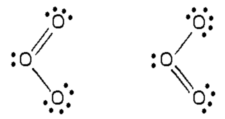
We would like to point out, however, that the analogy between the electronic structure of the FeO_2 moiety and the ozone molecule can be explained on the grounds of totally paired structures.[39,40] According to resonance theory the structure of ozone can be regarded as a hybrid of the forms[40]



Each oxygen atom has four outer electron pairs, either shared or unshared, and each bond can be considered as a hybrid of a single and a double covalent bond. These resonance structures ressemble those of I and II for the FeO_2 moiety. Totally paired structures are also supported by the absence of contact, temperature dependent, paramagnetic chemical shifts (Table I).

Our results clearly indicate that ^{17}O NMR spectroscopy is a highly promising tool in rationalizing the structure, electronic arrangement, and dynamics of the FeO_2 linkage.

Acknowledgment. We thank Dr. M. Marraud (Laboratoire de Chimie-Physique Macromolēculaire, ENSIC-INPL, Nancy) for the access on the Bruker AM-400 spectrometer at the University of Nancy, France, the Research Committee of the University of Ioannina, Greece, and the Institut National de la Santē et de la Recherche Mēdicale (France) for partial finantial support.

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(38) Savicki, J. P.; Lang, G.; Ikeda-Saito, M. *Proc. Natl. Acad. Sci. U.S.A.* **1984**, *81*, 5417–5419.

(39) Pauling, L. *Stanford Med. Bull.* **1948**, *6*, 215–222.

(40) Pauling, L.; Pauling, P. *Chemistry*; W. H. Freeman, Co.: San Francisco, 1975.

Transition Structures of Ene Reactions of Ethylene and Formaldehyde with Propene

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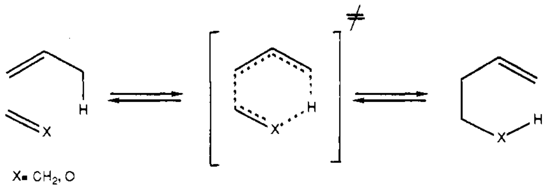
Abstract: The transition structures for the Alder ene reactions of propene with ethylene to form 1-pentene and of propene with formaldehyde to form 3-buten-1-ol have been located with the STO-3G and 3-21G basis sets. Energetics have been evaluated with the 6-31G* basis set and MP2 correlation energy corrections. Our best estimate of the activation energy (35 kcal/mol) of the propene–ethylene reaction is 14 kcal/mol higher than previous estimates, which were based on the measured activation energy of the reverse process, but it agrees with measured activation energies of similar ene reactions. Although the reaction of formaldehyde has a 5 kcal/mol lower activation energy than the reaction of ethylene, the transition structures of the two reactions are remarkably similar. The details of geometry provided by these calculations assist in the development of interpretations of the stereochemistries of intramolecular ene reactions.

The Alder ene reaction and its reverse, the retro-ene reaction, are common paths of hydrocarbon rearrangement[1,2] and an increasingly useful tool in synthesis.[3-5] Although there have been suggestions about the likely geometry of the transition structure,[1-5] no calculations have been reported for hydrocarbon versions of this reaction. We report here the STO-3G and 3-21G transition structures of the parent Alder ene reaction between propene and ethylene and show how the geometry helps account for some stereochemical aspects of the reaction. A new estimate of the activation energy of the parent reaction is also provided. We have also studied the reaction of propene with formaldehyde and show that although the activation energy is lowered by 5 kcal/mol the transition structure is changed only slightly.



The transition structures obtained with Pople's GAUSSIAN 80 and 82 programs[6] are shown in Figures 1–4. The calculated energetics are compared to available experimental data in Tables I and II. The exothermicities of both reactions are much too large with the STO-3G basis set,[7a] and consequently, very early transition states are predicted. With the 3-21G basis set,[7b] the reaction energetics are more accurate, and later transition states with more

Table I. Energetics of the Ene Reaction of Propene with Ethylene

computational level	activation energy[a]	reaction energy
STO-3G	52.1[a]	−54.2
3-21G	51.7	−23.6
6-31G*//3-21G	61.0	−23.5
MP2/6-31G*//3-21G	31.2	−29.4
experimental	21.4[b] (35)[c]	−28.5
ΔZPE(3-21G)	+0.7	
$\Delta S^{\ddagger}$(3-21G)	−43.0 eu	

[a] The STO-3G and 3-21G total energies of the transition structures are −192.65127 and −193.94254 au, respectively. The reaction energies were calculated with propene and ethylene energies found in: Whiteside, R. A.; Frisch, M. J.; Pople, J. A. *The Carnegie-Mellon Quantum Chemistry Archive*, 3rd ed.; Carnegie-Mellon University: Pittsburgh, PA. 1983. [b] Estimated from the activation energy[8] of 49.9 kcal/mol for the retro-ene reaction of 1-pentene and the heat of reaction[9] of 1-pentene (−11.2 kcal/mol), to form propene (4.88 kcal/mol) and ethylene (12.50 kcal/mol). [c] Estimate of barrier made here (see text).

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* University of California.

(1) The generality of the "ene synthesis" was recognized by Alder in 1943: Alder, K.; Pascher, F.; Schmitz, A. *Berichte* **1943**, *76*, 27. Reviews: (a) Snider, B. B. *Acc. Chem. Res.* **1980**, *13*, 426. (b) Keung, E. C.; Alper, H. *J. Chem. Educ.* **1972**, *49*, 97. (c) Hoffmann, H. M. R. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 556. (d) Roth, W. R. *Chimia* **1966**, *20*, 229.

(2) Gajewski, J. J. *Hydrocarbon Thermal Isomerizations*; Academic: New York, 1981.

