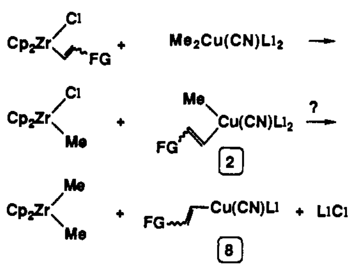
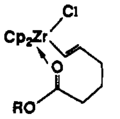
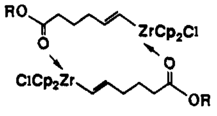
Scheme III



above led to only olefinic products **4** (R = OEt, OMe) (Scheme II). These failures to transmetalate may be a consequence of intra- and/or intermolecular chelation of the ester carbonyl with the Zr(IV) present (cf. **6** and **7**).[10] This notion stems from the



6



7

observation that for all known HO cyanocuprate-based transmetalations (involving Sn,[11] Te,[12] Al,[13] Zr[8,13]), whatever the mechanism involved, the common denominator is the Lewis acidic nature of the participating organometallic. Thus, occupation of the remaining coordination site as in **6**/**7** shuts down ligand exchange with $Me_2Cu(CN)Li_2$ and, hence, vinylcuprate formation. However, replacement of R = OEt or OMe in **3a**,**b** with R = $OSi(i\text{-}Pr)_3$ (OTIPS), on steric[15] or stereoelectronic grounds (or both),[16] completely restores the transmetalation pathway. In support of the argument above, we also find that (1) introduction of ethyl heptanoate to reactions of **3e** *completely inhibits* formation of **5** (R = OTIPS) and (2) all attempts to effect the sequence with amides **3c**,**d** likewise produced the alkene **4** rather than the desired Michael adducts **5**.

The true nature of the species formed in the transmetalation process has yet to be established. Although formulated here initially as a HO cuprate (cf. Scheme I), it is possible that **2** reacts to some degree with the presumed $Cp_2Zr(Me)Cl$ byproduct of the transmetalation to produce an LO lithiocyanocuprate **8** (Scheme III). Spectroscopic studies are anticipated to elucidate this issue.

In summary, the extreme mildness and rapidity with which vinylzirconates undergo transmetalations with HO cyanocuprates have led to the first examples of functionalized lithiocuprates.[17] Applications, in particular to polyene macrolide chemistry, are currently in progress and will be reported in due course.

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(10) See, for examples: Yamamoto, Y.; Komatsu, T.; Maruyama, K. *J. Organomet. Chem.* **1985**, *285*, 31. Buchwald, S. L.; Nielsen, R. B.; Dawan, J. C. *Organometallics* **1988**, *7*, 2324.

(11) For example, see Behling, J. R.; Babiak, K. A.; Ng, J. S.; Campbell, A. L.; Moretti, R.; Koerner, M.; Lipshutz, B. H. *J. Am. Chem. Soc.* **1988**, *112*, 7440.

(12) Comasseto, J. V.; Berriel, J. N. *Synth. Commun.* **1990**, *20*, 1681.

(13) Ireland, R. E.; Wipf, P. *J. Org. Chem.* **1990**, *55*, 1425.

(14) Babiak, K. A.; Behling, J. R.; Dygos, J. H.; McLaughlin, K. T.; Ng, J. S.; Kalish, V. J.; Kramer, S. W.; Shone, R. L. *J. Am. Chem. Soc.* **1990**, *112*, 7441.

(15) Use of the corresponding t-$BuMe_2Si$ ester gave low (15–20%) yields.

(16) Frye, S. V.; Eliel, E. L. *Tetrahedron Lett.* **1986**, *27*, 3223; *J. Am. Chem. Soc.* **1988**, *110*, 484. Chen, X.; Hortelano, E. R.; Eliel, E. L.; Frye, S. V. *Ibid.* **1990**, *112*, 6130. Magnus, P.; Mugrage, B. *Ibid.* **1990**, *112*, 462.

