

minimize the geometries. Table III contains some information on the energy-minimized $H_4N_2^+$ geometries obtained in this work. Complete information on the calculated energies, geometries, and spin densities is available by writing the authors.

Acknowledgment. We thank the National Science Foundation and the National Institutes of Health for partial financial support of this work under grants CHE-8026111 and GM 29549, re-

spectively, and the NSF for a Fellowship to J.E.C. We thank Dan Kapp for assistance in construction of the flow electrochemical cell.

Registry No. 1, 62781-95-7; 2, 82666-13-5; 3, 86711-99-1; 4, 90046-51-8; 5, 93601-00-4; 6, 60512-67-6; 7, 93473-65-5; 8, 34504-32-0; 9, 93473-66-6; 10, 93473-67-7; 11, 93473-68-8; 12, 93473-69-9; 13, 42843-04-9; 14, 93601-01-5; 15, 93473-70-2; $H_4N_2^+$, 34504-42-2.

Theoretical Studies of [1,*n*]-Sigmatropic Rearrangements Involving Hydrogen Transfer in Simple Methyl-Substituted Conjugated Polyenes

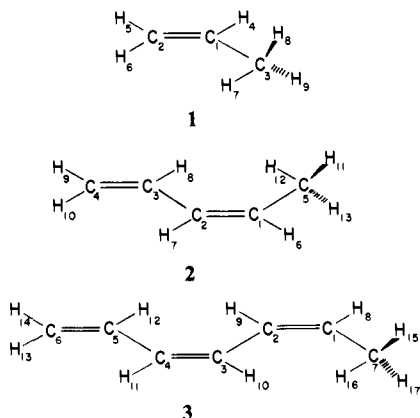
B. Andes Hess, Jr.,* L. J. Schaad,* and J. Pancir†

Contribution from the Department of Chemistry, Vanderbilt University, Nashville, Tennessee 37235. Received April 3, 1984

Abstract: Transition structures for the [1,*n*]-sigmatropic hydrogen shift in 1-propene (*n* = 3), (*Z*)-1,3-pentadiene (*n* = 5), and (3*Z*,5*Z*)-1,3,5-heptatriene (*n* = 7) have been studied by using ab initio SCF and correlated wave functions with several basis sets from STO-2G to 6-31G*. Antarafacial transition structures were found for propene and heptatriene and suprafacial for pentadiene, as predicted by the Woodward-Hoffmann rules. Activation energies were also obtained and were found to decrease significantly from the [1,3]- to the [1,5]- to the [1,7]-hydrogen shift in agreement with earlier experimental results. The deuterium isotope effect for the [1,5] shift has been computed ab initio and found in poor agreement with experiment.

Sigmatropic rearrangements that involve hydrogen transfer have been of considerable theoretical¹⁻⁵ and experimental⁶ interest since the stereochemistry of their transition structures was predicted by Woodward and Hoffmann.⁷ They stated that the [1,3]-, [1,7]-, ... hydrogen migrations would have transition structures corresponding to an antarafacial hydrogen migration while the [1,5]-, [1,9]-, ... hydrogen migration would have transition structures with suprafacial stereochemistry. Quite recently Dewar has questioned the synchronous nature of many concerted reactions.⁸ However, he noted that [1,*n*]-sigmatropic rearrangements that involve hydrogen transfer are likely to be an exception to his rule that "synchronous multibond mechanisms are normally prohibited" and therefore are likely to have symmetric transition structures.

We have undertaken a systematic theoretical study of the [1,3]-, [1,5]-,⁹ and [1,7]-sigmatropic hydrogen-transfer rearrangements in the corresponding methyl-conjugated linear polyenes (1-3). Both transition structures and activation energies have been examined.



Results

All computations were done on Vanderbilt University's DEC-10 and DEC-20 computers with use of Pople's GAUSSIAN 80 program¹⁰

*Permanent address: J. Heyrovský Institute of Physical and Electrochemistry, Czechoslovak Academy of Sciences, Prague.

Table I. Optimized Geometry of Propene (1)^{a,b}

| coordinate | 3-21G | 6-31G | 6-31G* |
|--|-------|-------|--------|
| C ₁ -C ₂ | 1.316 | 1.324 | 1.318 |
| C ₁ -C ₃ | 1.510 | 1.502 | 1.503 |
| C ₁ -H ₄ | 1.076 | 1.074 | 1.079 |
| C ₂ -H ₅ | 1.073 | 1.074 | 1.076 |
| C ₂ -H ₆ | 1.075 | 1.075 | 1.077 |
| C ₃ -H ₇ | 1.083 | 1.083 | 1.084 |
| C ₃ -H ₈ | 1.086 | 1.086 | 1.087 |
| C ₃ -H ₉ | 1.086 | 1.086 | 1.087 |
| ∠C ₂ C ₁ C ₃ | 124.7 | 125.1 | 125.1 |
| ∠C ₁ C ₂ H ₅ | 121.9 | 121.8 | 121.6 |
| ∠C ₁ C ₂ H ₆ | 121.8 | 121.9 | 121.9 |
| ∠C ₂ C ₁ H ₄ | 119.6 | 119.1 | 118.9 |
| ∠C ₁ C ₃ H ₇ | 111.1 | 111.4 | 111.4 |
| ∠C ₁ C ₃ H ₈ | 110.6 | 111.0 | 110.9 |
| ∠C ₁ C ₃ H ₉ | 110.6 | 111.0 | 110.9 |
| ∠C ₂ C ₁ C ₃ H ₇ | 180.0 | 180.0 | 180.0 |
| ∠C ₂ C ₁ C ₃ H ₈ | 120.5 | 120.5 | 120.6 |
| ∠C ₂ C ₁ C ₃ H ₉ | 120.5 | 120.5 | 120.6 |

^aBond distances in angstroms and angles in degrees. ^bC_s symmetry assumed.

for the SCF runs and an MP2 program¹¹ written to take advantage of molecular symmetry for the correlation energy calculations.