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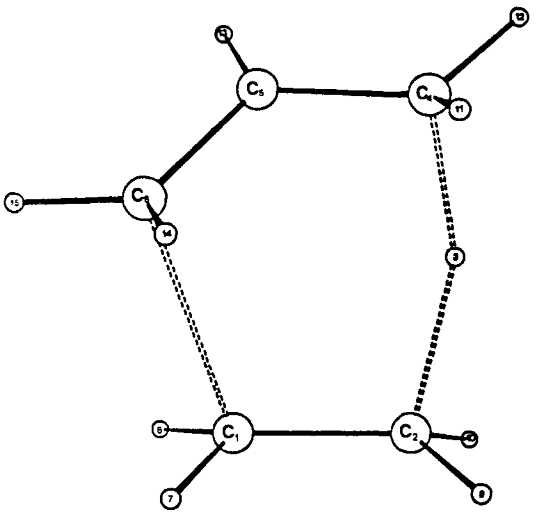


Bond Lengths

	STO-3G	3-21G
C_1C_2	1.388	1.397
C_1C_6	1.999	2.110
C_1H_7	1.082	1.073
C_1H_8	1.083	1.073
C_2H_3	1.524	1.447
C_2H_9	1.080	1.077
C_2H_{10}	1.080	1.077
H_3C_4	1.218	1.349
C_4C_5	1.437	1.402
C_4H_{11}	1.085	1.080
C_4H_{12}	1.085	1.077
C_5C_6	1.372	1.374
C_5H_{13}	1.085	1.076
C_6H_{14}	1.083	1.075
C_6H_{15}	1.083	1.074

Bond Angles

	STO-3G	3-21G
$C_1C_2H_3$	102.4	103.2
$C_1C_2H_9$	119.3	118.7
$C_1C_2H_{10}$	119.1	118.4
$C_1C_6C_5$	103.1	100.6
$C_1C_6H_{14}$	94.3	93.4
$C_1C_6H_{15}$	101.9	100.5
$C_2C_1C_6$	112.1	110.6
$C_2C_1H_7$	118.6	119.2
$C_2C_1H_8$	118.1	119.0
$C_2H_3C_4$	155.5	156.6
$H_3C_2H_9$	100.1	100.8
$H_3C_2H_{10}$	93.9	94.7
$H_3C_4C_5$	99.1	96.2
$H_3C_4H_{11}$	101.7	96.9
$H_3C_4H_{12}$	110.4	108.5
$C_4C_5C_6$	117.0	119.3
$C_4C_5H_{13}$	118.7	118.6
$C_5C_4H_{11}$	115.5	117.7
$C_5C_4H_{12}$	116.6	118.9
$C_5C_6H_{14}$	117.9	118.7
$C_5C_6H_{15}$	119.9	120.3
$C_6C_1H_7$	91.6	90.3
$C_6C_1H_8$	97.4	95.9
$C_6C_5H_{13}$	119.3	118.7
$H_7C_1H_8$	113.2	114.2
$H_9C_2H_{10}$	114.9	114.6
$H_{11}C_4H_{12}$	111.6	113.7
$H_{14}C_6H_{15}$	113.6	114.8

Torsional Angles

	STO-3G	3-21G
$C_1C_2H_3C_4$	-9.0	-12.8
$C_1C_6C_5C_4$	63.3	66.2
$C_1C_6C_5H_{13}$	-91.3	-92.5
$C_2C_1C_6C_5$	-39.7	-37.8
$C_2C_1C_6H_{14}$	80.3	82.3
$C_2C_1C_6H_{15}$	-164.5	-161.7
$C_2H_3C_4C_5$	25.5	30.4
$C_2H_3C_4H_{11}$	-93.2	-88.5
$C_2H_3C_4H_{12}$	148.3	153.7
$H_3C_2C_1C_6$	11.3	11.2
$H_3C_2C_1H_7$	116.5	113.7
$H_3C_2C_1H_8$	-100.3	-98.3
$H_3C_4C_5C_6$	-55.0	-59.4
$H_3C_4C_5H_{13}$	99.8	99.3
$C_4H_3C_2H_9$	114.2	110.4
$C_4H_3C_2H_{10}$	-129.8	-133.5
$C_4C_5C_6H_{14}$	-38.8	-33.4
$C_4C_5C_6H_{15}$	175.4	175.1
$C_5C_6C_1H_7$	-161.6	-159.4
$C_5C_6C_1H_8$	84.7	86.2
$C_6C_1C_2H_9$	-97.5	-99.2
$C_6C_1C_2H_{10}$	112.6	114.1
$C_6C_5C_4H_{11}$	52.7	41.7
$C_6C_5C_4H_{12}$	-173.3	-174.5
$H_7C_1C_2H_9$	7.3	3.4
$H_7C_1C_2H_{10}$	-142.6	-143.4
$H_7C_1C_6H_{14}$	-41.6	-39.3
$H_7C_1C_6H_{15}$	73.6	76.7
$H_8C_1C_2H_9$	150.5	151.4
$H_8C_1C_2H_{10}$	0.6	4.6
$H_8C_1C_6H_{14}$	-155.3	-153.7
$H_8C_1C_6H_{15}$	-40.1	-37.7
$H_{11}C_4C_5H_{13}$	-152.5	-159.6
$H_{12}C_4C_5H_{13}$	-18.5	-15.8
$H_{14}C_6C_5H_{13}$	166.6	167.6
$H_{15}C_6C_5H_{13}$	20.9	16.4

Figure 1. The STO-3G and 3-21G propene–ethylene ene reaction transition structures.

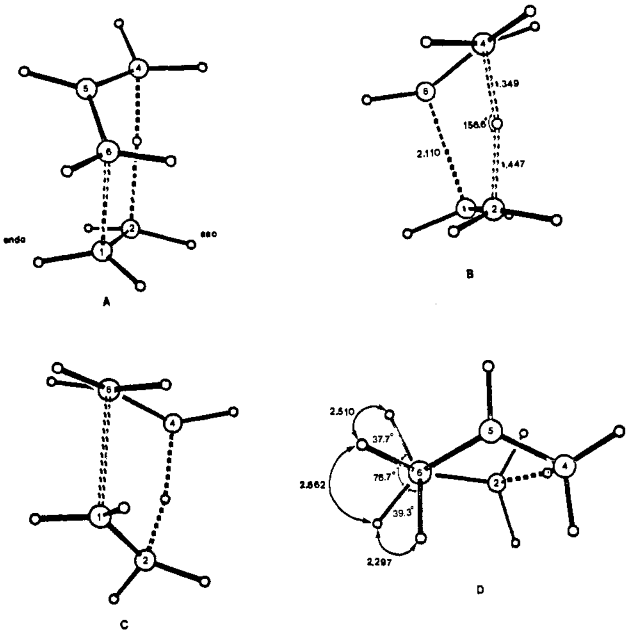
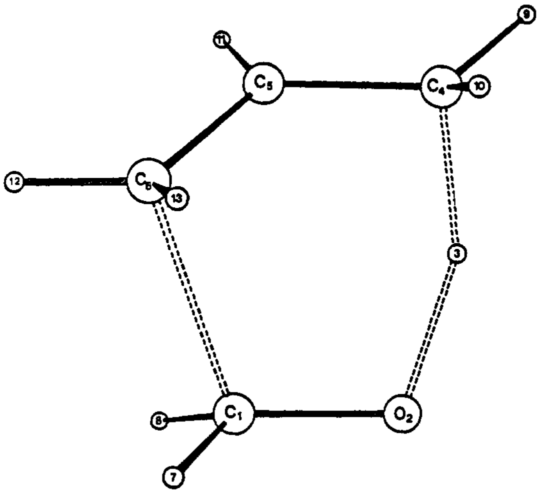


Figure 2. Four views of the 3-21G transition structure of the propene–ethylene ene reaction.



