30-3; (2*R*)-**4c**, 82110-33-6; (2*S*)-**4c**, 82110-34-7; **4d**, 82065-31-4; (2*R*)-**4d**, 82110-35-8; (2*S*)-**4d**, 82110-36-9; (2*R*,4*R*)-**5a**, 82065-32-5; (2*S*,4*S*)-**5a**, 82065-33-6; (2*R*,4*R*)-**5b**, 82065-34-7; (2*S*,4*S*)-**5b**, 82065-35-8; (2*R*,4*R*)-**5c**, 82065-36-9; (2*S*,4*S*)-**5c**, 82065-37-0; (2*R*,4*R*)-**5d**, 82065-38-1; (2*S*,4*S*)-**5d**, 82065-39-2; (2*R*,4*S*)-**6a**, 82065-40-5; (2*S*,4*R*)-**6a**, 82065-41-6; (2*R*,4*S*)-**6b**, 82065-42-7; (2*S*,4*R*)-**6b**, 82065-43-8; (2*R*,4*S*)-**6c**, 82065-44-9; (2*S*,4*R*)-**6c**, 82065-45-0; (2*R*,4*S*)-**6d**, 82065-46-1; (2*S*,4*R*)-**6d**, 82065-47-2; (−)-(2*R*,3*R*)-2,3-butanediol, 24347-58-8; (+)-(2*S*)-α-methoxy-α-(trifluoromethyl)phenylacetyl chloride, 20445-33-4.

# *Communications to the Editor*

## Observations on the Geometry of Hydrogen Transfer in [1,5] Sigmatropic Rearrangements

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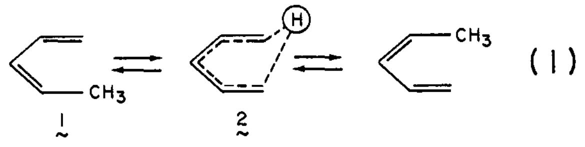
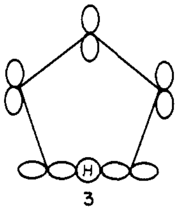
A [1,5] sigmatropic hydrogen-transfer process[1] must possess a six-membered pericyclic[2] transition state (TS$^\ddagger$) in accordance with the requirements of orbital symmetry conservation.[1] The validity of this regulation has been repeatedly confirmed[3] for retroene reactions in which either an O–H or a C–H bond has undergone suprafacial, linear hydrogen transfer to a carbon center in the pericyclic array. The criterion applied to assess the occurrence of concerted, linear H transfer was the temperature dependence of the primary H–D isotope effect.[4-11] Consistent with transition-state-derived theory,[12] a symmetrical or concerted[13] TS$^\ddagger$ will tend to exhibit an activation-energy difference between corresponding H and D bonds equal to their ground-state zero-point energy difference, i.e., $[\Delta E_a]_D^H \simeq [\Delta E_0]_D^H$, and a frequency factor ratio of no greater value than $2^{1/2}$, or, as established by model calculations,[14] $0.7 << A_H/A_D << 1.2$. Nonetheless, examples can be found in the literature where a 1,5 sigmatropic rearrangement of hydrogen has been depicted with a TS$^\ddagger$ of nonlinear H-transfer.

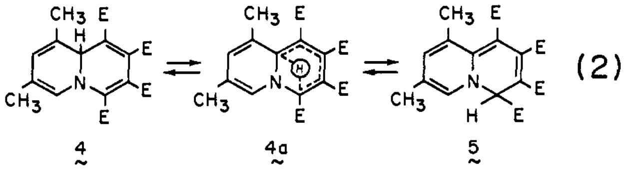


An exemplary case in point is that of the rearrangement of the pentadiene **1** shown[15] in eq 1, in which the temperature dependence of $k_H/k_D$ has been determined over a considerable temperature range, and the isotope effect parameters are reported to be $[\Delta E_a]_D^H \simeq 1.4$ kcal/mol and $A_H/A_D = 1.15$. When corrected for the α-secondary deuterium isotope effects, these values are closely coincident with expectations for a concerted, linear H-transfer mechanism. However, the authors[15] represented this pericyclic process with a bent TS$^\ddagger$ (**2**) in eq 1. Though they took note of the symmetry features of the TS$^\ddagger$ in keeping with the isotope effect results, they failed to recognize that these results also demanded a linear H-transfer TS$^\ddagger$. Apparently, the acyclic structure of conjugated double bonds in their cisoid conformation is capable of sufficient distention to permit linear H transfer, the minimum-energy configuration of this sigmatropic TS$^\ddagger$, as shown in **3**. The present investigation was undertaken with the objective of identifying a [1,5] sigmatropic rearrangement occurring in a cyclic system which is not capable of such distention of the π framework.