- (1) Bingham, R. C.; Dewar, M. J. S. *J. Am. Chem. Soc.* **1972**, *94*, 9107.
- (2) Castenmiller, W. A. M.; Buck, H. M. *Tetrahedron* **1979**, *35*, 397.
- (3) Bouma, W. J.; Vincent, M. A.; Radom, L. *Int. J. Quantum Chem.* **1978**, *14*, 767.
- (4) Rodwell, W. R.; Bouma, W. J.; Radom, L. *Int. J. Quantum Chem.* **1980**, *18*, 107.
- (5) Bernardi, F.; Robb, M. A.; Schlegel, H. B.; Tonachini, G. *J. Am. Chem. Soc.* **1984**, *106*, 1198.
- (6) Reviews of experimental results: (a) Gajewski, J. J. In "Mechanisms of Molecular Rearrangements"; Thyagarajan, B. S., Ed.; Wiley-Interscience: New York, 1971; Vol. 4, pp 1-53. (b) Gajewski, J. J. "Hydrocarbon Thermal Isomerizations"; Academic Press: New York, 1981. (c) Spangler, C. W. *Chem. Rev.* **1976**, *76*, 187. (d) Gilchrist, T. L.; Storr, R. C. "Organic Reactions and Orbital Symmetry"; Cambridge University Press: London, 1972. (e) Gill, G. B. *Q. Rev. Chem. Soc.* **1968**, *22*, 338.
- (7) Woodward, R. B.; Hoffmann, R. "The Conservation of Orbital Symmetry"; Academic Press: New York, 1970.
- (8) Dewar, M. J. S. *J. Am. Chem. Soc.* **1984**, *106*, 209.

Table II. Optimized Geometries of the Three Transition Structures Considered [4(C_2), 5(C_s), 6(C_{2v})] for the 1,3-Hydrogen Shift of Propene^a

| coordinate | 4 | | | 5 | | | 6 | | |
|--|-------|-------|--------|-------|-------|--------|-------|-------|--------|
| | 3-21G | 6-31G | 6-31G* | 3-21G | 6-31G | 6-31G* | 3-21G | 6-31G | 6-31G* |
| C ₁ -C ₂ | 1.404 | 1.405 | 1.401 | 1.410 | 1.410 | 1.402 | 1.461 | 1.455 | 1.436 |
| C ₁ -H ₄ | 1.075 | 1.077 | 1.079 | 1.076 | 1.075 | 1.078 | 1.051 | 1.053 | 1.057 |
| C ₁ -H ₇ | 1.854 | 1.838 | 1.812 | 1.248 | 1.244 | 1.219 | 2.060 | 2.055 | 2.036 |
| C ₂ -H ₅ | 1.078 | 1.077 | 1.076 | 1.071 | 1.072 | 1.074 | 1.090 | 1.091 | 1.097 |
| C ₂ -H ₆ | 1.080 | 1.081 | 1.085 | 1.068 | 1.068 | 1.071 | 1.090 | 1.091 | 1.097 |
| C ₂ -H ₇ | 1.538 | 1.530 | 1.503 | 1.673 | 1.645 | 1.612 | 1.356 | 1.339 | 1.299 |
| ∠C ₂ C ₁ C ₃ | 108.5 | 108.7 | 108.0 | 127.2 | 127.3 | 127.2 | 82.0 | 81.0 | 78.6 |
| ∠H ₄ C ₁ C ₂ | 125.8 | 125.7 | 126.0 | 116.2 | 115.8 | 116.1 | 139.0 | 139.5 | 140.7 |
| ∠C ₁ C ₂ H ₅ | 115.9 | 116.9 | 116.4 | 120.5 | 121.0 | 120.9 | 122.5 | 122.8 | 123.4 |
| ∠C ₁ C ₂ H ₆ | 122.3 | 122.4 | 122.4 | 119.9 | 119.9 | 119.8 | 122.5 | 122.8 | 123.4 |
| ∠H ₄ C ₁ H ₇ | 180.0 | 180.0 | 180.0 | 111.3 | 112.8 | 112.5 | 180.0 | 180.0 | 180.0 |
| ∠H ₄ C ₁ C ₂ H ₅ | 110.8 | 111.6 | 110.8 | 174.8 | 178.2 | 174.8 | 81.1 | 80.6 | 80.5 |
| ∠H ₄ C ₁ C ₂ H ₆ | 33.3 | 33.9 | 33.8 | 0.2 | 2.9 | 1.2 | 81.1 | 80.6 | 80.5 |

^a Bond distances in angstroms and angles in degrees.**Table III.** Calculated Total Energies (hartrees) of 1-Propene (1) and the Transition Structures Considered for the 1,3-Sigmatropic Hydrogen Migration

| method | propene | transition structure | | |
|-------------------------|------------|----------------------|------------|---------------|
| | | 4(C_2) | 5(C_s) | 6(C_{2v}) |
| 3-21G | -116.42401 | -116.25249 | -116.23414 | -116.17627 |
| 6-31G | -117.02828 | -116.85758 | -116.84238 | -116.78235 |
| 6-31G* | -117.07147 | -116.90259 | -116.89478 | -116.84336 |
| 6-31G*/MP2 ^a | -117.46893 | -117.32481 | -117.32080 | -117.25012 |

^a Computed at the optimized 6-31G* geometry.

The basis sets used were those stored internally in GAUSSIAN 80.

The transition structures studied possess different symmetry elements than do the reactants. This makes them particularly easy to locate by allowing GAUSSIAN 80 to vary the geometry to minimize the energy within the given symmetry constraints. This can be done even for the transition structures of C_s symmetry since the single reflection plane here is different than that of C_2 reactants.

The GAUSSIAN 80 program minimizes molecular energy by searching for a zero energy gradient, and first derivatives with respect to the geometrical parameters are computed in each SCF calculation. The force constant matrix can be obtained by numerical difference of the gradients gotten from further SCF calculations with the geometrical parameters varied from their equilibrium values. Except where noted the force constant matrix for each transition structure below was computed, diagonalized, and found to have exactly one negative eigenvalue as required.