Bond Lengths

	STO-3G	3-21G
C_1O_2	1.291	1.298
C_1C_6	1.973	2.016
C_1H_7	1.098	1.078
C_1H_8	1.099	1.078
O_2H_3	1.332	1.311
H_3C_4	1.227	1.322
C_4C_5	1.438	1.406
C_4H_9	1.082	1.076
C_4H_{10}	1.084	1.080
C_5C_6	1.377	1.382
C_5H_{11}	1.088	1.076
C_6H_{12}	1.082	1.075
C_6H_{13}	1.082	1.076

Bond Angles

	STO-3G	3-21G
$C_1O_2H_3$	107.0	108.8
$C_1C_6C_5$	98.2	96.5
$C_1C_6H_{12}$	104.6	103.7
$C_1C_6H_{13}$	95.8	96.6
$O_2H_3C_4$	156.3	153.5
$O_2C_1C_6$	111.2	110.1
$O_2C_1H_7$	118.6	118.1
$O_2C_1H_8$	119.1	119.2
$H_3C_4C_5$	96.5	94.0
$H_3C_4H_9$	112.1	110.7
$H_3C_4H_{10}$	102.6	98.5
$C_4C_5C_6$	118.0	120.5
$C_4C_5H_{11}$	118.7	118.4
$C_5C_6H_{12}$	119.8	119.7
$C_5C_6H_{13}$	117.9	117.9
$C_5C_4H_9$	116.3	118.1
$C_5C_4H_{10}$	115.2	117.0
$C_6C_1H_7$	92.2	91.7
$C_6C_1H_8$	97.7	97.4
$C_6C_5H_{11}$	118.9	118.3
$H_7C_1H_8$	112.2	113.8
$H_9C_4H_{10}$	112.1	114.1
$H_{12}C_6H_{13}$	114.2	115.2

Torsional Angles

	STO-3G	3-21G
$C_1O_2H_3C_4$	-16.3	-22.3
$C_1C_6C_5C_4$	63.3	67.2
$C_1C_6C_5H_{11}$	-93.0	-93.7
$O_2C_1C_6C_5$	-41.8	-41.0
$O_2C_1C_6H_{12}$	-165.6	-163.8
$O_2C_1C_6H_{13}$	77.5	78.1
$O_2H_3C_4C_5$	29.5	35.7
$O_2H_3C_4H_9$	151.3	157.7
$O_2H_3C_4H_{10}$	-88.2	-82.4
$H_3O_2C_1C_6$	16.3	17.7
$H_3O_2C_1H_7$	121.2	121.2
$H_3O_2C_1H_8$	-96.0	-93.4
$H_3C_4C_5C_6$	-55.8	-61.0
$H_3C_4C_5H_{11}$	100.3	99.9
$C_4C_5C_6H_{12}$	175.2	177.1
$C_4C_5C_6H_{13}$	-37.9	-33.8
$C_5C_6C_1H_7$	-163.7	-161.9
$C_5C_6C_1H_8$	83.5	83.8
$C_6C_5C_4H_9$	-174.4	-177.1
$C_6C_5C_4H_{10}$	51.5	40.7
$H_7C_1C_6H_{12}$	72.5	75.3
$H_7C_1C_6H_{13}$	-44.4	-42.8
$H_8C_1C_6H_{12}$	-40.3	-39.0
$H_8C_1C_6H_{13}$	-157.1	-157.1
$H_9C_4C_5H_{11}$	-18.2	16.2
$H_{10}C_4C_5H_{11}$	-152.4	-158.4
$H_{11}C_5C_6H_{12}$	19.1	16.2
$H_{11}C_5C_6H_{13}$	166.0	165.2

Figure 3. The STO-3G and 3-21G propene–formaldehyde ene reaction transition structures.

extensive bond reorganization are predicted.

The activation energy of the parent ene reaction can be estimated from the activation energy[8] for the fragmentation of 1-pentene and the heat of this reaction.[9] The value thus obtained (21 kcal/mol) is remarkably low, considering that the parent reaction has never been observed experimentally. The experi-

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(3) (a) Oppolzer, W. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 876. (b) Oppolzer, W.; Snieckus, V. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 476.

(4) Taber, D. F. *Intramolecular Diels-Alder and Ene Reactions*; Springer-Verlag: New York, 1984.

(5) (a) Vandewalle, M.; De Clercq, P. *Tetrahedron* **1985**, *41*, 1767. (b) Desimoni, G.; Tacconi, G.; Barco, A.; Pollini, G. P. *Natural Product Synthesis Through Pericyclic Reactions*; ACS Monograph 180, American Chemical Society: Washington, D.C., 1983, Chapter 8. (c) Martin, S. F. *Tetrahedron* **1980**, *36*, 419. (d) Conia, J. M.; Le Perchec, P. *Synthesis* **1975**, 1.

(6) (a) Binkley, J. S.; Whiteside, R. A.; Raghavachari, K.; Seeger, R.; Defrees, D. J.; Schlegel, H. B.; Frisch, M. J.; Pople, J. A.; Kahn, L. R. GAUSSIAN 82, Carnegie-Mellon University, Pittsburgh, 1982. (b) Binkley, J. S.; Whiteside, R. A.; Krishnan, R.; Seeger, R.; DeFrees, D. J.; Schlegel, H. B.; Topiol, S.; Kahn, L. R.; Pople, J. A. GAUSSIAN 80, Quantum Chemistry Program Exchange No. 406, Indiana University, Bloomington, Indiana.

(7) (a) Hehre, W. J.; Stewart, R. F.; Pople, J. A. *J. Chem. Phys.* **1969**, *51*, 2657. (b) Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 939.

(8) Walsh, R., unpublished results cited by: Egger, K. W.; Vitius, P. *Int. J. Chem. Kinet.* **1974**, *6*, 429.