(17) A typical procedure for the preparation of an ω-functionalized cyanocuprate is as follows: The vinyl zirconate is formed by treating a slurry of $Cp_2Zr(H)Cl$ (0.5 mmol) in anhydrous THF (2 mL) with the 1-alkyne (0.5 mmol, added neat) for 15 min at room temperature. The solution is then cooled to −78 °C and treated for 10 min with a −78 °C THF solution of $Me_2Cu(CN)Li_2$ (prepared from 2MeLi (1 mmol) and CuCN (0.5 mmol) at −78 °C in 2 mL of THF). If necessary, $BF_3{\cdot}Et_2O$ (0.5 mmol in 1 mL of Et_2O or THF) can be added at this time in a dropwise fashion. The enone (0.25 *mmol, neat or in 0.5 mL* of THF) is then introduced and the solution stirred at −78 °C until the reaction is complete (5 min to 1 h), as determined by TLC. The mixture is then quenched by pouring it into saturated aqueous NH_4Cl/concentrated NH_4OH solution (9:1) and is extracted with Et_2O. Normal handling and chromatography affords the pure 1,4-addition product.

Acknowledgment. Financial support provided by the NIH (GM 40287) and the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged. We are indebted to Dr. Toshio Tanaka (Teijin Ltd.) for a generous sample of the nonracemic cyclopentenone used in Table I, entry 8.

Registry No. **1**, 139461-23-7; **3a**, 108545-38-6; **3b**, 77758-51-1; **3c**, 139461-32-8; **3d**, 139461-33-9; **3** (R = $OSiMe_2Bu$-t), 139461-36-2; **4a**, 54653-25-7; **4b**, 2396-80-7; **4c**, 139461-34-0; **4d**, 139461-35-1; $Cp_2Zr(H)Cl$, 37342-97-5; $Me_2Cu(CN)Li_2$, 80473-70-7; $HC{\equiv}C(CH_2)_3CN$, 14918-21-9; $HC{\equiv}C(CH_2)_2OCOPh$, 122471-85-6; $HC{\equiv}C(CH_2)_2Cl$, 51908-64-6; 2-cyclohexenone, 930-68-7; 2-methyl-2-cyclopentenone, 1120-73-6; 4-methylpent-3-en-2-one, 107-86-8; 3-methyl-2-cyclopentenone, 1193-18-6; (*R*)-4-(dimethyl-*tert*-butylsiloxy)-2-cyclopentenone, 61305-35-9; (*E*)-3-(5-cyano-1-pentenyl)cyclohexanone, 139461-24-8; (*E*)-3-[6-(triisopropylsiloxy)-6-oxo-1-hexanyl]cyclohexanone, 139461-25-9; (*E*)-3-[4-(phenylcarbonyloxy)-1-butenyl]cyclohexanone, 139461-26-0; (*E*)-3-(4-chloro-1-butenyl)cyclohexanone, 139461-27-1; 2-methyl-3-[6-(triisopropylsiloxy)-6-oxo-1-hexenyl]cyclopentanone, 139461-28-2; triisopropylsilyl (*E*)-7,7-dimethyl-9-oxodec-5-enoate, 139461-29-3; (*E*)-3-methyl-3-[6-(triisopropylsiloxy)-6-oxo-1-hexenyl]cyclohexanone, 139461-30-6; (*E*)-2(*R*)-(dimethyl-*tert*-butylsiloxy)-3(*S*)-[6-(triisopropylsiloxy)-6-oxo-1-hexenyl]cyclopentanone, 139461-31-7.

Supplementary Material Available: Listings of spectral data for the products in Table I and ^1H and ^{13}C NMR spectra for these and other products of the reactions of lithiocuprates (18 pages). Ordering information is given on any current masthead page.

Dynamics of Solute Motion: Photoisomerization Shows Linear Dependence on Solvent Mass

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Received May 28, 1992

In the general theory of solute motion based on Kramers' equation,[1] the control of reaction dynamics is divided into two limiting categories. At low friction (i.e., at low viscosity), the reaction rate is expected to increase with the number of collisions with solvent, as these supply the energy required to cross a potential barrier. At high viscosity, solvent will obstruct the path along the reaction coordinate and decrease the rate. Experiments have shown that Kramers' theory regularly fails when the potential barrier of the reaction is small (relative to kT) or no activation energy is required.[2] Several attempts have been made to account for behavior in this low-barrier regime.[3] Grote and Hynes[4] replaced the friction coefficient in Kramers' equation (ξ), with a frequency-dependent function, $\xi(\omega)$, which permits the viscosity to vary with the rate of the reaction. Velsko and Fleming[2] added a reaction coordinate-dependent sink function to Kramers' theory and obtained an improved fit to experimental observation. In an approach developed by Åkesson, Sundström, and Gillbro,[5] the barrier height, large or small, is made to depend on the solvent. When this approach is applied to a homologous solvent series such as the *n*-alcohols, adjusting the barrier generates a good fit to experimental data. Dote, Kivelson, and Schwartz[6] introduced "free spaces" in the solvent where rotation can take place unhindered

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(1) Kramers, H. A. *Physica* **1940**, *7*, 284.

