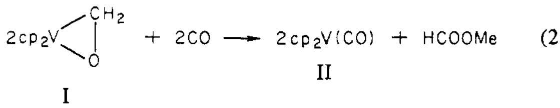
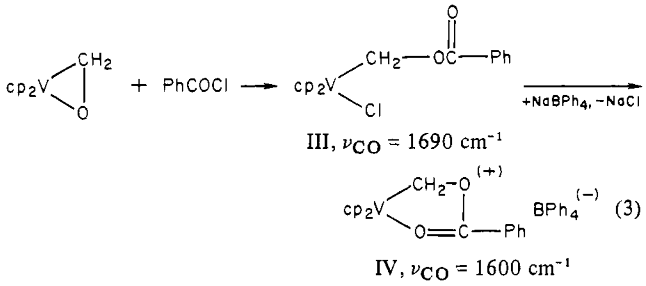
Formaldehyde in complex I is displaced by carbon monoxide in the form of methyl formate[10] (eq 2). In reaction 2, which is



(2)

rather slow, the vanadocene moiety is transformed into the corresonding monocarbonyl, II.[11] Complex II itself is active in promoting the slow transformation of paraformaldehyde into HCOOMe.[12] Disproportionation of formaldehyde to HCOOMe can be viewed as the classic Cannizzaro reaction in the version call "the Tishchenko reaction".[13] The occurrence of such a transformation would suggest that the formation of HCOOMe from H_2/CO catalyzed by transition-metal complexes could be the consequence of a preliminary metal-promoted formation of formaldehyde.[14] In case of an early transition metal,[3] the data cited above can be easily explained by Scheme I[15] (A ≡ paraformaldehyde). The scheme requires, mostly, the conversion of a formaldehydo into a hydrido–formyl complex. Such a transformation was observed both for the osmium complex $Os(CO)_2(PPh_3)_2(\eta^2\text{-}CH_2O)$[2] and in the oxidative addition of CH_2O to an iridium complex to form $(PMe_3)_4Ir(H)(CHO)^+$.[16]

The interaction of a Lewis acid on the metal-bonded CH_2O may represent a useful modeling reaction as concerns its possible activation by a bifunctional acid–base system.[1] This reaction would simulate the change from η^2-C,O to a bridging bonding mode of formaldehyde[4] and other possible pathways that formaldehyde, eventually formed from CO and H_2 on a metal center, could evolve through by a subsequent action of Lewis acids. Electrophiles attack the oxygen in complex I by a rather unexpected reaction because of the high oxophilicity of vanadium. Reaction 3 describes the transformation of η^2-C,O-bonded formaldehyde into an acyloxymethylene complex.[17] Complexes III and IV are unexpectedly stable being vanadium(IV) derivatives containing metal–carbon σ bonds.[17] The transformation of formaldehyde into an acyloxymethylene group was recently proposed as the intermediate step in the ruthenium-catalyzed reduction of CO to ethylene glycol esters.[18] Conversion of the formaldehydo group into oxymethylene derivatives, $cp_2V\text{–}CH_2OX$, exemplified in reaction 3, can be achieved by different Lewis acids [X = BF_3, $^1/_2TiCl_4$). Detailed investigations both on the action of different acids on complex I and on the reaction of carbon monoxide with the resulting oxymethylene complexes are in progress.



III, ν_{CO} = 1690 cm^{-1}

(3)

IV, ν_{CO} = 1600 cm^{-1}

Studies on metal–formaldehyde species will give interesting information on the products formed from CO and H_2, supposing that such systems produce formaldehyde as a primary intermediate in such a complex reaction.[19] Disproportionation, conversion to oxymethylene derivatives, and reductive coupling of formaldehyde may represent general pathways through which metallic systems are able to operate in synthesis gas conversion.

Acknowledgment. This work was supported by Italian National Research Council (CNR).

Registry No. I, 80737-39-9; II, 53339-41-6; III, 80737-40-2; IV, 80737-42-4; H-$[OCH_2]_n$-OH, 30525-89-4; Cp_2V, 1277-47-0; PhCOCl, 98-88-4.

Supplementary Material Available: Tables of positional (SI) and thermal (SII) parameters for $Cp_2V(CH_2O)$ and a listing of structure factor amplitudes (9 pages). Ordering information is given on any current masthead page.

