cis isomer, the preponderance of this rate enhancement is an inductive or other through-bond effect, and only the factor of 75 would be attributed to silicon participation. In open-chain systems previously studied, the factor of 75 would be sufficient to ensure predominant reaction from anti rather than gauche conformers and hence give the observed stereoselectivity. Previous interpretations in terms of

(13) The trans alcohol 4 was obtained by ring opening of cyclohexene oxide with (trimethylsilyl)lithium. The cis alcohol 3 was obtained by ring opening of 1-(trimethylsilyl)cyclohexene oxide with LiAlH<sub>4</sub>. Although the syntheses of the alcohols were relatively straightforward, problems arose with the choice of leaving group. The tosylates analogous to 3 and 4 decomposed rapidly after formation. The *p*-nitrobenzoates were unreactive. Previous kinetics on open-chain systems used halogen leaving groups, which are intermediate in rate compared with tosylate and *p*-nitrobenzoate. We rejected halogen, however, because of the likelihood of nonstereospecific syntheses and the sensitivity of product stability to reaction conditions. We chose trifluoroacetate because of its intermediate leaving group ability.<sup>14</sup> Formation of the trifluoroacetates occurred with high yield, and the rates, measured by standard conductance methods, were convenient for the temperature range 25-70 °C.

(14) Noyce, D. S.; Virgilio, J. A. *J. Org. Chem.* **1972**, *37*, 2643-2647.

(15) A boat form could offer a viable stereochemistry for such participation. This alternative appears to be excluded even for the powerful participative capacity of acetoxy, in the molecule exactly analogous to 3: Winstein, S.; Grunwald, E.; Buckles, R. E.; Hanson, C. *J. Am. Chem. Soc.* **1948**, *70*, 816-821.

(16) Although the  $A$  values are not known for trifluoroacetoxyl or for trimethylsilyl, they should not be far, respectively, from those of acetoxy (0.71)<sup>17</sup> and trimethylstannyl (0.94).<sup>18</sup>

(17) Jensen, F. R.; Bushweller, C. H. *J. Am. Chem. Soc.* **1969**, *91*, 344-351.

(18) Modir, R. I. *J. Org. Chem.* **1980**, *45*, 1008-1010. Kitching, W.; Doddrell, D.; Grutzner, J. *J. Organomet. Chem.* **1976**, *107*, C5.

(19) Schadt, F. L.; Bentley, T. W.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1976**, *98*, 7667-7674.

(20) Cyclohexyl was chosen as the standard for comparison because it is known to solvolyze by solvent participation.<sup>21</sup> The *tert*-butyl analogues of 3 and 4 would not be appropriate because of direct steric interactions of the bulky *tert*-butyl group ( $A > 4.5$ ) with the leaving group and because of the inability of the trans form to attain the diaxial conformation. If the extrapolation to 97% trifluoroethanol is nonlinear, the rate constant for cyclohexyl would be a minimum and the relative rates for both 3 and 4 would be lower. This possibility does not alter our mechanistic conclusion, which is based primarily on the small size of the  $4/3$  rate ratio. Even so, the stated factor of  $10^4$  for  $3/1$  is in line with previous estimates of the  $\beta$ -silyl acceleration.<sup>1</sup>

(21) Lambert, J. B.; Putz, G. J. *J. Am. Chem. Soc.* **1973**, *95*, 6313-6319.

participation should be qualified by the statement that the effect is not strong.

In summary, by the use of cyclic structures, we have measured the first reaction rate for a  $\beta$ -silyl system in which the geometry between silicon and the leaving group is restricted to a skew arrangement (3/3'). The very large rate acceleration ( $3.35 \times 10^4$ ) of this compound in comparison with cyclohexyl trifluoroacetate demonstrates that the inductive or another through-bond effect of silicon is sufficient to provide the well-known reactivity of  $\beta$ -silyl systems.<sup>22</sup> The trans arrangement provides an additional acceleration of about 75, so that there is some neighboring-group participation, although the effect is not large.<sup>23</sup> We cannot distinguish between the two modes of participation, whereby silicon either displaces the leaving group in the transition state to give a three-membered ring siliconium ion (1) or stabilizes the developing empty p orbital hyperconjugatively without movement of the C-Si bond (2). Neither participative mode should be invoked to explain high  $\beta$  effects unless the inductive mode has been factored out by the use of sterically defined systems.

**Acknowledgment.** We are indebted to the National Science Foundation (Grant CHE-80-25601) for support of this work.

**Registry No.** 3, 80866-33-7; 4, 80866-34-8; cyclohexene oxide, 286-20-4; 1-(trimethylsilyl)cyclohexene oxide, 60484-85-7.

(22) The strong  $\alpha$  inductive effect of silicon frequently is masked by a variety of  $\pi$  effects, which can involve electron withdrawal.

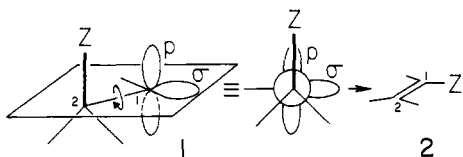
(23) We should not ignore the very intriguing possibility that silicon can participate nucleophilically from the skew geometry. In this case, the high rate for 3/3' would be attributed to participation rather than induction. Such a role for silicon is equivalent to frontside displacements by silicon nucleophiles on carbon centers. We are exploring this unprecedented possibility by appropriate experiments.

