Table I. Rate Constants for Diels-Alder Reactions

solvent	additional component	$k_2 \times 10^5$, $M^{-1} s^{-1}$[a]
(a) Cyclopentadiene + Butenone, 20 °C		
isooctane[b]		5.94 ± 0.3
MeOH		75.5
H_2O		4400 ± 70
H_2O	LiCl (4.86 M)	10800
H_2O	$C(NH_2)_3^+Cl^-$ (4.86 M)	4300
H_2O	β-cyclodextrin (10 mM)[c,f]	10900
H_2O	α-cyclodextrin (10 mM)[c,f]	2610
(b) Cyclopentadiene + Acrylonitrile, 30 °C		
isooctane[b]		1.9
MeOH		4.0
H_2O		59.3
H_2O	β-cyclodextrin (10 mM)[d,f]	537
H_2O	α-cyclodextrin (5 mM)[d,f]	47.9
(c) Anthracene-9-carbinol + *N*-Ethylmaleimide, 45 °C		
isooctane[b]		796 ± 71
1-butanol		666 ± 23
MeOH		344 ± 25
CH_3CN		107 ± 8
H_2O		22600 ± 700
H_2O	β-cyclodextrin (10 mM)[e]	13800

[a] Second-order rate constants. All data are the result of at least three runs at a given set of concentrations; error limits are given for cases in which triplicate runs were performed at more than one dienophile concentration. [b] 2,2,4-Trimethylpentane, >99% pure. [c] Initial conditions: cyclopentadiene (0.4 mM), butenone (10 mM). [d] Initial conditions; cyclopentadiene (0.4 mM), acrylonitrile (200 mM). [e] Initial conditions: anthracenecarbinol (0.03 mM), *N*-ethylmaleimide (1.0 mM). [f] The reactions were actually performed with 1 mol % of methanol and small amounts of HCl or formate buffer present; these had no effect on the reaction rate in pure water.

of reagents into a cyclodextrin cavity, compared with the reaction of *unassociated* molecules, is considerable.[7]

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Temperature and Matrix Effects on Migratory Aptitude and Stereochemistry in 1,2-Migration to a Divalent Carbon

Sir:

The 1,2-migration to divalent carbon generating an alkene has been of theoretical and synthetical interest, and hence considerable efforts[1] have been made to clarify the stereochemistry, migratory aptitude, and roles of multiplicity in the rearrangement. During the course of our studies[2] on the effect of temperature on carbene processes, we found that the migratory aptitude as well as the stereochemistry of a 1,2-H shift is highly sensitive to temperature and the reaction phase. The results provide important information concerning energetic and conformational controls in the carbenic rearrangement.

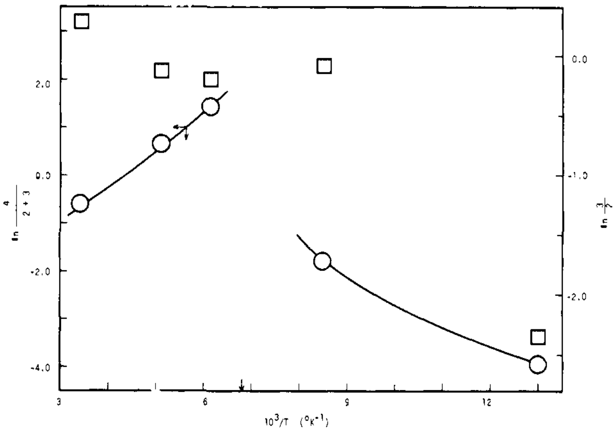
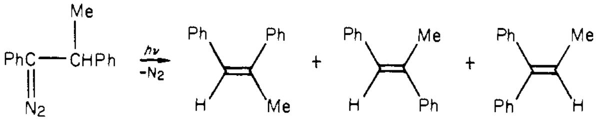


Figure 1. ln ([Ph migration product]/[H migration product]) (○) and ln {[(*E*)-olefin]/[(*Z*)-olefin]} (□) as a function of temperature in the photolysis of 1 in methylcyclohexane. Arrows show the freezing point of the solvent.

Direct irradiation of 1,2-diphenyl-1-diazopropane (**1**)[3] in methylcyclohexane in a sealed Pyrex tube was carried out with a 300-W high-pressure Hg lamp until all of the diazo compound was destroyed. A Corning CS-052 filter (**1**)[3] in cutoff at 350 nm was used in order to avoid product isomerization.[5] GC analysis of the reaction mixture showed that three olefins, i.e., 1,2-diphenylpropenes **2** and **3** and 1,1-diphenyl-1-propene (**4**), are formed in roughly equal amounts at ambient temperature along with α-phenylpropiophenone and its azine. Temperature studies (+20 to −196 °C) revealed, however, that the relative amounts of olefins **2** and **3**, which result from H migration, and **4**, which results from phenyl migration, vary dramatically with temperature (Figure 1). Thus, as temperature decreases, phenyl migration product continues to increase as far as the solvent is fluid (81% at −110 °C), but its formation becomes remarkably suppressed once the environment becomes solid and is almost completely eliminated (<2%) at −196 °C.



