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 β-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 (3.35×10^4) 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 β-silyl systems.[22] The trans arrangement provides an additional acceleration of about 75, so that there is some neighboring-group participation, although the effect is not large.[23] 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 β 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.

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(22) The strong α inductive effect of silicon frequently is masked by a variety of π 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

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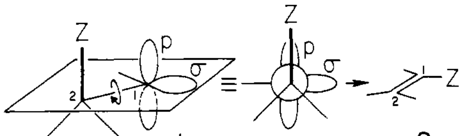
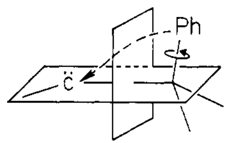
For isomerization of a thermally generated singlet carbene to an olefin (**1** → **2**), a preference for perpendicular *alignment* of



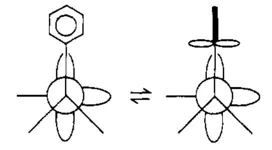
1 2

the C–Z bond has been established experimentally for Z = H and Z = Ph and has been supported theoretically for Z = H.[1] 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).

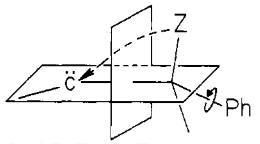
Geometric description is considerably simplified if we adopt, as reference, an imaginary plane perpendicular to the C(1)–C(2) bond axis. After the C–Ph bond is optimally *aligned* (**3**), the ring can take up two extreme orientations with respect to the reference plane. In one (**4a**), the face of 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 π cloud is well disposed[1b] for hominal[2] overlap with the carbene p orbital, whereas in M edge it can overlap with the carbene σ orbital.



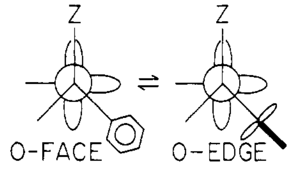
M-ORIENTATION
3



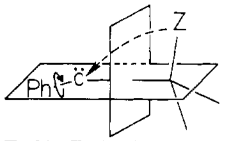
M-FACE M-EDGE
4a 4b



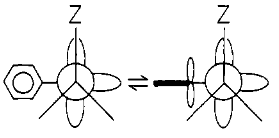
O-ORIENTATION
5



O-FACE O-EDGE
6a 6b



T-ORIENTATION
7



T-FACE T-EDGE
8a 8b

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,[1g,h] whereas O face (**6a**) could allow hominal interaction between the π cloud and the carbene orbitals (σ and/or p).[3]

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[4] and has also been invoked to interpret cis–trans olefin ratios when hydrogen shifts to an aryl carbene center.[5] No experimental (or theoretical) work has probed matters of M and O orientation.[6] 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

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(1) (a) Nickon, A.; Huang, F.-C.; Weglein, R.; Matsuo, K.; Yagi, H. *J. Am. Chem. Soc.* **1974**, *96*, 5264–5265. (b) Seghers, L.; Shechter, H. *Tetrahedron Lett.* **1976**, 1943–1946. (c) Press, L. S.; Shechter, H. *J. Am. Chem. Soc.* **1979**, *101*, 509–510. (d) Hoffmann, R.; Zeiss, G. D.; Van Dine, G. W. *Ibid.* **1968**, *90*, 1485–1499. (e) Bodor, N.; Dewar, M. J. S. *Ibid.* **1972**, *94*, 9103–9106. (f) Zimmerman, H. E. *Acc. Chem. Res.* **1972**, *5*, 393–401. (g) Altmann, J. A.; Csizmadia, I. G.; Yates, K. *J. Am. Chem. Soc.* **1974**, *96*, 4196–4201. (h) Altmann, J. A.; Csizmadia, I. G.; Yates, K. *Ibid.* **1975**, *97*, 5217–5222. (i) Altmann, J. A.; Tee, O. S.; Yates, K. *Ibid.* **1976**, *98*, 7132–7138. (j) Gordon, M. S.; Saatzer, P. M.; Koob, R. D. *Chem. Phys. Lett.* **1976**, *37*, 217–225. (k) Kyba, E. P. *J. Am. Chem. Soc.* **1977**, *99*, 8330–8332. This paper also compares calculated energies for rearrangement and conformational distortions in flexible systems.

(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.[7] For recent usage, see: Nickon, A.; Zurer, P. St. J. *J. Org. Chem.* **1981**, *46*, 4685–4694.