(2) Velsko, S. P.; Waldeck, D. H.; Fleming, G. R. *J. Chem. Phys.* **1983**, *78*, 249.

(3) Barbara, P.; Walker, G. C. *Rev. Chem. Interm.* **1988**, *10*, 1. Bagchi, B.; Fleming, G. R. *J. Phys. Chem.* **1990**, *94*, 9.

(4) Grote, R. F.; Hynes, J. T. *J. Chem. Phys.* **1980**, *73*, 2715. Grote, R. F.; Hynes, J. T. *J. Chem. Phys.* **1981**, *74*, 4465.

(5) Åkesson, E.; Sundstrom, V.; Gillbro, T. *Chem. Phys.* **1986**, *106*, 269.

(6) Dote, J. L.; Kivelson, D.; Schwartz, R. N. *J. Phys. Chem.* **1981**, *85*, 2169.

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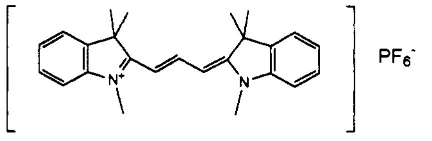
by viscosity.[7] The coupling factor between solute and solvent was corrected for this effect and agreement with experiment was improved.

These approaches to modeling the dynamics of solute motion have key features in common. All are based on Kramers' theory, which implies the existence of a reaction barrier. All include, as one of the solvent-dependent parameters, the hydrodynamic viscosity, directly, to a fractional power (typically in the range from $^1/_3$ to $^2/_3$), or indirectly.[8] Despite extensive effort there is no theoretical approach that fully accounts for the effect of solvent viscosity on dynamical molecular processes.

We report herein an examination of the deactivation rates for the singlet excited state of *N,N'*-dimethylindocarbocyanine hexafluorophosphate $[\mathrm{DMIC^+PF_6^-}]^{*1}$ in four solvent series. The excited state of this cationic dye undergoes torsional rotational motion about a carbon–carbon bond, which causes its relaxation and deactivation. We find that solvent viscosity cannot be used to account for the dynamics of this motion. Instead, there is a surprisingly good linear correlation of the observed deactivation rates with the molecular weight of the solvent.



DMIC+

The excited-state lifetime of $[\mathrm{DMIC^+PF_6^-}]^{*1}$ in various solvents was determined directly by transient absorption spectroscopy in solution (Nd:YAG, 532 nm, 18 ps, 200 μJ).[9] Complete time-resolved spectra were recorded from 400 to 650 nm. The dynamical behavior of these spectra shows decay of the excited state, absorption of the dye (λ = 435 nm), recovery of its ground-state absorption (λ = 565 nm), and decay of fluorescence stimulated by the probe beam (λ = 620 nm). The kinetic data were analyzed by the nonlinear least-squares Marquardt–Lenberg algorithm[10] and show no dependence on wavelength. With the exception of water, no deconvolution of the instrument response function was necessary since data fitting started well after (typically 35 ps) the end of the laser pulse. These results were confirmed by steady-state fluorescence experiments, which identically reproduce the solvent dependence. The data for the four solvent series investigated are presented graphically in Figure 1 where the experimentally determined lifetimes are plotted as a function of the solvent molecular weight. No other solvent-dependent parameter we considered, particularly viscosity, yields such a good correlation.

The data obtained for isomeric alcohols provide particularly clear evidence that any attempt to correlate the lifetime of $[\mathrm{DMIC^+PF_6^-}]^{*1}$ with hydrodynamic viscosity is hopeless. We examined all of the linear and branched isomers of propyl and butyl alcohols. At room temperature the viscosities[11] of *n*-propyl and isopropyl alcohols are 1.9 and 3.3 cP, respectively, but the measured lifetimes of $[\mathrm{DMIC^+PF_6^-}]^{*1}$ are nearly identical. Even more striking are the data for *n*-butyl, isobutyl, *sec*-butyl, and *tert*-butyl alcohols. The viscosities of these solvents vary from 2.6 to 4.4 cP, but the lifetime, 215 ± 5 ps, is independent of the solvent. Nonetheless, there is an excellent linear correlation of the lifetime of $[\mathrm{DMIC^+PF_6^-}]^{*1}$ with solvent molecular weight, from water (18 Da, 40 ± 10 ps) to *n*-decyl alcohol (158 Da, 440 ± 10 ps).