The structure of propene was optimized¹⁰ with Pople's 3-21G, 6-31G, and 6-31G* basis sets, and the optimized geometries are given in Table I. A second conformation of propene in which H₈ and H₄ are eclipsed rather than H₇ and C₂ as in **1** was computed to be 1.8 kcal/mol higher in energy than **1** in the 3-21G basis. For pentadiene and hexatriene only the conformations analogous to that of **1** were examined. Possible transition structures of three different symmetries (4-6) for the [1,3]-sigmatropic hydrogen transfer in 1-propene were studied. Structure **4** corresponds to the "allowed" antarafacial, and **5** to the "forbidden" suprafacial, transition structure. Optimized geometries with the same three basis sets used for 1-propene are given in Table II for structures of C_2 (**4**), C_s (**5**), and C_{2v} (**6**) symmetry. In each case the structure was optimized by minimization of the energy with the corresponding symmetry held fixed. Energies for propene (**1**) and transition structures **4-6** are summarized in Table

(9) A preliminary communication on the [1,5]-sigmatropic hydrogen transfer has appeared: Hess, B. A., Jr.; Schaad, L. J. *J. Am. Chem. Soc.* **1983**, *105*, 7185.

(10) Binkley, J. S.; Whiteside, R. A.; Krishnan, R.; Seeger, R.; DeFrees, D. J.; Schlegel, J. B.; Topiol, S.; Kahn, L. R.; Pople, J. A., GAUSSIAN 80, Quantum Chemistry Program Exchange, Indiana University, Bloomington, IN. We thank Professor John Yates, University of Pittsburgh, for a DEC version of this program.

(11) Čársky, P.; Hess, B. A., Jr.; Schaad, L. J. *J. Comp. Chem.* **1984**, *5*, 280. This program has been submitted to the Indiana University Quantum Chemistry Program Exchange, No. 482.

Table IV. Optimized Geometry (3-21G) of (Z)-1,3-Pentadiene (**2**)^{a,b}

| bond | distance | angle | value |
|---------------------------------|----------|--|-------|
| C ₁ -C ₂ | 1.324 | C ₁ C ₂ C ₃ | 126.9 |
| C ₁ -C ₅ | 1.509 | C ₂ C ₃ C ₄ | 123.3 |
| C ₂ -C ₃ | 1.467 | C ₂ C ₁ C ₅ | 127.6 |
| C ₃ -C ₄ | 1.321 | C ₂ C ₁ H ₆ | 117.8 |
| C ₁ -H ₆ | 1.076 | C ₃ C ₂ H ₇ | 114.9 |
| C ₂ -H ₇ | 1.076 | C ₄ C ₃ H ₈ | 119.2 |
| C ₃ -H ₈ | 1.073 | C ₃ C ₄ H ₉ | 121.8 |
| C ₄ -H ₉ | 1.073 | C ₃ C ₄ H ₁₀ | 121.8 |
| C ₄ -H ₁₀ | 1.075 | C ₁ C ₅ H ₁₁ | 110.2 |
| C ₅ -H ₁₁ | 1.086 | C ₁ C ₅ H ₁₂ | 112.8 |
| C ₅ -H ₁₂ | 1.081 | C ₁ C ₅ H ₁₃ | 110.2 |
| C ₅ -H ₁₃ | 1.086 | C ₂ C ₁ C ₅ H ₁₄ | 120.8 |
| | | C ₂ C ₁ C ₅ H ₁₂ | 180.0 |
| | | C ₂ C ₁ C ₅ H ₁₃ | 120.8 |

^a Bond distances in angstroms and angles in degrees. ^b C_s symmetry assumed.**Table V.** Optimized Geometry (3-21G) of the Transition structures (**7**) Considered in the 1,5-Hydrogen Shift of (Z)-1,3-Pentadiene (**2**)^a

| coordinate | C_s | C_{2v} |
|---|-------|----------|
| C ₁ -C ₃ | 1.385 | 1.375 |
| C ₃ -C ₅ | 1.405 | 1.479 |
| C ₁ -H ₂ | 1.073 | 1.074 |
| C ₃ -H ₇ | 1.076 | 1.070 |
| C ₅ -H ₉ | 1.078 | 1.087 |
| C ₅ -H ₁₀ | 1.076 | 1.087 |
| C ₅ -H ₁₃ | 1.448 | 1.265 |
| ∠C ₃ C ₁ C ₄ | 120.4 | 124.0 |
| ∠C ₃ C ₃ C ₁ | 123.2 | 118.5 |
| ∠C ₃ C ₁ H ₂ | 118.3 | 118.0 |
| ∠C ₁ C ₃ H ₇ | 116.5 | 124.3 |
| ∠C ₃ C ₃ H ₇ | 118.6 | 117.2 |
| ∠C ₃ C ₃ H ₁₃ | 98.1 | 103.5 |
| ∠C ₄ H ₁₃ C ₆ | 129.9 | 151.9 |
| ∠C ₃ C ₃ H ₉ | 116.8 | 119.9 |
| ∠C ₃ C ₃ H ₁₀ | 118.8 | 119.9 |
| ∠C ₁ C ₃ C ₅ H ₉ | 7.1 | 107.7 |
| ∠C ₁ C ₃ C ₅ H ₁₀ | 132.6 | 107.7 |

^a Bond distances in angstroms and angles in degrees.

III. Included in this table are single-point 6-31G*/MP2¹¹ energies obtained at the optimized 6-31G* geometry.

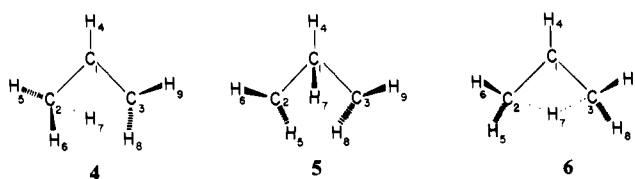


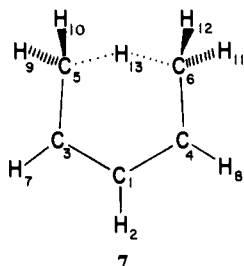
Table IV shows the optimized geometry found for (Z)-1,3-pentadiene (**2**) with the 3-21G basis set. In the case of the [1,5]-sigmatropic hydrogen transfer in **2**, transition structures **7**