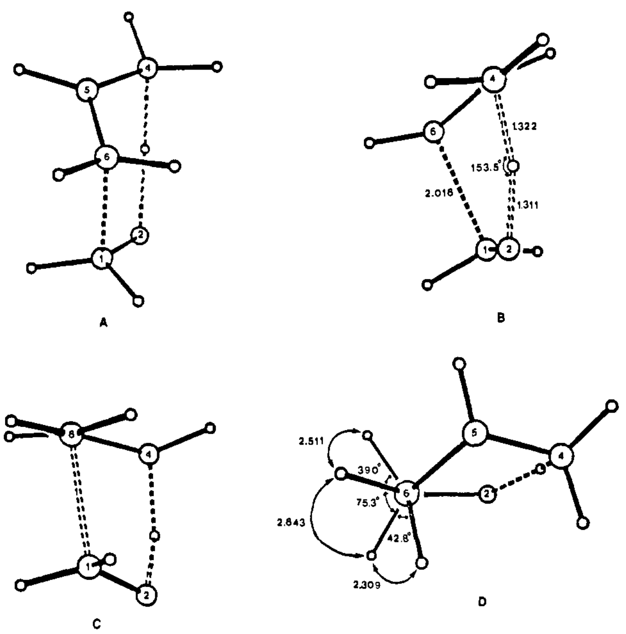

Figure 4. Four views of the 3-21G transition structure of the propene–formaldehyde ene reaction.

Table II. Energetics of the Ene Reaction of Propene with Formaldehyde

computational level	activation energy[a]	reaction energy
STO-3G	43.4[a]	−31.0
3-21G	38.2	−14.7
6-31G*//3-21G	53.4	−6.9
MP2/6-31G*//3-21G	27.5	−10.2
experimental	26.4[b]	−13.5[b]
ΔZPE(3-21G)	+1.2	
ΔS^*(3-21G)	−44.2 eu	
ΔS^*(exptl)	−40.1 eu	

[a] The STO-3G and 3-21G total energies of the transition structures are −227.94553 and −229.58503 au, respectively. The reaction energies were calculated from energies for propene and formaldehyde found in: Whiteside, R. A.; Frisch, M. J.; Pople, J. A. *The Carnegie-Mellon Quantum Chemistry Archive*, 3rd ed.; Carnegie-Mellon, University: Pittsburgh, PA. 1983. [b] Reference 19. [c] The activation entropy is determined from the experimental activation entropy[18] of −8.8 eu and the entropy of 3-buten-1-ol (84.8 eu), to form propene (63.8 eu) and formaldehyde (52.3 eu) found in footnote *b*.

mental activation energies[10] for the ene reactions of ethylene with *trans*-2-butene and *cis*-2-butene, to form 3-methylpent-1-ene, are 37.0 and 36.5 kcal/mol, respectively. In addition, intramolecular ene reactions of hydrocarbon dienes have activation energies of 32–40 kcal/mol.[2,3]

The calculated activation energies at the RHF level with the STO-3G or 3-21G basis sets are very high as compared to this estimated experimental value.[8] A larger basis set (6-31G*) produces an even higher activation energy. However, correlation energy corrections at the MP2 level give a value much closer to experimental, and indeed we believe that the parent reaction will have an activation barrier of about 35 kcal/mol. In computational studies of related pericyclic reactions involving hydrogen shifts,[11,12] we have found that correlation energy calculations generally lower the activation energy by about 10–20 kcal/mol as compared to RHF values. Those studies also show that the transition structures do not have appreciably different geometries upon inclusion of correlation energy, as will be described in more detail later in this paper. The energetics of the propene–ethylene reaction are calculated reasonably well at the 3-21G level, and so the transition state should not change position much upon going to larger basis sets and inclusion of correlation energy. On the other hand, the transition structure is likely to have appreciable diradical character, since the activation energy is lowered by an enormous 30 kcal/mol by inclusion of correlation energy. Our best estimate of the activation energy for this reaction, 35 kcal/mol, is very close to an estimate based upon formation of the hypothetical diradical, pentan-1,4-diyl. This diradical is estimated to have a heat of formation of 53.3 kcal/mol, using the Benson–O'Neal group equivalents.[13] Combined with the heats of reaction of propene and ethylene,[9] this leads to a 35.9-kcal/mol activation energy, if pentan-1,4-diyl were the transition state for the reaction. This is within 1 kcal/mol of our estimate for the experimental activation energy. Nevertheless, the stereospecificity of substituted cases implies that the reaction is concerted.[1]

The activation entropy of the parent reaction is not known. However, values of −30 to −45 eu are generally observed for intermolecular ene reactions,[1c] and the calculated activation entropy of −43.0 eu is in accord with these results.

The transition-state geometry resembles rather closely that proposed by Hoffmann,[1c] although the C---H---C angle is 156°, not the 180° usually postulated for hydrogen atom transfer. This 156° angle is similar to that which has been calculated for several hydride-transfer reactions.[14] The hydrogen is somewhat less than half-transferred, and the partially formed and broken CH bond lengths (1.447 and 1.349 Å at the 3-21G level) are similar to those calculated for the 1,5-sigmatropic hydrogen shift in 1,3-pentadiene (1.446 Å).[11] The forming CC single bond length of 2.11 Å is similar to the length calculated for the forming CC bonds (2.1–2.2 Å) in the Diels–Alder transition state.[15]

The transition structure is somewhat chairlike (Figure 2A), as has been postulated by Oppolzer,[16] but might better be characterized as an envelope conformation, like that of cyclopentane, but with two long CC bonds, and the transferring hydrogen atom placed between one of these long bonds. Structure **2A** in Figure 2 resembles the Hoffmann[1c] and Conia[5d] formulations to a remarkable degree. From the Newman projections along the C_4–C_5 and C_6–C_5 bonds shown in **B** and **C** of Figure 2, respectively, it is seen that C_5 distorts away from planarity, even though it is planar in both reactant and product. This occurs in order to maximize the overlap of the p orbital at C_5 with the p or slightly hybridized orbitals at C_4 and C_6. Thus, the π bonding between C_5 and C_6 is maintained as much as possible by this distortion, and the π bonding between C_4 and C_5 has already developed to a significant extent. This is also reflected in the corresponding C_4–C_5 and C_5–C_6 bond lengths of 1.37 and 1.40 Å, respectively. A similar maintenance of overlap and pyramidalization of C_2 and C_3 of butadiene was observed in the Diels–Alder transition structure.[15a]

The transition structure for the reaction of propene with formaldehyde is shown in Figures 3 and 4. Overall the perturbation of substituting the methylene group of the parent reaction with an oxygen, to give the corresponding transition state of propene with formaldehyde, does not significantly alter the geometry. The angle about the transferring hydrogen and the degree of staggering about the forming CC bond change only slightly. As shown best in D in Figures 2 and 4, the main difference in the two transition structures is the slightly larger dihedral angle,

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[9] (a) Benson, S. W. *Thermochemical Kinetics*; 2nd ed.; John Wiley and Sons, Inc.: New York, 1976. (b) Cox, J. D.; Pilcher, G. *Thermochemistry of Organic and Organometallic Compounds*; Academic: New York, 1970. (c) Stull, D. R.; Westrum, E. F., Jr.; Sinke, G. C. *The Chemical Thermodynamics of Organic Compounds*, John Wiley and Sons, Inc.: New York, 1969.

