Scheme III
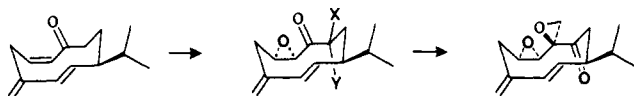

and have been converted separately to the *trans*-butadiene 7, a more convenient procedure avoided the chromatography. The two ring fusion stereocenters are returned to achiral, trigonal centers in the reaction sequence; thus both photoadducts converge on the same end product. Consequently, on large runs the 2:1 mixture of **3a** and **3b** was employed, allowing for greater material throughput. Stereospecific addition of vinylmagnesium bromide to the convex face of **3a** and **3b** provided the expected 2:1 mixture of allylic carbinols **4**.[10] Anion-accelerated oxy-Cope rearrangement[12] proceeded smoothly to provide the 2:1 mixture of cyclobutene bridgehead olefins **5** in 75% yield, despite the poor overlap of the 1,5-diene system present in **4** as judged by inspection of molecular models.[13] Electrocyclic ring opening provided a 2:1 mixture of cis- and trans-diene isomers (**5a** → 3:1 (**6:7**), **5b** → 2:3 (**6:7**)),[10] which could be separated by flash chromatography.[14] Photoisomerization of cis-diene **6** or trans-diene **7** in benzene established a photostationary equilibrium consisting of a 15:1 mixture enriched in the trans isomer.[10] Chromatography of thermolysis mixture was not required; the mixture could be directly photoisomerized to provide **7** in 70–75% isolated yield.

We have observed a high degree of regio- and stereoselectivity in the formation and trapping of 10-membered ring ketone enolates; one of these reactions provided the basis for the successful completion of the periplanone-B synthesis (Scheme II).[15] Lithium hexamethyldisilazide promoted enolization of **7** at −78 °C for 60 min and sulfenylation with Trost's reagent[16] provided a 16:1 regioisomeric mixture of monosulfenylated ketones (each as a single stereoisomer). The major C_2 (periplanone-B numbering) sulfide **8** was not separated from its minor regioisomer, since pyrolysis of the corresponding sulfoxides exhibited a substantial difference in rate, affording the readily separable cis enone and the more polar unreacted minor C_{10} sulfoxide.

At this stage, completion of the synthesis required incorporation of the two remaining epoxides and the C_{10} ketone. The Still synthesis of periplanone-B provided the expectation that stereochemically controlled bisepoxidation of the enone could be achieved (Scheme III).[3] Support for this premise was forthcoming.

Stereoselective epoxidation of **9** provided a 4:1 mixture of cis epoxides in which the major component was the desired isomer **10**.[3] Introduction of the C_{10} keto functionality began with the regio- and stereospecific selenenylation of epoxy ketone **10** to provide the selenide **11**. Oxidation afforded the corresponding selenoxides which could be isolated without complications resulting from selenoxide elimination. Selena–Pummerer rearrangement[17] and saponification afforded the α-diketone **12**. Monoepoxidation with dimethylsulfonium methylide provided, as the major product, (±)-periplanone-B, which exhibited spectral properties (UV, MS, IR, ^{13}C NMR, ^1H NMR) in accord with the structure. Comparison with the 300-MHz ^1H NMR spectrum of the natural material[2c] indicated these substances were the same. Furthermore, bioassay of the synthetic material, according to the reported method,[4] provided the response expected for the sex pheromone.

(12) Evans, D. A.; Golob, A. M. *J. Am. Chem. Soc.* 1975, *97*, 4765.
(13) The anion-accelerating property of the oxido substituent[12] was critical to the success of this reaction as thermal 3-hydroxy or 3-siloxy Cope rearrangements in this series were unsuccessful, affording elimination products at 200 °C.
(14) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* 1978, *43*, 2923.
(15) For related observations, see: Still, W. C.; Galynker, I. *Tetrahedron* 1981, *37*, 3981. Kuroda, C.; Hirota, H.; Takahashi, T. *Chem. Lett.* 1982, 249. Still, W. C.; Novack, V. J. *J. Am. Chem. Soc.* 1984, *106*, 1148.
(16) Trost, B. M.; Salzmann, T. N.; Hiroi, K. *J. Am. Chem. Soc.* 1976, *98*, 4887.
(17) Marshall, J. A.; Royce, R. D. *J. Org. Chem.* 1982, *47*, 693.