Table VI. Calculated Total Energies (hartrees) of (Z)-1,3-Pentadiene and the Two Transition Structures (7) Considered

| method | (Z)-1,3-pentadiene | transition structures | |
|---------------------|--------------------|-----------------------|------------|
| | | C_s | C_{2v} |
| 3-21G | -192.87980 | -192.79253 | -192.68465 |
| 6-31G* ^a | -193.95625 | -193.86273 | -193.75908 |

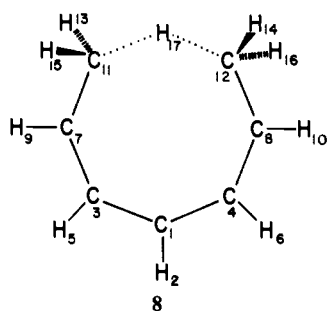
^a Computed at the optimized 3-21G geometry.

of two different symmetries (C_s and C_{2v}) were optimized with the 3-21G basis (Table V). In the transition structure with C_{2v}



symmetry all atoms in 7 lie in the plane of the page except for H₉, H₁₀, H₁₁, and H₁₂. The two local planes formed by H₉, C₅, and H₁₀ and H₁₁, C₆, and H₁₂ are perpendicular to the plane of the other atoms. The transition structure with C_s symmetry has a mirror plane that passes through atoms H₂, C₁, and H₁₃ (see Discussion). The 3-21G energies for the diene 2 and the transition structures 7 as well as those for single-point calculations (6-31G*) at the optimized 3-21G geometries are in Table VI. In addition a search (3-21G) was made for the "forbidden" antarafacial transition structure. Several starting point geometries were chosen with C_2 symmetry, but in all cases geometry optimization of these led to the collapse of the structure to that of 7 with C_{2v} symmetry, and this C_{2v} structure in turn can decrease monotonically in energy to the suprafacial C_s transition state.

The triene required for the [1,7]-sigmatropic hydrogen migration is (3Z,5Z)-1,3,5-heptatriene (3). Its geometry was fully optimized (C_s symmetry assumed) with the 3-21G basis and is given in Table VII. A single transition structure 8 of C_2 symmetry was considered for the hydrogen migration, and its geometry was optimized with both the STO-3G and 3-21G basis sets (Table VIII). The optimum energy of the triene 3 is -269.33598 hartrees (3-21G) and that of 8 is -267.46316 (STO 3G) and -269.26562 hartrees (3-21G).



Discussion

1,3-Hydrogen Shift in 1-Propene. Radom has published extensive computations on the 1,3-hydrogen shift in 1-propene.^{3,4} By performing geometry optimizations with the 4-31G basis for 4 and 5 he located two transition structures on the potential surface, one of C_2 symmetry (4) and the other of C_s symmetry (5). Our results with the 6-31G* basis show very little effect of the increase in basis size on the geometries. His finding that the transition structure that corresponds to an antarafacial rearrangement (C_2) is only slightly lower in energy than that for a suprafacial rearrangement is confirmed in the 6-31G* basis (Table IX). In a single-point calculation the inclusion of correlation by MP2 (6-31G*/MP2) lowers the energies for formation of 4 and 5 to about the same degree, in agreement with Radom's CEPA

Table VII. Optimized Geometry (3-21G) of (3Z,5Z)-1,3,5-Heptatriene (3)^{a,b}

| bond | distance | angle | value |
|---------------------------------|----------|--|-------|
| C ₁ -C ₂ | 1.326 | C ₁ C ₂ C ₃ | 125.9 |
| C ₁ -C ₇ | 1.510 | C ₂ C ₁ C ₇ | 127.9 |
| C ₂ -C ₃ | 1.463 | C ₂ C ₃ C ₄ | 126.2 |
| C ₃ -C ₄ | 1.329 | C ₃ C ₄ C ₅ | 127.0 |
| C ₄ -C ₅ | 1.465 | C ₄ C ₅ C ₆ | 123.2 |
| C ₅ -C ₆ | 1.322 | C ₅ C ₆ H ₈ | 117.8 |
| C ₁ -H ₈ | 1.075 | C ₃ C ₂ H ₉ | 116.1 |
| C ₂ -H ₉ | 1.074 | C ₄ C ₃ H ₁₀ | 117.4 |
| C ₃ -H ₁₀ | 1.073 | C ₅ C ₄ H ₁₁ | 115.0 |
| C ₄ -H ₁₁ | 1.076 | C ₅ C ₆ H ₁₃ | 121.8 |
| C ₅ -H ₁₂ | 1.073 | C ₅ C ₆ H ₁₄ | 121.7 |
| C ₆ -H ₁₃ | 1.075 | C ₆ C ₅ H ₁₂ | 119.1 |
| C ₆ -H ₁₄ | 1.073 | C ₁ C ₇ H ₁₅ | 110.2 |
| C ₇ -H ₁₅ | 1.086 | C ₁ C ₇ H ₁₆ | 112.9 |
| C ₇ -H ₁₆ | 1.080 | C ₁ C ₇ H ₁₇ | 110.2 |
| C ₇ -H ₁₇ | 1.086 | C ₂ C ₁ C ₇ H ₁₅ | 120.8 |
| | | C ₂ C ₁ C ₇ H ₁₆ | 180.0 |
| | | C ₂ C ₁ C ₇ H ₁₇ | 120.8 |