**3**

The case chosen for study was the rearrangement of the 9a*H*-quinolizine (**4**) to the 4*H*-quinolizine (**5**) expressed in eq 2. The temperature dependence of the isotope effect was again applied as the criterion of TS$^\ddagger$ geometry in H transfer. It has frequently been demonstrated, though not directly derivable (at present) from conventional transition-state theory of the isotope effect,[12] that a bent TS$^\ddagger$, i.e., one involving H transfer at an acute angle, can be correlated with a temperature-independent $k_H/k_D$. That is to say, the finding of isotope effect parameters of $[\Delta E_a]_D^H \simeq 0$ and $A_H/A_D >> 1.2$ has been empirically shown[17] to be most congruent with a bent TS$^\ddagger$.



Where E = –COOMe

The manner in which the isotope effect data for the reaction of eq 2 have been run, as well as the data gathered in these experiments, is presented in Table I. The determination that

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(12) Westheimer, F. H. *Chem. Rev.* **1961**, *61*, 265. See also: Bigeleisen, J.; *Pure Appl. Chem.* **1964**, *8*, 217. Melander, L. "Isotope Effects on Reaction Rates"; Ronald Press: New York, 1960.

(13) See ref 12 as well as ref 3 for discussion.

(14) Schneider, M. E.; Stern, M. J. *J. Am. Chem. Soc.* **1972**, *94*, 1517.

(15) Roth, W. R.; König, J. *Liebigs Ann. Chem.* **1966**, *699*, 24.

(16) Acheson, R. M.; Taylor, G. A. *J. Chem. Soc.* **1960**, 1691.

(17) For further discussion see ref 10 and other references cited therein.

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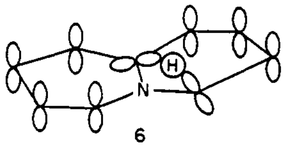
Table I. Temperature Dependence of $k_H/k_D$ in the Sigmatropic Rearrangement of 9a*H*-Quinolizine (4) to Its 4*H* Analogue (5): Eq 3

| sample designation | temp, °C | reaction, % | $m_L/m_H$ | reciprocal $m_H/m_L$ | starting $m_H/m_L$ | $k_H/k_D$ (at 100%) | $k_H/k_D$ (corr)[a,b] |
|---|---|---|---|---|---|---|---|
| 1 | 66.2 | 30.8 | 0.2082 ± 0.0002 | 4.803 ± 0.005 | | 4.942 + 0.012; cc = 0.9970 | 5.095 ± 0.012 |
| 3 | 66.2 | 54.1 | 0.2064 ± 0.0001 | 4.846 ± 0.003 | | | |
| 5 | 66.2 | 67.6 | 0.2050 ± 0.0003 | 4.879 ± 0.0072 | | | |
| 7 | 80.85 | 28.5 | 0.2054 ± 0.0002 | 4.869 ± 0.005 | | 4.967 ± 0.008; cc = 0.9904 | 5.121 ± 0.008 |
| 9 | 80.85 | 38.8 | 0.2046 ± 0.0003 | 4.887 ± 0.001 | | | |
| 11 | 80.85 | 54.9 | 0.2039 ± 0.0003 | 4.905 ± 0.006 | | | |
| 13 | 98.15 | 38.5 | 0.2063 ± 0.0002 | 4.849 ± 0.047 | | 4.920 ± 0.013; cc = 0.9980 | 5.131 ± 0.013 |
| 15 | 98.15 | 57.2 | 0.2054 ± 0.00003 | 4.869 ± 0.0006 | | | |
| 17 | 98.15 | 65.8 | 0.2049 ± 0.0002 | 4.881 ± 0.005 | | | |
| 19 | 126.6 | 73.8 | 0.2081 ± 0.0003 | 4.805 ± 0.007 | | 4.934 ± 0.012; cc = 0.9976 | 5.107 ± 0.012 |
| 21 | 126.6 | 80.8 | 0.2065 ± 0.0002 | 4.844 ± 0.004 | | | |
| 23 | 126.6 | 89.3 | 0.2049 ± 0.0002 | 4.881 ± 0.005 | | | |
| 31 | | 0.0 | 1.0429 ± 0.002 | | 0.9589 ± 0.0002 | | |
| 32 | | 0.0 | 1.0307 ± 0.0031 | | 0.9702 ± 0.0029 | | |
| 33 | | 0.0 | 1.0350 ± 0.0029 | | 0.9662 ± 0.0029 | | |

[a] The computed value of the isotope effect at each temperature is corrected for the deviation from a 50:50 mixture of the starting material proceeding to the (extrapolated) product composition. The corrected value of $k_H/k_D$ is therefore the value in column seven divided by the appropriate value in column six. [b] Mean $k_H/k_D$ = 5.113 ± 0.016.