Tunneling in the Automerization of Cyclobutadiene

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Carpenter[1] recently has communicated the possiblity that tunneling is the major pathway for the automerization (1) of

$$(1)$$
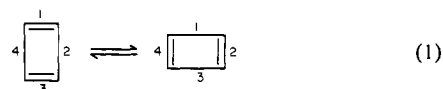
cyclobutadiene below 0 °C. He emphasized that the narrowness of the barrier makes this bond-shifting reaction "especially susceptible to tunneling" although heavy (carbon) atoms are involved. Carpenter carried out a one-dimensional tunneling calculation based on a vibrational frequency of cyclobutadiene multiplied by the transmission coefficient (TC) expression of Bell[2] for a barrier that is an inverted truncated parabola. The purpose here is to point out that such tunneling rates are much lower than those obtained by considering one-dimensional tunneling in a symmetric double-minimum potential in terms of the energy splittings (ES) ΔE_i characteristic of the levels of such a potential; $\Delta E_i = E_{i^-} - E_{i^+}$ where + and − refer to symmetries of the wave functions, 0^+ is the ground state, $E_{i\pm} < E_{(i+1)\pm}$ and $\Delta E_i < \Delta E_{i+1}$. For a one-dimensional symmetric potential, the ES method is the correct one for calculating tunneling rates. The finding that the TC method underestimates the tunneling rates confirms earlier calculations[3] and has been rationalized in terms of quantum mechanical resonance between the levels in the two symmetric wells, ignored in the TC method.

Carpenter modeled the reaction coordinate as a single stretching motion; in his model an inverted parabolic potential energy barrier separates the diatomic molecule (26–26) configuration with internuclear separation corresponding to the minimum energy of the C=C bond from the configuration with internuclear separation corresponding to the C—C bond. The potential and correspondingly the transmission coefficients are completely determined by the height of the potential barrier and the difference between the lengths of the single and the double bonds, chosen by Carpenter as 10.8 kcal/mol and 0.198 Å, respectively. Carpenter assumed a harmonic oscillator frequency of 1000 cm^{-1} along the reaction coordinate in the initial configuration, a Boltzmann distribution of pseudo-diatomic molecules among states corresponding to this frequency, and a tunneling rate from each of these states equal to the frequency times the transmission coefficient. Rates obtained at −50 and −10 °C were 8.08×10^4 and 4.65×10^5 s^{-1}, respectively.

The ES calculations here were carried out with a symmetric double-minimum potential, $V(R) = AR^2 + Be^{-CR^2}$, where A, B, and C are parameters, and $R = r_1 + r_3 - r_2 - r_4$, with r_i the ith carbon–carbon distance as indicated in (1). The parameters A,

(1) Carpenter, B. K. *J. Am. Chem. Soc.* 1983, *105*, 1701.
(2) Bell, R. P. "The Proton in Chemistry", 2nd ed.; Cornell University Press: Ithaca, NY, 1973.
(3) See, for instance: (a) Brickmann, J.; Zimmermann, H. *J. Chem. Phys.* 1969, *50*, 1608. (b) Harmony, M. D. *Chem. Soc. Rev.* 1972, *1*, 1211. (c) Limbach, H. H.; Hennig, J. *J. Chem. Phys.* 1979, *71*, 3120.

B, and C can be varied to fit preset values of the barrier height b, the distance between the two minima ΔR, and the curvature at each minimum [or, alternatively, the energy difference between 0 (the average of 0^+ and 0^-) and 1]. R equals 0 for the square configuration of the top of the potential barrier, and ΔR equals 4 times the difference between C—C and C=C.