^a Bond distance in angstroms and angles in degrees. ^b C_s symmetry assumed.**Table VIII.** Optimized Geometry of the Transition Structure (8) in the 1,7-Hydrogen Shift of (3Z,5Z)-1,3,5-Heptatriene (3)^a

| coordinate | STO-3G | 3-21G |
|--|--------|-------|
| C ₁ -C ₃ | 1.397 | 1.392 |
| C ₃ -C ₇ | 1.384 | 1.384 |
| C ₇ -C ₁₁ | 1.412 | 1.397 |
| C ₁ -H ₂ | 1.086 | 1.078 |
| C ₃ -H ₅ | 1.084 | 1.077 |
| C ₇ -H ₉ | 1.084 | 1.076 |
| C ₁₁ -H ₁₃ | 1.085 | 1.081 |
| C ₁₁ -H ₁₅ | 1.083 | 1.077 |
| C ₁₁ -H ₁₇ | 1.327 | 1.374 |
| ∠C ₃ C ₁ C ₄ | 132.2 | 132.2 |
| ∠C ₁ C ₃ C ₇ | 130.2 | 130.4 |
| ∠C ₃ C ₇ C ₁₁ | 125.7 | 125.6 |
| ∠C ₇ C ₁₁ H ₁₇ | 105.4 | 104.6 |
| ∠C ₁₁ H ₁₇ C ₁₂ | 151.6 | 149.6 |
| ∠C ₃ C ₁ H ₂ | 113.9 | 113.7 |
| ∠H ₂ C ₃ C ₁ | 114.5 | 114.4 |
| ∠H ₉ C ₇ C ₃ | 116.7 | 116.6 |
| ∠H ₁₃ C ₁₁ C ₇ | 116.0 | 117.0 |
| ∠H ₁₅ C ₁₁ C ₇ | 116.5 | 117.7 |
| ∠H ₂ C ₃ C ₁ H ₂ | 14.0 | 14.4 |
| ∠C ₇ C ₃ C ₁ H ₂ | 160.2 | 159.6 |
| ∠H ₉ C ₇ C ₃ H ₅ | 13.5 | 13.5 |
| ∠C ₁₁ C ₇ C ₃ H ₅ | 168.0 | 166.8 |
| ∠H ₁₃ C ₁₁ C ₇ H ₉ | 146.3 | 150.5 |
| ∠H ₁₅ C ₁₁ C ₇ H ₉ | 9.2 | 7.5 |

^a Bond distances in angstroms and angles in degrees.**Table IX.** Calculated Activation Energies (kcal/mol) for 1,3-Sigmatropic Hydrogen Migration in 1-Propene

| method | via structure | | |
|-------------------------|---------------|-------|----------|
| | C_2 | C_s | C_{2v} |
| 3-21G | 108 | 119 | 155 |
| 6-31G | 107 | 117 | 154 |
| 6-31G* | 106 | 111 | 143 |
| 6-31G*/MP2 ^a | 90 | 93 | 137 |
| DZP ^b | 104 | 105 | |
| DZP/CEPA ^b | 93 | 96 | |

^a Computed at the optimized 6-31G* geometry. ^b Reference 4, computed at the optimized 4-31G geometry.

results. However, very recent MC-SCF calculations by Bernardi, Robb, Schlegel, and Tonachini⁵ show that the C_s structure 5 becomes a minimum (the trimethylene biradical) when the geometry is reoptimized at the CI level. Thus it appears that a "forbidden" suprafacial pathway does not exist for the 1,3-sigmatropic hydrogen shift in propene. In light of the MC-SCF results,⁵ it is not surprising that a "false" transition structure was found by using a single-determinant SCF wave function. On the

Table X. Calculated Activation Energies (kcal/mol) for the 1,5-Sigmatropic Hydrogen Migration in (*Z*)-1,3-Pentadiene

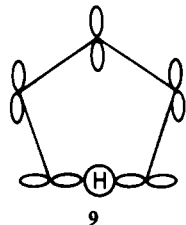
| method | structure | |
|---------------------|-----------|----------|
| | C_s | C_{2v} |
| 3-21G | 55 | 122 |
| 6-31G* ^a | 59 | 124 |
| STO-3G ^b | 62 | |

^a Computed at the optimized 3-21G geometry. ^b Reference 3, partial geometry optimization only.

other hand, the antarafacial transition structure **4** is changed very little by inclusion of CI. We did not repeat Radom's check of the eigenvalues of the force constant matrices for **4** and **5**.

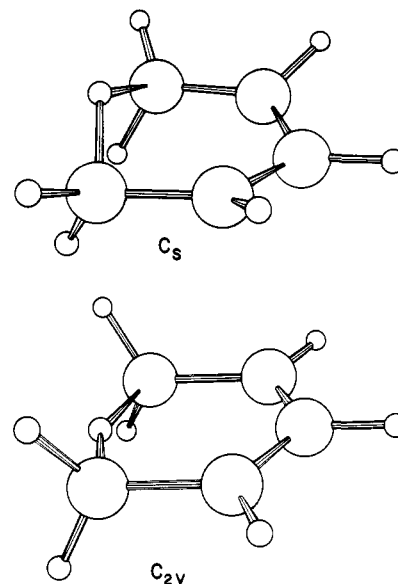
Finally we have considered a third possible transition structure which has C_{2v} symmetry (**6**). It is seen from Table IX that it is considerably higher in energy than **4** and **5** and is therefore unlikely to lie along the reaction pathway of the hydrogen shift in 1-propene. For this reason the force constant matrix was not checked to be sure that **6** is a transition structure.

1,5-Hydrogen Shift in (*Z*)-1,3-Pentadiene. Radom has carried out a preliminary investigation (STO-3G) on the transition structure for the 1,5-hydrogen shift in (*Z*)-1,3-pentadiene by assuming C_s symmetry and a planar carbon skeleton and found an activation energy of 62 kcal/mol.³ Kwart, Brechbiel, Acheson, and Ward¹² have more recently concluded that the transition structure should involve a linear transfer of the hydrogen (**9**).



Their conclusion was based on the kinetic results of Roth and König¹³ which they claim are consistent with model predictions for a collinear hydrogen transfer by Schneider and Stern.¹⁴ However, note that **9** has C_{2v} symmetry, and, were it the transition structure, it presumably would have been located in the partial geometry optimization performed by Radom. In his search the carbon skeleton was held planar; and the restriction of C_s symmetry would not have prevented the finding of a transition structure of C_{2v} symmetry such as **9**, unless of course there are two saddle points (one of C_s and the other of C_{2v} symmetry) on the potential surface. We therefore considered both possibilities by locating minimum-energy structures with the constraint of C_s and C_{2v} symmetry. ORTEP¹⁵ drawings of these (3-21G) are given in Figure 1. The structure of C_{2v} symmetry does not have a collinear arrangement of the migrating hydrogen and two terminal carbons which means the structure proposed by Kwart would be of even higher energy. Energies of activation for the two possible transition structures are given in Table X, and it is seen that that of C_s symmetry lies far below that of C_{2v} symmetry. Gradients for the single-point calculations (6-31G*) in Table VI were obtained, and from these it can be concluded that the 6-31G* activation energy in Table X (59 kcal/mol) is likely to be within 1 kcal/mol of that obtained had geometry optimizations been carried out at this level.