## Migrating-Group Orientation in Carbene Rearrangements

Alex Nickon\* and June K. Bronfenbrenner

Department of Chemistry, The Johns Hopkins University  
Baltimore, Maryland 21218  
Received November 30, 1981

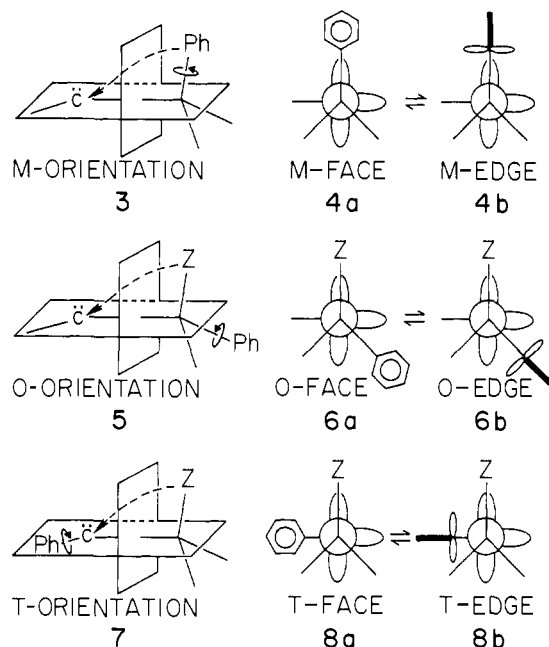
For isomerization of a thermally generated singlet carbene to an olefin (1  $\rightarrow$  2), a preference for perpendicular alignment of



the C-Z bond has been established experimentally for Z = H and Z = Ph and has been supported theoretically for Z = H.<sup>1</sup> When Z itself lacks axial symmetry, rotation about the C-Z bond introduces another stereochemical variable (termed here the *orientation factor*) that could influence ease of rearrangement. We illustrate this aspect with Z = Ph and extend our description to include the case where phenyl is at C(2) (i.e., at the migration

origin) but is not the migrating group and also where phenyl is attached to the carbene carbon (i.e., to the migration terminus).

Geometric description is considerably simplified if we adopt, as reference, an imaginary plane perpendicular to the C(1)-C(2) bond axis. After the C-Ph bond is optimally aligned (3), the ring



can take up two extreme orientations with respect to the reference plane. In one (4a), the face of the phenyl ring projects onto the reference plane. In the other (4b), the edge of the ring projects onto this plane. This degree of freedom in the migrating group may be called the *M-orientation factor* and, for phenyl, the two extremes are termed M face (4a) and M edge (4b). Both orientations have optimum alignment, but in M face the phenyl  $\pi$  cloud is well disposed<sup>1b</sup> for hominal<sup>2</sup> overlap with the carbene p orbital, whereas in M edge it can overlap with the carbene  $\sigma$  orbital.

When phenyl is not the migrating group but is nevertheless attached to the migration origin (5) its possible conformations (termed the *O-orientation factor*) also include the two extremes, O face (6a) and O edge (6b). Resonance interaction between phenyl and the migrating C-Z bond should be best in O edge (6b), especially for an early transition state,<sup>1a,b</sup> whereas O face (6a) could allow hominal interaction between the  $\pi$  cloud and the carbene orbitals ( $\sigma$  and/or p).<sup>3</sup>

The carbene carbon represents the *terminus* for a 1,2 shift, and so the conformational possibilities at that center (7) may be labeled the *T-orientation factor*, with T face (8a) and T edge (8b) being the two extremes for phenyl. T-orientation geometry appears important in resonance stabilization of aryl carbenes<sup>4</sup> and has also been invoked to interpret cis-trans olefin ratios when hydrogen shifts to an aryl carbene center.<sup>5</sup> No experimental (or theoretical) work has probed matters of M and O orientation.<sup>6</sup> We now report a study dealing with M orientation in rearrangement of a phenyl group. Our approach involved competitive H vs. Ph shift in the

(2) *Hominal* refers to a 1,3 relationship in the same way that *geminal* and *vicinal* represent a 1,1 and a 1,2 relationship, respectively.<sup>7</sup> For recent usage, see: Nickon, A.; Zurer, P. *St. J. J. Org. Chem.* 1981, 46, 4685-4694.

(3) Rotation about C(1)-C(2) can place phenyl syn or anti to the substituent at the carbene center. Formulas 6a and 6b display only the anti forms.

(4) (a) Miller, R. J.; Yang, L. S.; Shechter, H. *J. Am. Chem. Soc.* 1977, 99, 938-939. (b) Miller, R. J.; Shechter, H. *J. Am. Chem. Soc.* 1978, 100, 7920-7927 and references cited there.

(5) Dellacolella, B. A.; Shechter, H. *Tetrahedron Lett.* 1979, 4817-4820.

(6) We use phenyl to illustrate M, O, and T factors, but, orientation geometry also applies to other Z groups that lack full axial symmetry (e.g.,  $-\text{CH}=\text{CH}_2$ , OR, SR, NR<sub>2</sub>,  $-\text{CH}_2\text{R}$ , etc.), and each can have its own additional subtleties. For example, an ortho-substituted phenyl has two *face* and two *edge* forms. The stereochemical terminology suggested here for aryl rings in carbene systems can also aid discussion of 1,2 rearrangements in carbocations, carbanions, and radicals.