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[10] Reaction 2 can be followed by the IR spectrum of a toluene solution (30 mL) of complex I (0.60 g) treated with carbon monoxide. The appearance of two bands, at 1880 and at 1730 cm^{-1}, in a few hours are diagnostic for the presence of $cp_2V(CO)$ and HCOOMe, respectively. The absorption of CO was found to be 0.85 mol per mol of vanadium in 24 hours. After 2 days HCOOMe can be distilled from the solution and determined by a standard procedure.

[11] Fachinetti, G.; Del Nero, S.; Floriani, C. *J. Chem. Soc., Dalton Trans.* **1976**, 1046–9.

[12] Paraformaldehyde added to a toluene solution of $cp_2V(CO)$ causes a partial but significant displacement of CO from the complex, which promotes its disproportionation to HCOOMe.

[13] March, J. "Advanced Organic Chemistry: Reaction, Mechanisms and Structure"; McGraw-hill: New York, 1968; p 910.

[14] Disproportionation of metal-bonded CH_2O can occur by a mechanism like that recently proposed for the disproportionation of metal–formyl groups: Casey, C. P.; Andrews, M. A.; McAlister, D. R. *J. Am. Chem. Soc.* **1979**, *101*, 3371–3. Casey, C. P.; Neumann, S. M.; Andrews, M. A.; McAlister, D. R. *Pure Appl. Chem.* **1980**, *52*, 625–33.

[15] The steps depicted in the scheme are supported by the results given in ref 6, 9, 10, and 12 and by the observation that vanadocene is unreactive with HCOOMe.

[16] Thorn, D. L. *J. Am. Chem. Soc.* **1980**, *102*, 7109–10 and references cited therein.

[17] A toluene solution (50 mL) of I (0.91 g, 4.31 mmol) was reacted with distilled PhCOCl (0.50 mL, 4.31 mmol). The resulting green-yellow solution gave in a few seconds light green needles of $cp_2V(Cl)(CH_2O_2CPh)$ (0.85 g). Anal. Calcd for $C_{18}H_{17}O_2VCl$: C, 61.45; H, 4.83; Cl, 10.10. Found: C, 60.47; H, 5.17; Cl, 11.16. $\nu_{C\text{–}O}$ (Nujol) = 1690 cm^{-1} (vs). Complex III (0.52 g, 1.48 mmol) dissolved in THF (50 mL) was reacted with $NaBPh_4$ (0.60 g, 1.75 mmol). The resulting solution was kept standing overnight. A crystalline deep blue solid formed (0.35 g). Anal. Calcd for $[Cp_2V\text{–}CH_2OC(O)\text{-}Ph](BPh_4)$, $C_{42}H_{37}O_2VB$: C, 79.37; H, 5.83. Found: C, 78.97; H, 5.89. $\nu_{C\text{–}O}$ (Nujol) = 1600 cm^{-1} (vs). Proposed structures are based on preliminary X-ray analysis results.

[18] Dombek, B. D. *J. Am. Chem. Soc.* **1980**, *102*, 6855–7. *Ibid.* **1979**, *101*, 6466–8.

[19] Fahey, D. R. *J. Am. Chem. Soc.* **1981**, *103*, 136–41.

Modes of β-Silyl Involvement in Solvolysis

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Received November 12, 1981

A β-silicon atom strongly activates the departure of groups under both solvolytic and pyrolytic conditions.[1,2] The overall result is an elimination reaction (eq 1), whose mechanism has at one

$$Me_3SiCH_2CH_2X + ROH \rightarrow CH_2{=}CH_2 + Me_3SiOR + HX \qquad (1)$$

time been considered to involve rate-determining expulsion of a silylenium ion[3,4] or a four-centered transition state with concerted departure of Me_3SiX.[5] Most authors currently subscribe to a

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[1] Jarvie, A. W. P. *Organomet. Chem. Rev., Sect. A* **1970**, *6*, 153–170.

[2] Sommer, L. H.; Whitmore, F. C. *J. Am. Chem. Soc.* **1946**, *68*, 485–487.

[3] We use the term silylenium for electron-deficient positive silicon (R_3Si^+) and siliconium for electron-sufficient positive silicon (R_5Si^+).

[4] Sommer, L. H.; Baughman, G. A. *J. Am. Chem. Soc.* **1961**, *83*, 3346–3347.