The cyclobutadiene molecule here is a four-atom system with each carbon atom assigned a mass of 13 daltons. Tunneling is taken as one dimensional corresponding to concerted stretching of bonds 1 and 3 in (1) and an equivalent shortening of bonds 2 and 4 (or vice versa) with the above potential energy. The E_i and ΔE_i values were obtained numerically.[4]

A number of parameter sets were employed for b and ΔR: α[5] – 8.58 kcal/mol, 0.18 Å; β[6] – 12.0 kcal/mol, 0.23 Å; γ[7] – 14.0 kcal/mol, 0.25 Å, δ[8] – 10.8 kcal/mol, 0.198 Å. While no normal coordinate analysis has been carried out here, probably none of the normal modes of cyclobutadiene corresponds quite to the motion of the reaction coordinate. One cannot deduce the appropriate curvature at the minima in the potential directly from the vibrational spectrum of cyclobutadiene. Thus, the curvature at the minima has been varied here to give in various calculations energies for the 0 → 1 transition varying between 800 and 1900 cm^{-1}. Variations corresponding to such a range changed the rates (vide infra) at −10 °C by less than a factor of 3.

Tunneling rates were calculated for each doublet of levels from the ΔE_i values by the formula[9] $k_i = 2\Delta E_i/h$ (i = 0, 1, ...), and the effective tunneling rate is obtained by appropriate Boltzmann averaging.[10] Most of the effective tunneling rate arises from the 0 state, with small contribution from 1 and negligible contributions from higher states. As expected, the highest rates are obtained for α calculations, where ΔE_0 is typically ~ 2 cm^{-1}, and a rate of $\sim 2 \times 10^{11}$ s^{-1} is typically obtained at −10 °C. The lowest rates are given by the γ calculations with $\Delta E_0 \sim 0.009$ cm^{-1} and a rate $\sim 5 \times 10^8$ s^{-1} at −10 °C. β and δ calculations lead to rates of $\sim 3 \times 10^9$ and $\sim 3 \times 10^{10}$ s^{-1}, respectively.

The temperature dependence of the effective tunneling rates is very small, so that between −50 and −10 °C the enthalpy of activation is found to be slightly negative for the various parameter sets, −0.3 to −0.5 kcal/mol. Corresponding entropies of activation are quite negative varying from −8 to −20 kcal/(deg mol). A relatively large negative ΔS^* value agrees with Carpenter's calculation and also appears to be implied by Whitman and Carpenter's[11] measurements.

The one-dimensional tunneling rates for symmetric potentials here are considerably larger than values evaluated by Carpenter by the TC approximation. On the other hand, it is expected from experience in the NH_3 system[12] that more realistic multidimensional models will tend to yield lower rates. If the double-minimum problem were unsymmetric tunneling rates would decrease.[3a] Possibly such lack of symmetry must be considered for cyclobutadiene in solution. Finally one should note that Whitman and Carpenter's[11] experiment with respect to reaction 1 involved vicinally dideuterated cyclobutadiene. In a one-dimensional calculation, the extra mass does not change the conclusions presented

(ΔS^* tends to decrease by ~ 0.5 cal/(deg mol)). In a multidimensional calculation, conceivably the effect of lack of symmetry caused by isotopic substitution might be nonnegligible.

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Tunneling Dynamics of Cyclobutadiene

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It is now generally accepted that cyclobutadiene (1) has a rectangular singlet ground state, the square structure (2) being the transition state (TS) for automerization of 1 (i.e., 1 to 2). Estimates[1–6] of the barrier height range from 8 to 15 kcal/mol, implying that is should be possible to freeze out a single isomer at low temperatures.