[10] Richard, C.; Scacchi, G.; Back, M. H. *Int. J. Chem. Kinet.* **1978**, *10*, 307.

[11] Rondan, N. G.; Houk, K. N. *Tetrahedron Lett.* **1984**, *25*, 2519.

[12] Jensen, F.; Houk, K. N. *J. Am. Chem. Soc.* **1987**, *109*, 3139.

[13] O'Neal, H. E.; Benson, S. W. In *Free Radicals*; Kochi, J. K., Ed.; John Wiley and Sons: New York, 1973; Vol. 11, pp 275–359.

[14] Wu, Y.-D.; Houk, K. N. *J. Am. Chem. Soc.* **1987**, *109*, 906.

[15] (a) Brown, F. K.; Houk, K. N. *Tetrahedron Lett.* **1984**, 25, 4609. (b) Lin, Y.-T.; Brown, F. K.; Houk, K. N. *J. Am. Chem. Soc.* **1986**, *108*, 554. (c) Bernardi, F.; Bottini, A.; Robb, M. A.; Field, M. J.; Hillier, I. H.; Guest, M. F. *J. Chem. Soc., Chem. Commun.* **1985**, 1051.

[16] (a) Oppolzer, W.; Mirza, S. *Helv. Chim. Acta* **1984**, *67*, 730. (b) Oppolzer, W.; Robbiani, C.; Bättig, K. *Tetrahedron* **1984**, *40*, 1391. (c) Oppolzer, W.; Robbiani, C. *Helv. Chim. Acta* **1980**, *63*, 2010. (d) Oppolzer, W.; Robbiani, C.; Bättig, K. *Ibid.* **1980**, *63*, 2015.

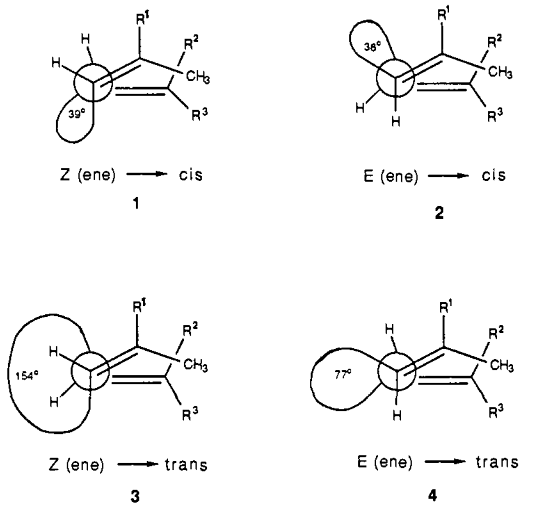
∠2165, which is accompanied by a change of ∠1234 from its value −13° in the hydrocarbon transition state to −22° in the propene–formaldehyde transition structure. The angle of hydrogen transfer, 154°, is very similar to that found for hydrogen atom transfer in intramolecular radical reactions.[17] Although such reactions prefer a nearly linear hydrogen transfer, the preference is small, and angles of around 155° are common in order to maintain approximately tetrahedral C—O- - -H and H- - -C—C angles.[17]

The activation energy of the reaction of propene with formaldehyde (Table II) has been determined from the activation energy of the retro-ene reaction of 3-buten-1-ol[18] and the heat of this reaction.[19] The trends in calculated activation energies previously mentioned for the parent reaction are also seen here. The Hartree–Fock activation energy is much too high, but MP2 correlation energy estimates lower the activation energy by 26 kcal/mol to a value within 1 kcal/mol of the experimental value. The estimated heat of formation of the potential diradical intermediate, 1-oxapentan-1,4-diyl, is 30.2 kcal/mol,[13] which gives an estimate of 53.0 kcal/mol for the activation energy of the reaction, if it were to involve a diradical transition state. This value is much higher (27 kcal/mol) than the experimental activation energy of 26.4 kcal/mol. The relative difficulty in forming this diradical as compared to the all-carbon case arises from the greater π bond strength of the carbonyl group in formaldehyde as compared to the π bond of ethylene. This is also reflected in the lower overall exothermicity of the reaction of formaldehyde. The diradical in the oxygen case has a very much higher energy than that estimated either experimentally or computationally for the transition state of the ene reaction. A concerted mechanism is highly favored in the carbonyl reaction. Also of note is the fact that the lowering of the activation energy calculated for formaldehyde must arise from the greater electophilicity of formaldehyde as compared to ethylene and not from differences in diradical intermediate stabilities.

The entropy of activation at the 3-21G level is calculated to be −44.2 eu, in reasonable agreement with the experimental value[18,19] of −40.1 eu.

The retro-ene decomposition of 3-buten-1-ol to form propene and formaldehyde has been studied previously with the MINDO/3 method.[20] An energy of activation of 33.2 kcal/mol and an entropy of activation of −48.8 cal/(mol·K) were calculated for the reaction of propene with formaldehyde to form 3-buten-1-ol. These can be compared to experimental values of 26.4 and −40.1, and to MP2/6-31G*//3-21G values of 28.7 (after 3-21G ZPE corrections) and −44.2 eu.

As noted above, correlation energy corrections have a big influence on the calculated activation energies. In the hydrocarbon case, a diradical is also estimated to have a heat of formation very similar to that of the transition state for the reaction. Both of these facts lead to concerns that the transition structures might be substantially different when the MP2/6-31G* optimizations are carried out. However, the results of transition-structure calculations for other, closely related, pericyclic reactions, summarized in Table III, show that geometries do not change appreciably at higher levels of theory. The energetics of single-point calculations with correlation on the 3-21G geometries are very similar to the results of full geometry optimizations at the correlated level. As a consequence of these analogies, we believe that the geometries reported here for the ene reactions of propene with ethylene and with formaldehyde are very good approximations to the real situations.