Of course the finding of a minimum energy structure within C_s symmetry does not mean that it is necessarily a transition structure. It might be an intermediate connecting two saddle points (mirror image transition structures). We therefore carried out a vibrational analysis (3-21G) on the C_s structure and found

**Figure 1.** ORTEP drawings of the two transition structures considered in the [1,5]-sigmatropic hydrogen migration of **2**.

that it indeed is a transition structure since a single negative eigenvalue was found on diagonalization of the force constant matrix. Houk¹⁶ has just informed us that he has obtained results identical with ours for this C_s structure. A vibrational analysis was not done for the structure of C_{2v} symmetry since it is of so much higher energy than the C_s structure and is therefore unlikely to be on the reaction pathway under consideration.

Roth and König obtained an activation energy of 35 kcal/mol for the [1,5]-hydrogen migration. This is considerably lower than our calculated values, but inclusion of correlation would presumably lower the computed activation energy.¹⁷ We have also computed the activation energies for the two possible transition structures considered (C_s and C_{2v}) by the topological method of Pandiř and found values of 25 and 92 kcal, respectively.¹⁸ This semiempirical method does take into account correlation energy, and the large difference in activation energies found for the two pathways gives further support to the conclusion that the [1,5]-sigmatropic hydrogen shift in (*Z*)-1,3-pentadiene is suprafacial with a transition structure of C_s symmetry and not C_{2v} as proposed by Kwart.

It is natural to ask how much higher in energy is the "forbidden" antarafacial path than the "allowed" suprafacial path. However, since there appears to be no transition structure of C_2 symmetry, there is no unique line on the potential surface that could be called the antarafacial reaction path; and the question is perhaps meaningless.

1,7-Hydrogen Shift in (3*Z*,5*Z*)-1,3,5-Heptatriene. Here a transition structure that corresponds to an antarafacial shift has been predicted by Woodward and Hoffmann.⁷ This would presumably be of C_2 symmetry, and unlike propene,^{3,4} heptatriene could lead to a transition structure with relatively little strain because of the greater flexibility of the larger carbon skeleton. Because of the size of this system only a transition structure with C_2 symmetry was considered directly although in the course of the search for this structure it was found that one of C_{2v} symmetry is unlikely (see below).

To save computer time the initial search of the potential surface was done with the small STO-2G basis. Searches starting from several initial guesses of the C_2 transition structure geometry failed with GAUSSIAN 80. It was then decided first to optimize within the higher C_{2v} symmetry (all atoms were held in a plane with the

(12) Kwart, H.; Brechbiel, M. W.; Acheson, R. M.; Ward, D. C. *J. Am. Chem. Soc.* **1982**, *104*, 4671.

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

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

(15) Johnson, C. K. "ORTEP II: A FORTRAN Thermal-Ellipsoid Plot Program for Crystal Structure Illustrations"; Oak Ridge National Laboratory Report ORNL-5138, 1976.

(16) Rondan, N. G.; Houk, K. N., University of Pittsburgh, private communication.

(17) Pople, J. A. *Pure Appl. Chem.* **1983**, *55*, 343.

(18) (a) Panciř, J. *Collect. Czech. Chem. Commun.* **1980**, *45*, 2452-2463. (b) Panciř, J. *J. Am. Chem. Soc.* **1982**, *104*, 7424.

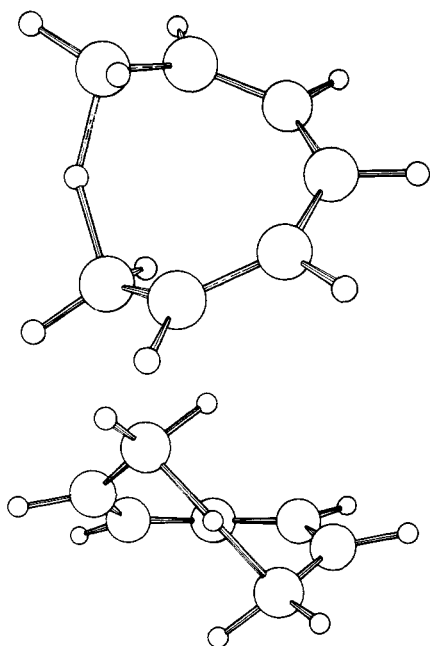


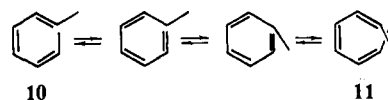
Figure 2. ORTEP drawings of the transition structure (C_2) considered in the [1,7]-sigmatropic hydrogen migration of **3**.

exception of H_{13} , H_{14} , H_{15} , and H_{16} in **8** with the C_2 axis passing through H_2 , C_1 , and H_{17} . This symmetry constraint was next relaxed to C_2 , and the C_{2v} structure was distorted by changing the dihedral angles $H_2C_1C_3H_5$ and $H_2C_1C_4H_6$ from 0° to 5° . This geometry was then used as a starting point for further geometry optimization with GAUSSIAN 80. The optimization proceeded extremely slowly, and 70 cycles of the Schlegel optimization procedure in GAUSSIAN 80 were required before the absolute value of the largest component of the Cartesian gradient was less than 0.005 hartree/bohr. The energy of this structure was 100 kcal lower than that for the optimized structure with C_{2v} symmetry which indicates that the transition state for the [1,7]-sigmatropic hydrogen shift is unlikely to have C_{2v} symmetry. This is not surprising when the results for the [1,5] shift above are taken into account.