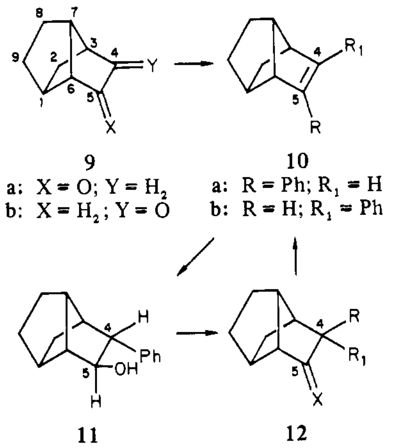
(3) Rotation about C(1)–C(2) can place phenyl syn or anti to the substituent at the carbene center. Formulas **6a** and **6b** display only the anti forms.

(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) Dellacoletta, 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., $-CH{=}CH_2$, OR, SR, NR_2, $-CH_2R$, 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.

Scheme I



9

a: $X = O; Y = H_2$

b: $X = H_2; Y = O$

10

a: $R = Ph; R_1 = H$

b: $R = H; R_1 = Ph$

11

12

	X	R	R$_1$
a:	O	H	Ph
b:	O	Ph	H
c:	NNHTs	H	Ph
d:	NNHTs	Ph	H

epimeric pair of rigid carbene precursors **12c** and **12d** to produce olefinic products **10a** and/or **10b**. Our findings indicate that carbene rearrangements can be M-orientation controlled rather than alignment controlled.

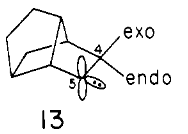
Known 5-brexanone (**9a**)[7] (Scheme I) was converted, via Grignard addition and dehydration, to liquid 5-phenyl-4-brexene [**10a**: δ (CDCl$_3$) 6.33 (H(4)); M^+ 196.1249 (calcd 196.1248)].[8] A similar sequence on known 4-brexanone (**9b**)[9] gave liquid 4-phenyl-4-brexene [**10b**: δ 6.20 (H(5)); M^+ 196.1249 (calcd 196.1248)]. Hydroboration of **10b** produced (84%) crystalline *endo*-4-phenyl-*exo*-5-brexanol [**11**: δ 4.00 (H(5)), 2.80 (H(4))], which was oxidized to its crystalline ketone *endo*-4-phenyl-5-brexanone [**12a**: δ 3.40 (H(4)); ν 1730, 1745 cm^{-1} (split C=O)]. Epimerization of **12a** in 4-picoline gave a 2:1 mixture, from which the minor epimer, liquid *exo*-4-phenyl-5-brexanone (**12b**) was separated by column chromatography [**12b**: δ 3.04 (H(5)); ν (C=O) 1748 cm^{-1})]. Each epimeric ketone, **12a** and **12b**, was converted to its respective crystalline *p*-tosylhydrazone **12c** and **12d**, from which each parent ketone was regenerated[10] with 98.3–98.6% preservation of stereochemical integrity at C(4).

The dry, sodium salts of **12c** and **12d** (prepared with NaOCH$_3$/CH$_3$OH) were individually pyrolyzed (155–215 °C). The volatile product (53–60%) from each precursor consisted of 4-phenyl-4-brexene (**10b**), with no detectable ($<0.1\%$) 5-phenyl-4-brexene (**10a**). These results were reproducible and indicate an H/Ph migration preference of at least 1000 for each substrate.

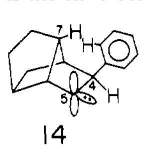
To exclude the possibility of epimerization in preparation and thermolysis of the sodium salts, we recovered each salt (40–60%) from an interrupted pyrolysis and regenerated its parent ketone.[10] For each epimer the original stereochemistry at C(4) was preserved to the extent of 97.3–99%. Separate controls established that absence of 5-phenyl-4-brexene (**10a**) in the olefinic product is not due to selective loss or destruction of this isomer during the reaction or during workup.

The H/Ph migration preferences of >1000 in **12c** and **12d** exceed by far those exhibited in nonrigid carbenes.[11] For example, in PhCH(CH$_3$)–CH: the H/Ph preference is ca. 1.6; and in PhCH$_2$–CD: it is ca. 4.5.[12-14] When phenyl migrates from an optimum bond alignment in these uncomplicated, mobile systems, it would adopt its preferred M orientation; and when hydrogen shifts, the (nonmigrating) Ph could adopt any preferred O orientation that would help hydrogen move. Thus, these open-chain substrates with their optimum M and O factors provide an approximate reference H/Ph "norm", which differs markedly from the exceptionally high (>1000) ratios in our brexyl substrates **12c** and **12d**.

For epimer **12c** (exo H, endo Ph), *alignment* alone might provide a rationale for the high H/Ph ratio, because the exo bond at C(4) is better situated for shift than is the endo bond (see **13**).[1a]



13



14

Consequently, the outcome for **12c** does not necessarily augur a new geometric factor. But, epimer **12d** (exo Ph, endo H) has phenyl better aligned than hydrogen and might have led to a lower than "normal" H/Ph ratio (or even possibly to reversal, i.e., a preference of Ph over H.[15] Therefore, the unusually high H/Ph ratio in **12d** is not understandable on *alignment* considerations alone or on an exaltation of H shift through O orientation.