Z (ene) → cis
1

E (ene) → cis
2

Z (ene) → trans
3

E (ene) → trans
4

Figure 5. Four model transition structures for the intramolecular ene reaction. The *E* and *Z* notation refers to the allyl component of the ene reaction where R^1 = H. The terms cis and trans refer to the geometrical relationship of the substituents on the ring after CC bond formation.

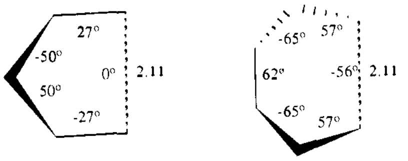


Figure 6. The MM2 optimized geometries of "stretched" cyclopentane and cyclohexane. The constrained bond length of each structure is in Å.

The results on both of these reactions provide us with considerable detail about the steric relationships between the various hydrogens, which may be replaced by substituents in the transition states of useful reactions. Figures 2D and 4D show that there is partial staggering about the forming CC bonds in both reactions. The steric environment of exo and endo hydrogens on the ethylene or formaldehyde group is quite different, as indicated by the H–H distances shown in the figure. In particular, the exo hydrogen on ethylene is in the more sterically crowded position, and so groups in this position will be more crowded than endo groups. The experimental preference for endo addition has been noted previously.[1,21] For example, upon reaction of cyclopentene with maleic anhydride the erythro isomer is formed predominantly in a 3.5:1 ratio. Reaction of maleic anhydride and *cis*-2-butene gives 80–85% of the *threo*-3-(1-butenyl)succinic anhydride, while reaction of *trans*-2-butene gives 57% of the erythro diastereomer. In each of these reactions the major product arises from endo addition. The geometries of the transition states imply that part of the endo preference could arise from the greater crowding of the exo positions.

It is well established[1,4] that intramolecular ene reactions occur with a preference for the formation of cis-disubstituted five-membered rings and trans-disubstituted six-membered rings. In order to explain this stereoselectivity, we postulate the transition structure models, **1**–**4**, shown in Figure 5. To arrive at these transition structure models, we first carried out MM2 calculations of "stretched" cyclopentane and cyclohexane. In the calculation of "stretched cyclopentane" two CC atoms of the cyclopentane ring were fixed at a distance of 2.11 Å. The structure was then optimized by MM2[22] with this bond length constrained. Likewise, to generate "stretched cyclohexane", two CC atoms of the 6-membered ring were set apart at the 3-21G transition state forming CC distance of 2.11 Å, and this structure was optimized by MM2.[22] The CC dihedral angles for optimized "stretched" cyclopentane and cyclohexane are shown in Figure 6. As a further development of the transition structure models we considered the

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(17) Dorigo, A.; Houk, K. N. *J. Am. Chem. Soc.* **1987**, *109*, 2195.

(18) Smith, G. G.; Yates, B. L. *J. Chem. Soc.* **1965**, 7242.

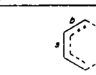
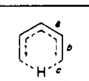
(19) Benson, S. W.; O'Neal, H. E. *Kinetic Data on Gas Phase Unimolecular Reactions*; National Standard and Reference Data Series, National Bureau of Standards: Washington, D.C., 1970; p 135.

(20) Brown, S. B.; Dewar, M. J. S.; Ford, G. P.; Nelson, D. J.; Rzepa, H. S. *J. Am. Chem. Soc.* **1978**, *100*, 7832.

(21) Berson, J. A.; Wall, R. G.; Perlmutter, H. D. *J. Am. Chem. Soc.* **1966**, *88*, 187.

(22) (a) Burkert, U.; Allinger, N. L. *Molecular Mechanics*; American Chemical Society: Washington D.C., 1982. (b) Allinger, N. L. *J. Am. Chem. Soc.* **1977**, *79*, 8127. (c) Allinger, N. L.; Yuh, Y. H. Molecular Mechanics II, QCPE No. 395, Indiana University, Bloomington, IN.

Table III. Summary of Relevant Calculations on Pericyclic Reactions[a]

								
	3-21G[b] bond length	CAS1-4-31G[c] bond length		3-21G[d] bond length	MP2/6-31G*[d] bond length		3-21G[e] bond length	MP2/6-31G*[e] bond length
a	1.402	1.376	*a*	1.385	1.396	*a*	1.369	1.379
b	1.370	1.389	*b*	1.405	1.418	*b*	1.421	1.423
c	2.210	2.244	*c*	1.448	1.411	*c*	2.138	2.133
d	1.376	1.398						
		E_a(corr)[f]			E_a(corr)[f]			E_a(corr)[f]
RHF/3-21G		38.3	RHF/3-21G		51.2	RHF/3-21G		40.1
exptl I[g]		27.5	MP2/6-31G*//3-21G		37.6	MP2/6-31G*//3-21G		35.1
exptl II[i]		32.8-34.3	MP2/6-31G*		34.1	MP2/6-31G*		36.1[h]
			exptl[j]		35.2 ± 2.2	exptl[k]		32.5