$k_H/k_D$ is temperature independent over a ca. 65 °C range of study of this reaction and that $A_H/A_D$ has a value of 5.11 is consonant only with angular H transfer. The only plausible formulation in keeping with the structural restraints imposed by the six-membered pericyclic TS$^‡$ is represented by the orbital diagram in **6**.



**6**

Orbital Diagram

This value of $A_H/A_D$ is the largest found thus far among a variety of bent H-transfer transition states identified by means of the temperature dependence of the isotope effect criterion.[6,8-10] It suggests that a far greater probability here attends the reaction of hydrogen compared to deuterium. This can be best understood as a consequence of the higher energy bending vibration amplitudes[18] of the H and D experienced in the course of approaching the reaction TS$^‡$. When the bending vibration modes of (say) an C–H bond are far from their equilibrium configurations, they become inseparable and undergo facile energy exchanges. the circumstances of the higher energy bending vibration amplitudes of hydrogen compared to deuterium create a more efficient means by which the hydrogen pumps energy from a nonreactive mode into the reaction coordinate mode. The same situation does *not* obtain in linear H transfer because the higher frequency stretching vibrational modes are still quite separable.

The large, temperature-independent $k_H/k_D$ found here for a reaction in which H transfer can only occur at an angle of less than 180° must be regarded as experimental verification of the TDKIE criterion for a bent TS. Moreover, O'Ferrall[19] has reported detailed model calculations that show that at a constant (single) temperature, i.e., where any temperature-dependent factor in $k_H/k_D$ is inoperative, the isotope effect is a steep function of this angle. Consequently, TS theory, which is the basis of these model calculations, has been shown to support the thesis that the temperature-independent component of $k_H/k_D$, namely $A_H/A_D$, is directly relatd to the angle of H transfer in the TS. Using these calculations and results for a typical C–H bond transfer, where $A_H/A_D$ = 5.1 (in the eq 2 process), we estimate the angle to be approximately 145°.

**Acknowledgment.** We are obliged for support of this work by the National Science Foundation under Grant CHE 7911110.

**Registry No.** 4, 983-36-8; 5, 1055-24-9.

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## Effects of 15-Crown-5 on Reactions of Dialkylmagnesium Compounds[†,1]

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Although the electron-deficient structure R–Mg–X (where X = R, halogen, etc.) is commonly written for organomagnesium compounds, magnesium is usually bonded to four or more groups.[2] The extra bonds at a magnesium that reduce its electron deficiency are ordinarily to donor atoms (usually O or N) of solvent molecules or to bridging groups (R or X) that are bonded to another magnesium. As part of an effort to develop a greater understanding of the effects of the extent and nature of this additional bonding on the reactions of organomagnesium compounds, we have discovered that 15-crown-5 significantly affects some reactions of dialkylmagnesium compounds.[3]

As shown by the data in Table I, addition of 15-crown-5 accelerated metalation of fluorene (FlH, eq 1) by a tetrahydrofuran

$$Et_2Mg + FlH \rightarrow Fl^- \, {}^+MgEt + EtH \qquad (1)$$

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[†] Dedicated to Professor W. von E. Doering on the occasion of his 65th birthday.

(1) This work is taken from: King, B. A. Ph.D. Dissertation, The Pennsylvania State University, University Park, PA, 1981.

(2) In a few instances, there is evidence for bonding to only three groups: Pinkus, A. G. *Coord. Chem. Rev.* **1978**, *25*, 173.

(3) We know of only two prior references to effects of crown ethers upon organomagnesium compounds:[4] Bogatskii, A. V.; Chumachenko, T. K.; Luk'yanenko, N. G.; Lyamtseva, L. N.; Starovoit, I. A. *Dokl. Chem.* (*Engl. Transl.*) **1980**, *252*, 105; *Dokl. Akad. Nauk SSSR, Ser. Khim.* **1980**, *252*, 113.

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