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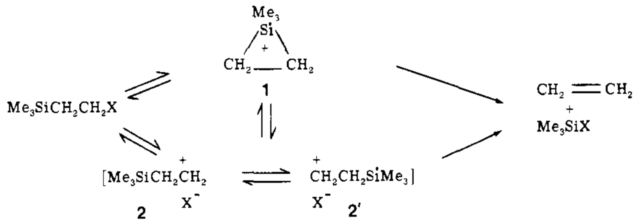
Scheme I

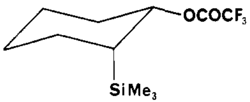


mechanism in which silicon-assisted cleavage of the C–X bond is rate determining,[6,7] because the reaction is sensitive to ionizing power rather than nucleophilicity of the solvent, because it exhibits a strong stereoselectivity for anti elimination of the elements of Me_3SiX, and because deuterium is partially scrambled between the α and β 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).

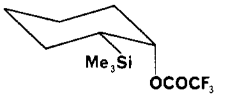
Silicon involvement can be viewed in terms of induction (silicon is electropositive with respect to carbon), vertical stabilization[8] (σ–π participation without nuclear motion, as in the formation of the carbenium ion in Scheme I), or direct nucleophilic attack (participation with nuclear motion to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

Previous mechanistic studies of β-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.[12]

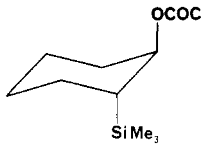
We selected the cyclohexyl systems **3** and **4** for our studies.



3



3'



4

They were prepared by standard, stereospecific reactions.[13] Each 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.[15] 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.[16] 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 ($N = -2.59$).[19] 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[20] 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, 7.05×10^{-10} s^{-1} (relative rate 1.0);[20] cis-2-(trimethylsilyl)cyclohexyl 2.36×10^{-5} s^{-1} (relative rate 3.35×10^{4}); *trans*-2-(trimethylsilyl)cyclohexyl, 1.74×10^{-3} s^{-1} (relative rate 2.47×10^{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 σ 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

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(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 β-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.

(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 $LiAlH_4$. 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.[14] 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 acetoxyl, 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 acetoxyl (0.71)[17] and trimethylstannyl (0.94).[18]

(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.[21] 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 β-silyl acceleration.[1]

(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 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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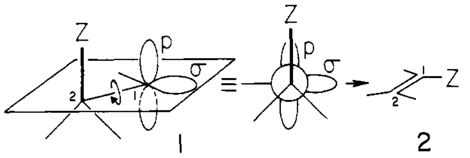
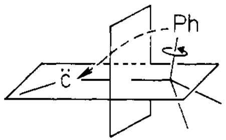
Received November 30, 1981

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

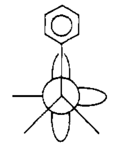


the C–Z bond has been established experimentally for Z = H and Z = Ph and has been supported theoretically for Z = H.[1] When Z itself lacks axial symmetry, rotation about the C–Z bond introduces another stereochemical variable (termed here the *orientation factor*) that could influence ease of rearrangement. 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).

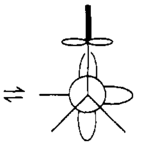
Geometric description is considerably simplified if we adopt, as reference, an imaginary plane perpendicular to the C(1)–C(2) bond axis. After the C–Ph bond is optimally *aligned* (**3**), the ring can take up two extreme orientations with respect to the reference plane. In one (**4a**), the face of 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.



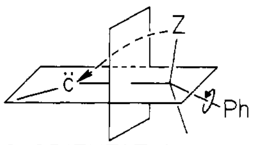
M-ORIENTATION
3



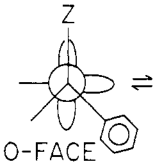
M-FACE
4a



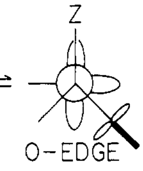
M-EDGE
4b



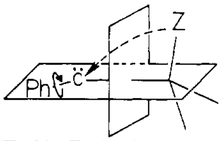
O-ORIENTATION
5



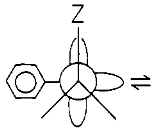
O-FACE
6a



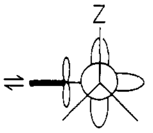
O-EDGE
6b



T-ORIENTATION
7



T-FACE
8a



T-EDGE
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.

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