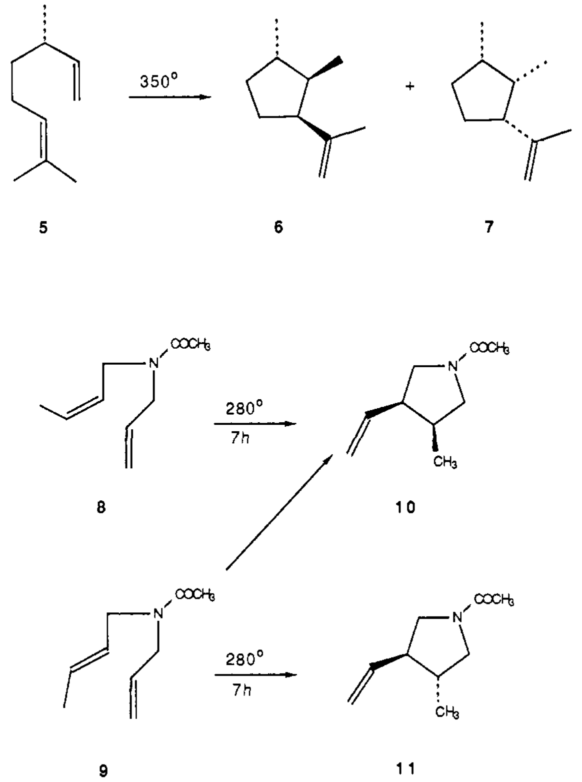
[a] Bond lengths in Å, energies in kcal/mol. [b] Reference 14b. [c] MCSCF with the 4-31G basis set and a four electron CASCF, ref 14c. [d] Jensen, F.; Houk, K. N. *J. Am. Chem. Soc.* **1987**, *109*, 3139. [e] Spellmeyer, D. C.; Houk, K. N. *J. Am. Chem. Soc.*, submitted for publication. [f] The E_a are the calculated ΔE plus zero-point energy and heat capacity corrections. [g] Rowley, D.; Steiner, H. *Discuss. Faraday Soc.* **1951**, *10*, 198. [h] A two configuration SCF optimization of the transition state for this reaction gives similar structure with calculated E_a of 39.4 kcal/mol: Breulet, J.; Schaefer, H. F., III *J. Am. Chem. Soc.* **1984**, *106*, 1221. [i] Calculated from E_a of cyclohexene cycloreversion and the experimental heat of reaction: Uchiyama, M.; Tomioka, T.; Amano, A. *J. Phys. Chem.* **1964**, *68*, 1878. Tsang, W. *J. Chem. Phys.* **1965**, *42*, 1805. Tardy, D. C.; Ireton, R.; Gordon, A. S. *J. Am. Chem. Soc.* **1979**, *101*, 1508. [j] Roth, W. R.; Konig, J. *Ann. Chem.* **1966**, *24*, 699. Roth, W. R. *Chimia* **1966**, *20*, 229. [k] (a) Kim, H.; Gwinn, W. D. *J. Chem. Phys.* **1965**, *42*, 3728; (b) Bak, B.; Led, J. J.; Nygaard, L.; Rastrup-Andersen, J.; Sorensen, G. O. *J. Mol. Struct.* **1969**, *3*, 369.

superimposition of the 3-21G transition structure and the MM2 stretched ring system. If the two carbon atoms of the "stretched cyclopentane" that are separated by 2.11 Å were superimposed on C_1 and C_6 of the 3-21G transition structure (Figure 2D), a 1,6-octadiene could be envisioned. Likewise a 1,7-nonadiene would result from superimposition of "stretched cyclohexane" on the 3-21G transition structure. The transition structure models can also be thought of by replacing a hydrogen on C_1 and one on C_6 (of Figure 2D) with two carbon atoms of the appropriate connecting-chain length.

The geometry of this connecting-chain (also known as the tether, or ansa) plays an important role in determining the preference for the cis- or the trans-disubstituted ene product. To illustrate this point, several dihedral angles about the forming CC bond, corresponding to the HC---CH angles in the 3-21G transition-state calculation, are shown in Figure 6. For a trimethylene connecting-chain, these ideal transition-state angles should be similar to the ideal dihedral angle of 0° for an envelope form of a "stretched cyclopentane". The dihedral angles about the forming CC bond of the two transition structures leading to the cis-disubstituted products (39° and 38°) are much smaller than those leading to the trans products (154° and 77°). Here we are merely looking at how the 3-21G transition structure would have to change to accommodate the appropriate connecting-chain. This accounts for the preference for the cis adduct, since only relatively small distortions of the transition structure are required to accommodate the trimethylene side chain. Cis stereoselectivity has been observed for the intramolecular ene reaction of 3,7-dimethyl-1,6-octadiene (**5**) at 350°.[23] The two cis-disubstituted cyclopentanes, **6** and **7**, are produced in a ratio of 3:1, corresponding to a 1.4 kcal/mol lower activation energy for the formation of **6** than for formation of **7**. Inspection of the transition-state models (Figure 5, R^1 = CH_3, R^2 = R^3 = H) shows that the cis product could arise via **1** or **2**.

As another example of the formation of cis-disubstituted, five-membered rings, Oppolzer[24] has synthesized substituted pyrrolidines via intramolecular ene reactions of the *N*-(*cis*- and *trans*-crotyl) *N*-allyl amides, **8** and **9**. Whereas the *cis*-pyrrolidine, **10**, is obtained exclusively from the intramolecular ene reaction of **8**, the reaction of the *trans*-alkene, **9**, gives a mixture of cis and trans ene adducts, **10** and **11**, in a ratio of 89:11. We postulate that the cyclization of the *cis*-crotyl amide, **8**, occurs through the exo transition state, **1** (R^1 = R^2 = R^3 = H), giving pyrrolidine **10**. The transition structure, **3**, would involve very high ring strain, and only one product, **10**, is observed for this reaction. The cyclization of the *trans*-crotyl amide, **9**, occurs through the endo transition state, **2**, to give the cis-disubstituted adduct, while the trans-substituted product is formed via the exo transition state, **4**. Here the two possible transition states for the reaction do not have as large a difference in ideal dihedral angles as is the case for **1** and **3**. The cis-disubstituted product is still preferred, but in general the preference should be smaller for *trans*-alkenes than for *cis*-alkenes.

Scheme I



Oppolzer[24] has postulated different transition structure models to explain the formation of the observed products, as reproduced

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(23) (a) Huntsman, W. D.; Curry, T. H. *J. Am. Chem. Soc.* **1958**, *80*, 2252. (b) Pines, H.; Hoffman, N. E.; Ipatieff, V. N. *Ibid.* **1954**, *76*, 4412. (c) Huntsman, W. D.; Lang, P. C.; Madison, N. L. *J. Org. Chem.* **1962**, *27*, 1983.

(24) Oppolzer, W.; Pfenninger, E.; Keller, K. *Helv. Chim. Acta* **1973**, *56*, 1807.

(25) (a) Snider, B. B.; Roush, D. M.; Killinger, T. A. *J. Am. Chem. Soc.* **1979**, *101*, 6023. (b) Snider, B. B.; Roush, D. M. *J. Org. Chem.* **1979**, *44*, 4229.

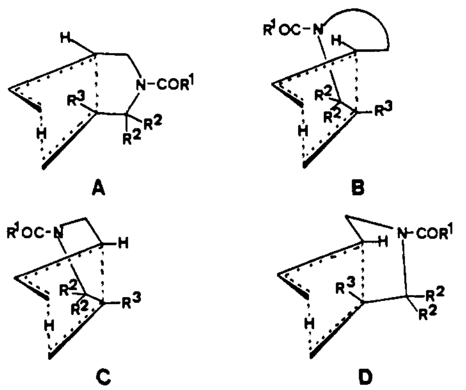
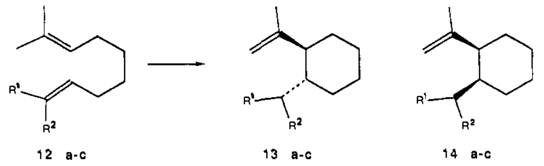


Figure 7. Transition structure models proposed by Oppolzer for the formation of the observed products from intramolecular ene reactions of the *N*-(*cis*- and *trans*-crotyl) *N*-allyl amides **8** and **9**. $R^1 = CH_3$ and $R^2 = R^3 = H$.