Recently, however, Carpenter[7] has proposed on the basis of a rather simplistic model that the automerization may take place predominantly by tunneling, a rather striking suggestion because it has always been assumed that heavy-atom tunneling can be neglected. Here, however, the distance (<0.2 Å) the carbon atoms move during the reaction is comparable with the de Broglie wavelength[14] of carbon, suggesting that tunneling may in fact play the role Carpenter suggests. To test this, we have now carried out detailed calculations for the automerization of 1 and its tetradeuterio (3) and tetra ^{13}C (4) derivatives, and also for the
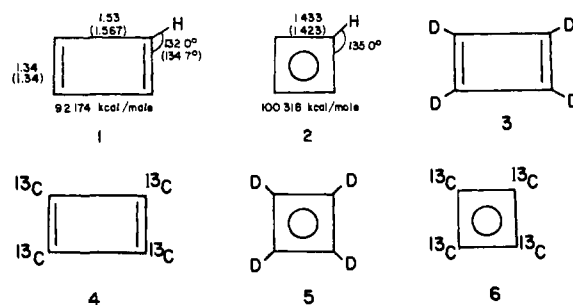
(square) TS, 2, 5, and 6, for their automerizations. The calculations were carried out using the "half-electron" version (MINDO/3/HE) of MINDO/3 with 3 × 3 CI because the square

(4) The method used here is a one-dimensional version of that used for NH_3 (Bopp, P.; McLaughlin, D. R.; Wolfsberg, M. *Z. Naturforsch., A.* **1982**, *37A*, 398) with the D_{4h} configuration at the top of the potential barrier as the reference configuration and with the normal coordinate of the reference configuration equal to a constant times R here.
(5) Parameter set based on various literature values[1] to yield high tunneling rate.
(6) Jafri, J. A.; Newton, M. D. *J. Am. Chem. Soc.* **1978**, *100*, 5012.
(7) Kollmar, H.; Staemmler, V. *J. Am. Chem. Soc.* **1977**, *99*, 3583.
(8) Set used in ref 1.
(9) Eyring, H.; Walter, J.; Kimball, G. E. "Quantum Chemistry"; Wiley: New York, 1954.
(10) ΔE_i values are calculated only for those levels lying below the top of the barrier. While Harmony[3b] has indicated how to include the classical rate (over the top of the barrier) in the total rate constant, this process is unnecessary here because this classical rate is negligible on account of the adverse Boltzmann factor.
(11) Whitman, D. W.; Carpenter, B. K. *J. Am. Chem. Soc.* **1982**, *104*, 6473.
(12) Bopp, P.; McLaughlin, D. R.; Wolfsberg, M. *Z. Naturforsch., A* **1982**, *37A*, 398.

(1) Dewar, M. J. S.; Komornicki, A. *J. Am. Chem. Soc.* **1977**, *99*, 6174.
(2) Schaad, L. J.; Hess, B. A., Jr. *J. Am. Chem. Soc.* **1979**, *101*, 2281.
(3) Kollmar, H.; Staemmler, V. *J. Am. Chem. Soc.* **1977**, *99*, 3583.
(4) Borden, W. T.; Davidson, E. R.; Hart, P. *J. Am. Chem. Soc.* **1978**, *100*, 388.
(5) Kollmar, H.; Staemmler, V. *J. Am. Chem. Soc.* **1978**, *100*, 4304.
(6) Jafri, J. A.; Newton, M. D. *J. Am. Chem. Soc.* **1978**, *100*, 5012.
(7) Carpenter, B. K. *J. Am. Chem. Soc.* **1983**, *105*, 1700.
(8) Dewar, M. J. S.; Ford, G. P. *J. Am. Chem. Soc.* **1977**, *99*, 1685.
(9) Masamune, S.; Souto Bachiller, F. A.; Machiguchi, T.; Bertie, J. E. *J. Am. Chem. Soc.* **1978**, *100*, 4889.
(10) (a) Schaad, L. J.; Hess, B. A., Jr. *J. Org. Chem.* **1982**, *47*, 2904. (b) Hess, B. A., Jr.; Carsky, P.; Schaad, L. J. *J. Am. Chem. Soc.* **1983**, *105*, 695.
(11) The parameters for MINDO/3 and MNDO are chosen to fit the calculated total energies to observed heats of formation. The calculated "total energies" therefore contain implicit corrections for thermal contributions.
(12) Bicerano, J.; Schaefer, H. F., III; Miller W. H. *J. Am. Chem. Soc.* **1983**, *105*, 2550.
(13) Miller, W. H. *J. Chem. Phys.* **1979**, *83*, 960 and references cited therin.
(14) Bell, R. P. "The Tunnel Effect in Chemistry"; Chapman and Hall: London, 1980.