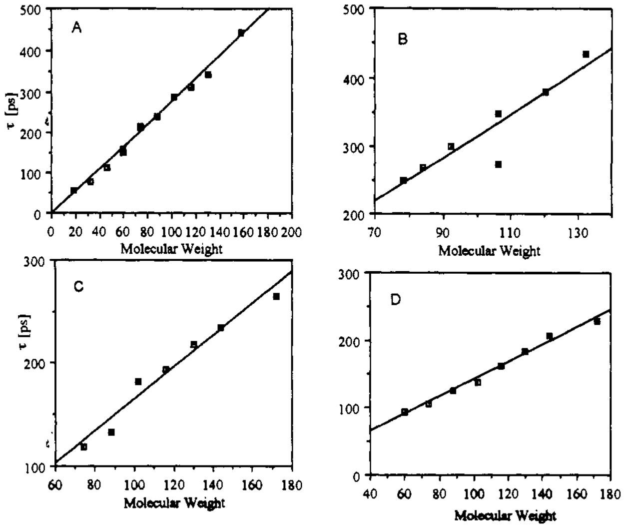


Figure 1. Nonradiative lifetime (τ) of $[\mathrm{DMIC^+PF_6^-}]^{*1}$ plotted against solvent molecular weight: (A) alcohol series, points are water, methanol, ethanol, 1-propanol, 2-propanol, *n*-, iso-, *sec*-, and *tert*-butyl alcohol, 1-pentanol, 1-hexanol, 1-heptanol, 1-octanol, and 1-decanol; (B) aromatic hydrocarbon series, points are benzene, benzene-d_6, toluene, *o*-xylene (off the line), *p*-xylene, mesitylene, and tetralin; (C) acetate series, points are methyl, ethyl, *n*-propyl, *n*-butyl, *n*-pentyl, *n*-hexyl, and *n*-octyl acetates; (D) ketone series, points are acetone, methyl ethyl ketone, 2-pentanone, 2-hexanone, 2-octanone, 2-nonanone, and 2-undecanone.

The other solvent classes examined behave similarly—in each case a linear correlation of lifetime with molecular weight is obtained. Also, within each class, extrapolation of the data to zero solvent molecular weight gives a lifetime for $[\mathrm{DMIC^+PF_6^-}]^{*1}$ within experimental error of zero. These observations indicate that there is no barrier to torsional rotational motion in the absence of solvent. In contrast, the proportionality constants relating solvent mass to lifetime (the slopes in Figure 1) depend on the solvent class (alcohols, hydrocarbons, acetates, ketones: 2.7, 3.2, 1.6, 1.3 ps/Da, respectively).

It is generally appreciated that a proper molecular level description of the interaction between molecules in solution will be very complex. Nonetheless, the linear dependence of lifetime on solvent molecular weight for $[\mathrm{DMIC^+PF_6^-}]^{*1}$ may provide important insight to the dominant features of this interaction. The experiments indicate that deactivation in the absence of solvent is barrierless (or nearly so). We assume that this reaction requires a small rotation of one end of the molecule with respect to the other since the internal conversion rate will increase rapidly as the twist angle increases.[12]

In one approach, we consider that twisting of $[\mathrm{DMIC^+PF_6^-}]^{*1}$ generates angular momentum equal to the product of the moment of inertia (I) and angular velocity ω. Collisions with solvent (mass m) at distance d from the rotational axis must displace solvent molecules a distance x to permit $[\mathrm{DMIC^+PF_6^-}]^{*1}$ to achieve a relaxation-prone geometry. If momentum is conserved and if little is transferred in each collision ($d^2m \gg I$), then the lifetime is directly proportional to m: $\tau \approx m[xd/2\omega I]$. In other words, for greater m, each collision is less effective since solvent motion, δx, is smaller and the twisting of $[\mathrm{DMIC^+PF_6^-}]^{*1}$ is less. Further, since the movement necessary to reach an internal conversion-prone geometry of $[\mathrm{DMIC^+PF_6^-}]^{*1}$ is small, no location exchange of solvent molecules need occur. Location exchange accounts for the macroscopic viscosity of a liquid. These considerations may explain why the mass of a solvent molecule[13] and not the ma-

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(7) Korppi-Tommola, E. I. J.; Hakkarainen, A.; Hukka, T.; Subbi, J. *J. Phys. Chem.* **1991**, *95*, 8482. Åkesson, E.; Hakkarainen, A.; Laitinen, E.; Helenius, V.; Gillbro, T.; Korppi-Tommola, J.; Sundström, V. *J. Chem. Phys.* **1991**, *95*, 6508.