(1)

1 2 3 4

Predominant Ph migration over H migration in a lower temperature liquid is quite interesting since the sequence of migratory aptitutde prevailing in ambient-temperature chemistry was given[6] as H > Ph > Me and since, moreover, it has often been assumed[1a,7] that 1,2-H migrations occur with essentially zero activation energy. Apparently, however, the phenomenon is interpretable as indicating that the activation energy for H migration marginally exceeds that for Ph migration. Drastic decrease in the formation of **4** in a low-temperature solid phase, in spite of the energetic advantage, is then ascribable not to a simple temperature effect but totally to a matrix effect (a change in environment). In a matrix environment, for example, in which molecular motions are known[8] to be severely restricted, migration of a larger group (Ph) becomes effectively suppressed, whereas migration of an extremely small particle (H) is still significant even at this low temperature.

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(1) For pertinent reviews, see: (a) Schaeffer, H. F., III. *Acc. Chem. Res.* **1979**, *12*, 288. (b) Moss, R. A.; Jones, M., Eds. "Carbenes"; Wiley: New York, 1973, 1975; Vol. I, II. (c) Kirmse, W., Ed. "Carbene Chemistry"; Academic Press: New York, 1971.

(2) (a) Tomioka, H.; Izawa, Y. *J. Am. Chem. Soc.* **1977**, *99*, 6128. (b) Tomioka, H. *Ibid*, **1979**, *101*, 256. (c) Tomioka, H.; Griffin, G. W.; Nishiyama, K. *Ibid.* **1979**, *101*, 6009. (d) Tomioka, H.; Inagaki, T.; Nakamura, S.; Izawa, Y. *J. Chem. Soc., Perkin Trans. 1* **1979**, 130. (e) Tomioka, H.; Suzuki, S.; Izawa, Y. *Chem. Lett.* **1980**, 293. (f) Tomioka, H.; Miwa, T.; Suzuki, S.; Izawa, Y. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 753.

(3) All diazo compounds used in this study were prepared[4] by oxidation of the corresponding hydrazones and purified just before use. That no olefins were present before irradiation was easily shown by NMR.

(4) Pomerantz, M.; Witherup, T. H. *J. Am. Chem. Soc.* **1973**, *95*, 5977.

(5) A control experiment indicated that the product olefins did not isomerize under these conditions.

(6) (a) Friedman, L.; Shechter, H. *J. Am. Chem. Soc.* **1961**, *83*, 3159. (b) Philp, B. H.; Keating, J. *Tetrahedron Lett.* **1961**, 523.

(7) This result is supported by MINDO calculations: Kyba, E. P. *J. Am. Chem. Soc.* 1977, *99*, 8330.

(8) See, for example: Wasserman, E.; Yager, W. A. *J. Phys. Chem.* **1967**, *71*, 201.

0002-7863/80/1502-7817$01.00/0

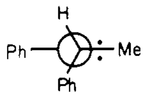
Table I. Photolysis of 5 at Various Temperatures[a]

R in 5	[(E)-6] [(Z)-6][b] 0 °C	−196 °C
Ph	1.4	1.9
Me	2.1	4.9
Et	1.7	2.2
i-Pr	4.0	0.9
t-Bu	8.0	2.1

[a] Methylcyclohexane solutions ca. 25 mM in diazo were used. All products were identified by gas chromatography comparisons with authentic samples and gas chromatography-mass spectroscopy techniques. Total product yields are 70–85%. Other minor products detected in each experimental condition were the ketone and its azine. No prominent formation of other products, e.g., C–H insertion product, was noted even at −196 °C. [b] Average of duplicate runs are tabulated; reproducibility was <±5%.

Support is lent to the above argument by the finding[9] that an H atom generated in a rigid neopentane crystal at −196 °C can travel a long distance and even intermolecularly. Furthermore, it has been generally accepted[10] that reactions in the solid state occur with minimum atomic or molecular movement even at ambient temperature since a large change of external shape of the reaction cavity, occupied by the molecules which will participate in the reaction, with the atomic movements constituting this reaction will be resisted by the close-packed environment. If one accepts[4,11] that H migration occurs from the singlet state of carbene, that, by analogy with the radical, a phenyl group can migrate in the triplet manifolds, and that these two arylcarbene electronic states can at least interconvert, if not come to equilibrium, the observed inversion of temperature dependency of migratory aptitude can be interpreted to indicate that cool solution favors the triplet-side reaction as a result of energetic advantage whereas the restricted mobility enforced by the solid matrix may place a premium on the triplet reaction and favor reaction from the singlet side.