We suggest that the high ratio stems from suppression of phenyl shift in **12d**, because of an M-orientation restriction. Molecular models show appreciable interference between the bridge H at C(7) and an ortho H, if phenyl is face oriented during migration (see **14**). In contrast, an M-edge orientation appears relatively free of steric adversity. Our findings imply that phenyl shift to a carbene prefers M-face geometry. In the brexyl system **12d**, the difficulty of adopting this transition-state orientation precludes Ph migration despite a bond alignment advantage over H migration.[16,17]

Acknowledgment. This work was supported by the National Science Foundation (Grant No. CHE-761450) and by the National Institutes of Health (Grant No. GM-06304). A Vernon K. Krieble Fellowship to J.K.B. is also gratefully acknowledged. Mass spectra were recorded at the Middle Atlantic Mass Spectrometry Laboratory, a National Science Foundation shared instrumentation facility.

Registry No. 9a, 53392-15-7; **9b**, 53439-20-6; **10b**, 80878-18-8; **11**, 80878-19-9; **12a**, 80878-20-2; **12b**, 80924-91-0; **12c**, 80878-21-3; **12c** Na salt, 80924-92-1; **12d**, 80924-93-2; **12d** Na salt, 80951-29-7; **10a**, 80878-22-4.

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[7] Nickon, A.; Weglein, R. C.; Mathew, C. T. *Can. J. Chem.* **1981**, *59*, 302–313.

[8] Unless otherwise indicated, NMR and IR data refer to CCl$_4$. New compounds were characterized spectroscopically and, except for **10a**, and **10b**, by elemental analyses. Liquids **10a** and **10b** decompose gradually at room temperature, and so precise, high-resolution mass spectra served for molecular formula characterization.

[9] Nickon, A.; Kwasnik, H. R.; Mathew, C. T.; Swartz, T. D.; Williams, R. O.; DiGiorgio, J. B. *J. Org. Chem.* **1978**, *43*, 3904–3916.

[10] (a) Rosini, G. *J. Org. Chem.* **1974**, *39*, 3504–3506. (b) Freeman, P. J.; Balyeat, J. R. *Ibid.* **1977**, *42*, 3205–3206.

[11] Jones, W. M. "Rearrangements in Ground and Excited States"; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 1, 95–160.

[12] Determined in the laboratories of Professor H. Shechter of The Ohio State University (private communication from Professor Shechter). The 4.5 is statistically corrected, and the 1.6 is reckoned on the expectation that methyl shift does not compete appreciably with Ph shift (ref 13 and 14).

[13] (a) Philip, H.; Keating, J. *Tetrahedron Lett.* **1961**, 523–526. (b) Havel, J. J. *J. Org. Chem.* **1976**, *41*, 1464–1465.

[14] (a) For PhCH(CH$_3$)–C(Ph): a H/Ph ratio of 5.5 ± 2 was reported [Pomerantz, M.; Witherup, T. H. *J. Am. Chem. Soc.* **1973**, *95*, 5977–5988]. In this substrate T orientation may also play a role.

[15] (a) These qualitative expectations presume that H and Ph are comparably sensitive to changes in dihedral angle. (b) For an intriguing reversal of an H/Ph migration preference as temperature is lowered from 20 to −110 °C in photolysis of a diazohydrocarbon, see: Tomiaka, H.; Ueda, H.; Kondo, S.; Izawa, Y. *J. Am. Chem. Soc.* **1980**, *102*, 7818–7820.

[16] M face also appears sterically unattractive for endo phenyl shift in epimer **12c**, and so probably the M factor also contributes to its high (>1000) H/Ph ratio. Published[1b] results on competitive axial H vs. equatorial Ph shift in a *tert*-butyl-anchored cyclohexylidene support this view. In that substrate Ph had no serious M-orientation restraint, and initial *alignment* decidedly favored the H. Yet, the observed H$_{ax}$/Ph$_{eq}$ migration ratio was 59.3, i.e., still considerably lower than the >1000 we found for **12c**.

[17] Irradiation (Pyrex filter, −20 °C, Hg lamp, medium pressure) of the sodium salt of **12c** suspended in hexane gave olefin **10b** but no detectable ($<0.1\%$) **10a**, whereas the salt from epimer **12d** gave **10b** containing 0.12–0.16% of **10a**, reproducibly detectable. Evidently, this represents yet another instance where photic and thermal Bamford–Stevens reactions differ in stereochemical behavior.[1a]