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(10) Marquardt, D. W. *J. Soc. Ind. Appl. Math.* **1963**, *11*, 431. Bevington, P. R. *Data Reduction and Error Analysis for the Physical Sciences*; McGraw-Hill: New York, 1969; Chapter 11.

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(12) Momicchioli, F.; Baraldi, I.; Berthier, G. *Chem. Phys.* **1988**, *123*, 103.

(13) The solvent-class-dependent slopes may be explained within the framework of the momentum conservation model by assuming different contact conditions. The angular momentum transferred to solvent in each collision may depend on the specific details of interaction between $[\mathrm{DMIC^+PF_6^-}]$ and the solvent. This interaction may be the same for all of the alcohols examined but different, for example, in the aromatic hydrocarbon solvents.

crcscopic viscosity can be used to predict the lifetime of $[\mathrm{DMIC^+PF_6^-}]^{*1}$.

In summary, Kramers' theory does not describe the dynamic behavior of $[\mathrm{DMIC^+PF_6^-}]^{*1}$. However, solvent molecular weight correlates surprisingly well with observed excited-state lifetimes. An explanation based simply on transfer of momentum seems to account for the findings. This approach may also assist in the interpretation of data reported previously for related systems.[7,8,14]

Acknowledgment. This work was supported by a grant from the National Science Foundation for which we are thankful. We are grateful to Professor J. Jonas of this department for his helpful comments.

Supplementary Material Available: Tables of the experimentally determined relaxation rates for $[\mathrm{DMIC^+PF_6^-}]^{*1}$ in various solvents and plots of the data taken from refs 7, 8, and 14 against solvent molecular weight (12 pages). Ordering information is given on any current masthead page.

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Silicon-Directed Aldol Reactions. Rate Acceleration by Small Rings

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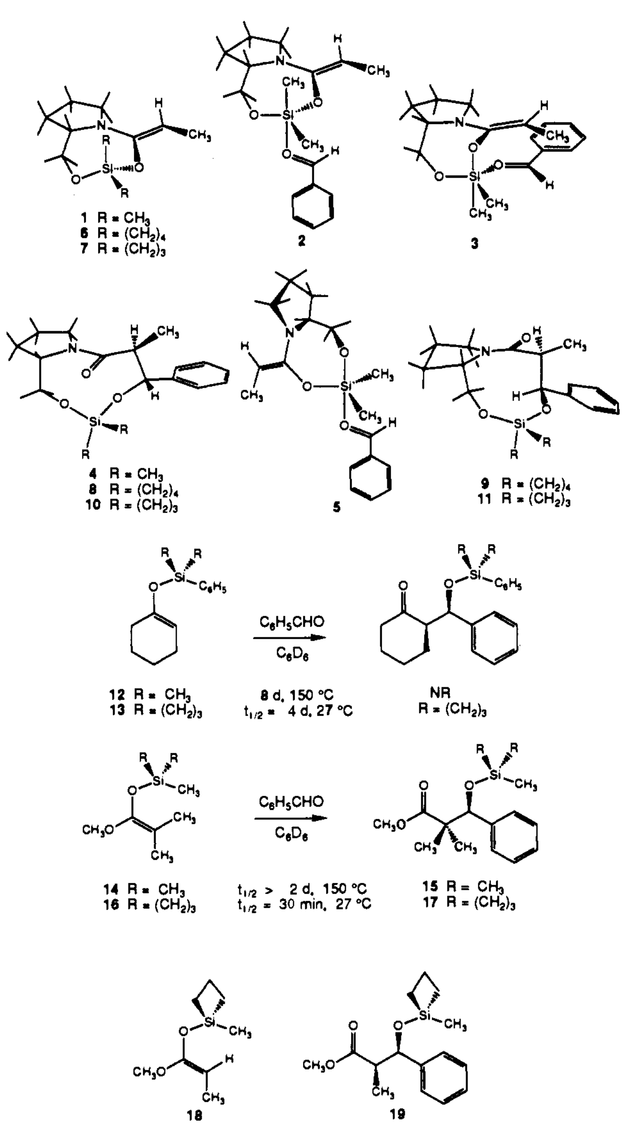
Noncatalyzed aldol addition reactions of silyl enol derivatives of ketones and esters with aldehydes do not occur or are exceedingly slow, even at elevated temperatures.[1] By contrast, silyl enol derivatives of amides (*O*-silyl *N*,*O*-ketene acetals) react readily with aldehydes, without catalysis, to form aldol addition products in a simple bimolecular process.[2] In further mechanistic studies of the latter transformation, we have learned that the rate of this reaction is dramatically accelerated by incorporation of the silicon atom within a four-membered ring. This observation extends to silyl enol derivatives of ketones and esters as well and likely represents a general strategy for carbon–carbon bond formation with organosilicon intermediates.