One more interesting feature of the results in Figure 1 is that the stereochemistry of the 1,2-H shift ([3]/[2] ratio) is also significantly sensitive to the reaction phase. Although the plot of [3]/[2] vs. T^{-1} shows some scatter, the obvious trend is that the *Z* isomer significantly increases once a rigid matrix is formed. Moreover, similar matrix effects on the stereochemistry of the 1,2-H shift were also observed in other arylcarbene systems (Table I). The mechanism of 1,2-H shift indicated[12] to be favorable involves an electrophilic pull of gauche hydride through the vacant p orbital of the singlet carbene, starting from approximate carbene conformations c and t for formation of *E* and *Z* olefins, respectively. The ratio of *E*/*Z* olefins produced will be then determined[12a] by the relative populations of the conformers, which are affected by steric as well as electrostatic factors. If one assumes that the steric interaciton between Ph–Ph is greater than Ph–Me, one would expect that the *E* isomer (**2**) would be favored in the rigid-matrix reaction since the more stable conformer predominates at low temperature and since the matrix imposes[2a] severe steric demands on the reaction within it. One notes from Table I, however, that more *E* isomer is formed from **5** (R = Me) than from **5** (R = Ph) at ambient temperature and that increase in the *E*/*Z* ratio caused by the matrix was more significant in **5** (R = Me) than in **5** (R = Ph), indicating that steric interaction between Ph–Me is greater than for Ph–Ph. This implies that the Ph ring on the carbenic carbon may be relatively perpendicular[12f,13] to the vacant carbene orbital and hence the steric interaction with the methyl group becomes important whereas the Ph ring on the β carbon may twist from the vacant orbital so as to reduce the steric repulsion with the adjacent Ph group. In order to obtain deeper insight into the nature of this interesting matrix effect on stereochemistry, we further examined the temperature dependence of stereoselectivity in the 1,2-H shift in the photolysis of a series of diazo compounds[3,5] (Table I). Contrary to the above results, indicating that the reaction is more stereoselective toward the more stable isomer in a rigid matrix, apparently the less stable olefin comes to predominate in a rigid matrix as the R group is successively displaced with a more bulky group. The origin of the anomalous matrix effect is quite interesting. It has been suggested[14] in the photochemical 1,2 shift of alkyl azide that the *tert*-butyl group is sufficiently large to experience significant nonbonded repulsion with the lone-pair electrons on adjacent nitrogen. It may be suggested, then, that such nonbonded repulsion between a bulky R group and the carbene unshared electrons, which is not important at ambient temperature, becomes significant in a rigid matrix due to the close packing. Alternatively, it is very tempting to assume that, in a matrix environment, the nascent carbene is forcibly paired with the leaving N_2 due to the limited diffusibility and hence rapid H migration occurs before leaving N_2 has completely left the neighborhood of the carbene center. Apparently, this would reduce the population of conformer leading to *E* olefin as a result of steric repulsion between the more bulky R group and N_2. We have recently demonstrated[2c] that such effect of leaving group on the intermolecular reaction courses of carbene is dominant in a rigid matrix.



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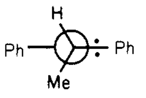

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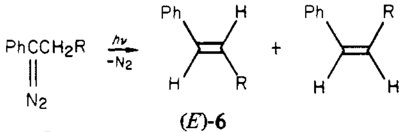

5 (*E*)-6 (2)

Expanded studies in this area are now in progress in order to probe the viability of our mechanistic hypothesis.

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(13) Recently, it has been demonstrated[12f] that stereochemistry is very sensitive to the conformation of the phenyl group in rearrangement of 1-phenyl-1-propylidenes. It has been suggested that electron-donor para substituents favor a planar conformation for singlet phenylcarbenes, whereas electron-withdrawing para substituents are presumed to enhance twisting of the phenyl group to a perpendicular conformation. MINDO/3 calculations indicate that an unsubstituted phenyl group favors a planar conformation: Miller, R. J.; Yang, L. S.; Shechter, H. *J. Am. Chem. Soc.* **1977**, *99*, 938.

(14) (a) Abramovitch, R. A.; Kyba, E. P. *J. Am. Chem. Soc.* **1971**, *93*, 1537. (b) Kyba, E. P.; Abramovitch, R. A. *Ibid.* **1980**, *102*, 735.

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Accurate and Sensitive Determination, by a New Cobalt-59 Nuclear Magnetic Resonance Method, of Electron Acceptance and Hydrogen Bond Donation by Protic Solvents

Sir:

The vast potential of ^{59}Co NMR, with a chemical shift range of over 14 000 ppm,[1] has remained almost untapped:[2-5] a large

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(1) Kidd, R. G.; Goodfellow, R. J. In "NMR and the Periodic Table"; Harris, R. K., Mann, B. E., Eds.; Academic Press: New York, 1978; pp 195–278.

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