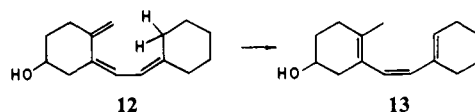
This STO-2G geometry was then used as a starting point for further geometry optimization with the 3-21G basis set. After 18 cycles of the Schlegel optimization the largest component of the Cartesian gradient was 0.0017 hartree/bohr. In the last six cycles the total energy change was less than 0.02 kcal/mol, and changes in geometry were very small. The final structure (Table VIII) is shown in Figure 2 and clearly shows the antarafacial nature of the transition structure for the [1,7]-hydrogen shift. The size of the system precluded a vibrational analysis with the 3-21G basis set. Therefore the structure was reoptimized with the STO-3G basis set (Table VIII), and the vibrational analysis, was carried out at this level. The single negative eigenvalue found on diagonalization of the computed force constant matrix of the C_2 structure confirms that it is a transition structure.

Finally the activation energy (3-21G) for the [1,7]-hydrogen shift was computed to be 44 kcal/mol which, when taken in light of the computed vs. experimental results for the [1,5]-hydrogen shift in pentadiene, suggests that the [1,7]-hydrogen shift in the heptatriene should be a relatively facile process. This is given further support by the results of the computation of activation energies with the topological method.¹⁸ The antarafacial hydrogen shift was computed to have an activation energy of 20 kcal/mol (again lower than that found for the suprafacial process in the [1,5]-hydrogen shift). There is experimental evidence that the [1,7]-hydrogen shift does occur relatively easily in substituted trienes. Marvell¹⁹ and Vogel²⁰ have shown that (2*Z*,4*Z*,6*E*)-2,4,6-octatriene (**10**) interconverts with (2*Z*,4*Z*,6*Z*)-2,4,6-octa-

triene (**11**) through a series of [1,7]-hydrogen shifts at 100 °C.



Havinga²¹ has also found that a [1,7]-hydrogen shift occurs readily ($E_a = 21.6$ kcal/mol) in the calciferol–precalciferol interconversion.



Kinetic Isotope Effects. To compute a kinetic isotope effect in the Eyring theory one needs partition functions for reactant and transition state of both isotopic species. It can be seen from eq 2.17 of ref 19 that, having carried out a vibrational analysis (3-21G) of the 1,5-transition structure, one needs only to do the same for (Z)-1,3-pentadiene in order to have the data necessary to compute the isotope effect for the 1,5-sigmatropic hydrogen shift. Isotopic substitution is assumed not to change potential surfaces so the deuterium compounds require no new computations of energy minima or of force constants; only a change of mass in the vibrational analysis programs is needed. This gave a calculated isotope effect for the rate of H migration in (Z)-1,3-pentadiene relative to D migration in 5-deuterio-(Z)-1,3-pentadiene of $k_H/k_D = 2.52$ at 200 °C which does not compare well with Roth and König's experimental value of 4.97 at the same temperature. These authors actually measured the rates of H transfer in 1,1-dideuterio-(Z)-1,3-pentadiene and of D transfer in the 5,5,5-trideuterio compound so that there are also secondary isotope effects to be considered. However, we estimate that these are not large since we compute the rate of a H transfer in the parent compound to be 0.995 times the H transfer rate in the 1,1,5,5-tetradeterio derivative.

These calculated isotope effects do not include any estimate of tunneling corrections. The magnitude of the imaginary frequency in the transition state for H transfer is computed to be 1927 and 1529 cm^{-1} for the D transfer. When these and the 6-31G* activation energy of 59 kcal/mol are used (uncorrected for zero-point energies which would have little effect), Bell's formula²³ gives $k_H/k_D = 4.33 \times 2.52 = 10.9$ which is much larger than the experimental value. However, the potential here must be a symmetric double minimum as in the interconversion of the two rectangular forms of cyclobutadiene where Wolfsberg²⁴ and Dewar²⁵ have shown this potential to give a very different tunnel correction than Bell's formula which is based on transmission through an inverted truncated parabola.²⁶

In view of these results we are not optimistic about the ab initio computation of kinetic hydrogen isotope effects.

Conclusions

Results for the three sigmatropic hydrogen shifts are in agreement with the predictions of Woodward and Hoffmann. While ab initio activation energies are computed to be significantly higher than experiment for the [1,5]- and [1,7]-hydrogen shifts, the finding that the [1,7]-shift would occur at a lower temperature than the [1,5]-shift agrees with experiment. No simple [1,3]-hydrogen shift has been observed, and our results support Radom's suggestions that other processes (for example, simple C–H bond dissociation) might be competitive with a concerted [1,3]-hydrogen shift.

(21) Schlattmann, J. L. M. A.; Pot, J.; Havinga, E. *Recl. Trav. Chim. Pays-Bas* **1964**, *83*, 1173.

(22) Melander, L.; Saunders, W. H., Jr. "Reaction Rates of Isotopic Molecules"; John Wiley and Sons: New York, 1980, p 19.

(23) Bell, R. P. *Trans. Faraday Soc.* **1959**, *55*, 1.

(24) Huang, M.-J.; Wolfsberg, M. *J. Am. Chem. Soc.* **1984**, *106*, 4039.

(25) Dewar, M. J. S.; Merz, K. M., Jr.; Steward, J. P. *J. Am. Chem. Soc.* **1984**, *106*, 4040.

(26) Carpenter, B. *J. Am. Chem. Soc.* **1983**, *105*, 1700.

(19) Marvell, E. N.; Caple, G.; Schatz, B. *Tetrahedron Lett.* **1965**, 385.

(20) Vogel, E.; Grimme, W.; Dlnne, E. *Tetrahedron Lett.* **1965**, 391.

Acknowledgment. We would like to thank the University Research Council, Vanderbilt University, which provided travel funds for Dr. Pančič. We are indebted to Professors J. A. Pople and A. J. Kresge for useful discussions on the tunnel and kinetic isotope effects. This work was supported in part by the Air Force

Office of Scientific Research, Air Force Systems Command, USAF, under Grant AFOSR-82-0100.

Registry No. 1, 115-07-1; 2, 1574-41-0; 3, 30915-44-7; deuterium, 7782-39-0.