We were led to these discoveries in the course of mechanistic studies of the reaction of *O*-silyl *N*,*O*-ketene acetal **1** with benzaldehyde. In order to further distinguish between a mechanism proposed in earlier work (**1** → **2** → **3** → **4**)[2] and an alternative pathway (**1** → **5** → **3** → **4**), the effect of constraining the silicon atom and silicon-bound carbon atoms within a small ring was examined.[3] In the proposed pathway, this change should lead to an accelerated reaction, whereas the alternative pathway involving **5** is predicted to be prohibitively strained. Silacyclopentane and silacyclobutane derivatives **6** and **7**, respectively, were prepared in analogy to **1**[2a] and were found to react with benzaldehyde at accelerated rates versus **1** to form mixtures of syn and anti aldol addition products (**8**–**11**).[4] Whereas the observed rate acceleration at 40 °C with silacyclopentane derivative **6** is roughly 10-fold (k = $(4.3 \pm 0.2) \times 10^{-4}$ and $(4.2 \pm 0.9) \times 10^{-5}$ M^{-1} s^{-1}, respectively, ^{1}H NMR analysis), reaction of the homologous silacyclobutane analog **7** is accelerated to such an extent that the reaction must be conducted at −80 °C to conveniently measure its rate ($k = (2.6 \pm 0.1) \times 10^{-4}$ M^{-1} s^{-1}, ^{1}H NMR analysis). From activation parameters previously determined,[2b] the rate of reaction of **1** and benzaldehyde at −80 °C can be estimated ($k \approx 1.2 \times 10^{-10}$ M^{-1} s^{-1}), leading to a calculated rate acceleration of $\sim 2 \times 10^6$ upon linking the silylmethyl groups of **1** with a carbon atom. Interestingly, across the series of substrates **1**, **6**, and **7**, the syn:anti ratio of benzaldehyde adducts is observed to increase uniformly (2:98, 50:50, 85:15, respectively). The origin of this variation in stereoselectivity is presently unclear, but is believed to be a consequence of bond angle distortion within the respective hypervalent transition states (Chart I).

Chart I



The results above suggest a general strategy for promotion of the aldol reaction of silyl enol derivatives of carbonyl compounds. Silyl enol derivatives of ketones, for example, do not react with aldehydes under simple thermal conditions. Thus, cyclohexanone

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(1) Silyl ketene acetals: Creger, P. L. *Tetrahedron Lett.* **1972**, 79. We are unaware of any precedent for noncatalyzed thermal aldol addition reactions of ketone silyl enol ethers with aldehydes.

(2) (a) Myers, A. G.; Widdowson, K. L. *J. Am. Chem. Soc.* **1990**, *113*, 9672. (b) Myers, A. G.; Widdowson, K. L.; Kukkola, P. J. *J. Am. Chem. Soc.* **1992**, *114*, 2765.

(3) This strategy is well-precedented in the study of phosphate ester hydrolysis: (a) Westheimer, F. H. *Acc. Chem. Res.* **1968**, *1*, 70. (b) Holmes, R. R. *Pentacoordinated Phosphorus*; American Chemical Society: Washington, D.C., 1980; Vol. 2, and references therein.

(4) Not surprisingly, silacyclobutane ethers are, in some cases, quite sensitive to hydrolysis (e.g., on silica gel); products **10** and **11** represent such a case.

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