Theoretical Examination of the S_N2 Reaction Involving Chloride Ion and Methyl Chloride in the Gas Phase and Aqueous Solution

Jayaraman Chandrasekhar,* Scott F. Smith, and William L. Jorgensen*

Contribution from the Department of Chemistry, Purdue University, West Lafayette, Indiana 47907. Received May 29, 1984

Abstract: The role of hydration on the course of the S_N2 reaction between chloride ion and methyl chloride has been studied by using quantum and statistical mechanical methods. The gas-phase reaction was examined at the ab initio molecular orbital level with the 6-31G* basis set. The calculated double-well potential surface is typical of gas-phase S_N2 profiles, featuring unsymmetrical ion-dipole complexes as minima and a symmetrical transition state. The complexation energy (10.3 kcal/mol) and intrinsic barrier (13.9 kcal/mol) compare favorably with experimental values. Monte Carlo simulations were then carried out for the solute cluster solvated by 250 water molecules at 25 °C and 1 atm by using solute-solvent potential functions derived from ab initio calculations in conjunction with the TIP4P model of water. In one set of simulations, importance sampling was employed to obtain the potential of the mean force in solution. The influence of the solvent is to make the reaction surface almost unimodal and to increase the barrier significantly. The calculated free energy of activation (26.3 kcal/mol) is in excellent agreement with the experimental estimate. Additional simulations were carried out in which the solute was held rigidly at geometries corresponding to the reactants/products and to the transition state. The solvation of the transition state relative to the separated species is characterized by less exothermic solute-solvent interaction as well as by a reduced solvent disruption energy. The increase in activation energy due to hydration is caused by reduction in strength rather than in the number of solute-solvent hydrogen bonds. The simulations provide detailed insights into the structural and energetic nature of the differential solvation of the reactants and transition state.

The rates of bimolecular nucleophilic substitution reactions involving anions and polar molecules vary over 20 orders of magnitude on going from the gas phase to polar, especially protic, media.¹⁻³ Even the qualitative nature of the reaction appears to be altered through solvation. The extensive studies of Brauman and co-workers have confirmed the double-well form of the potential surface for S_N2 reactions in the gas phase,^{1,2} while in solution the energy profiles are generally believed to be unimodal.³ The development of a detailed molecular level understanding of the role of solvation on the qualitative and quantitative nature of S_N2 reaction profiles has emerged as a fundamental goal in physical organic chemistry.

In his classic early work, Ingold noted that electrostatic solvation forces must be regarded as primary determinants of the activation energy for S_N2 reactions.^{3a} He explained the observed rate differences on the basis of the charge distribution of the reactants

and the transition state. For reactions involving anions and neutral substrates, one of the reactants has a localized charge while the transition state is characterized by a diffuse distribution. Application of Born's equation predicts a differential stabilization of the reactants by polar solvents, leading to increased activation barriers in such media. Later workers, especially Parker,^{3c} emphasized the importance of specific solute-solvent interactions like hydrogen bonding as well as variation in solvent reorganization energies for the reactants and the transition state in highly structured solvents. Initial desolvation of the nucleophile before its approach to the substrate has also been proposed as a major contributor to the activation energy in protic solvents.^{3e,f} Although these concepts have been of considerable interpretative value, largely empirical schemes have been adopted as predictive models.^{3c,d,4,5} For example, a sound thermodynamic description of the role of solvents in some S_N2 reactions has been based on solvent activity coefficients, i.e., the change in the standard chemical potential of a solute on transfer from a reference solvent to another solvent for the reactants, transition states, and products.^{3c} From a relatively small number of experimentally measurable quantities, a large body of rate data could be rationalized and often reduced to simple linear free-energy relationships. The Marcus equation has also been successfully applied to the prediction of S_N2 reactivity trends for nonidentity reactions in various solvents.^{3d} Recently the Marcus theory has been employed in conjunction with valence bond state correlation diagrams to provide a unified description of S_N2 reactivities in the gas phase and in solution.⁵

Nevertheless, all the solution reaction models have been incomplete for at least one of the following reasons. (i) They are

(1) Review: Nibbering, N. M. M. In "Kinetics of Ion-Molecule Reactions"; Ausloos, P., Ed.; Plenum Press: New York, 1979.

(2) (a) Lieder, C. A.; Brauman, J. I. *J. Am. Chem. Soc.* **1974**, *96*, 4029. (b) Brauman, J. I.; Olmstead, W. N.; Lieder, C. A. *Ibid.* **1974**, *96*, 4030. (c) Olmstead, W. N.; Brauman, J. I. *Ibid.* **1977**, *99*, 4019. (d) Pellerite, M. J.; Brauman, J. I. *Ibid.* **1980**, *102*, 5993. For more gas-phase mechanistic work, see; Bohme, D. K.; Young, L. B. *J. Am. Chem. Soc.* **1970**, *92*, 7354. Bohme, D. K.; Mackay, G. I.; Payzant, J. D. *Ibid.* **1974**, *96*, 4027. Tanaka, K.; Mackay, G. I.; Payzant, J. D.; Bohme, D. K. *Can. J. Chem.* **1976**, *54*, 1643.

(3) (a) Ingold, C. K. "Structure and Mechanism in Organic Chemistry", 2nd ed.; Cornell University Press: Ithaca, NY, 1969. (b) Hartshorn, S. R. "Aliphatic Nucleophilic Substitution"; Cambridge University Press: London, 1973. (c) Parker, A. J. *Chem. Rev.* **1969**, *69*, 1. (d) Albery, W. J.; Kreevoy, M. M. *Adv. Phys. Org. Chem.* **1978**, *16*, 87. (e) Ritchie, C. D. In "Solute-Solvent Interactions"; Coetzee, J. F., Ritchie, C. D., Eds.; Marcel Dekker: New York, 1969; p 284. (f) Dewar, M. J. S.; Dougherty, R. C. "The PMO Theory of Organic Chemistry"; Plenum Press: New York, 1975; pp 234, 266. (g) Carrion, F.; Dewar, M. J. S. *J. Am. Chem. Soc.* **1984**, *106*, 3531.

(4) McLennan, D. J. *Aust. J. Chem.* **1978**, *31*, 1897.

(5) Shaik, S. S. *J. Am. Chem. Soc.* **1984**, *106*, 1227.