Scheme II



	R^1	R^2	Yield			
a	CO_2Me	CO_2Me	73	99	:	1
b	CN	CN	71	92	:	8
c	CO_2Me	CN	89	96	:	4

in Figure 7. These have an eclipsing arrangement about the forming CC bond. Oppolzer postulated that the cyclization of the *cis*-crotyl amide, **8**, to give the cis adduct, **10**, occurs through the unstrained exo transition state **A**, rather than the highly strained endo transition state B (Figure 7). The cyclization of the *trans*-crotyl amide, **9**, is suggested to proceed through the endo and exo transition states, **C** and **D** (Figure 7). The hydrogens at R^2 and R^3 do not strongly influence the preferred transition state **C**. These structures do not provide an explanation for the preferential formation of the cis-disubstituted pyrrolidine upon cyclization of *trans*-crotyl amide, **9**. The actual transition structures should be somewhere between those in Figures 5 and 7, since the small connecting-chain will distort the ideal geometries in Figure 5 toward those in Figure 7. Substituents are also expected to lead to distortions away from the transition state calculated for the parent reaction.

Numerous other examples[4] of cis stereoselectivity in the formation of five-membered rings via intramolecular ene reactions have been reported. In all but two cases,[25] the cis-disubstituted five-membered ring is formed preferentially under kinetically controlled reaction conditions. These two highly substituted cases give a 1:1 ratio of cis and trans adducts.

In contrast to the cis stereoselectivity for the intramolecular ene reaction to form five-membered rings, there is a preference for the formation of trans-disubstituted six-membered rings. In this transition state, the atoms of a tetramethylene chain and the two carbon atoms undergoing CC bond formation form a cyclohexane ring with one long bond. In the chair form of "stretched cyclohexane" the ideal dihedral angle about the forming CC bond is 56°. This dihedral angle is between the values of the corresponding angles in the transition structure calculations which lead to the two cis and one of the trans ene products (Figure 5). Our model transition structures would thereby predict low stereoselectivity for this reaction, slightly favoring the formation of the cis-disubstituted six-membered ring, since the cis arrangements have dihedral angles which are closer to that of our model stretched cyclohexane. However, the stereoselectivity is also dependent upon substitution at R^1, R^2, and R^3. For example, the trans-disubstituted cyclohexanes, **13a–c**, are preferentially formed from 1,7-dienes, **12a–c**.[26] The trans-disubstituted products are formed via transition state **4** (Figure 5, $R^1 = CH_3$, R^2 and R^3 = CN or CO_2Me), while transition state **3** is disfavored because of ring strain. The formation of the cis-disubstituted product in low yield could occur through transition states **1** or **2**. The former suffers from steric repulsion between the connecting-chain and R^3, while the latter suffers from steric repulsion between the connecting-chain and the methyl group at R^1. Thus, substitution at each position, R^1, R^2, and R^3, gives a preference for the trans-disubstituted ene adduct. Other examples of the formation of six-membered rings via the intramolecular ene reaction have been reported;[23c,27] however, the stereochemical preference could not always be determined unambiguously.[23c] There is a need for further investigations into substituent effects upon the stereochemistry of the ene cyclization of 1,7-dienes.

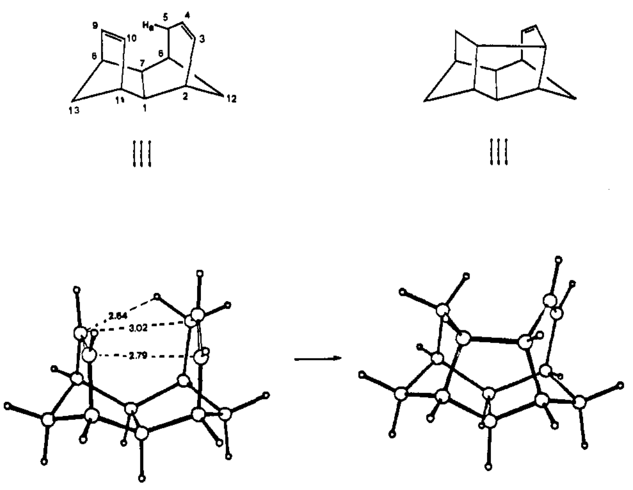


Figure 8. MM2 optimized structures of compounds **15** and **16**.

The extremely rapid intramolecular ene reaction of compound **15**[28] is a result of the relatively minor distortions required to convert the reactant into the transition state, as shown in Figure 8. Compound **15** rearranges to **16** at 45 °C ($\Delta G^\ddagger$ = 26 kcal/mol), and Brown has concluded that the rate of reaction of **15** is enchanced by the proximity of the allylic hydrogen and the terminal end of the olefin. While Drieding models of **15** suggest that the C_9–H_a distance is 1.75 Å,[28] MM2[22] calculations predict that this distance is 2.64 Å in the optimized structure of **15**. The forming CC distance need only decrease from 2.79 to 2.11 Å, and the carbons connecting the transferring hydrogen need only move to a distance of 2.74 Å in the transition state, as compared to the 3.02 Å in reactants.

Future investigations in our laboratories will include the calculation of ene reactions of more highly activated enophiles and force-field modeling of stereoselectivities of substituted cases.

Acknowledgment. We are grateful to the National Science Foundation for financial support of this research through research and supercomputer grants and to the Harris Corp. for use of a Harris H300 and grants of Harris H800 computers at Pittsburgh and Los Angeles.

Registry No. 5, 2436-90-0; **6**, 6876-17-1; 7, 53797-46-9; **8**, 50401-75-7; **9**, 50401-76-8; **10**, 50401-65-5; **11**, 50401-66-6; **12a**, 99298-55-2; **12b**, 99298-56-3; **12c**, 99298-57-4; **13a**, 110511-26-7; **13b**, 110570-44-0; **13c**, 99298-61-0; **14a**, 110511-27-8; **14b**, 110511-28-9; **15**, 110511-29-0; **16**, 24934-25-6; cyclopentane, 287-92-3; cyclohexane, 110-82-7; cyclopentene, 142-29-0; *erythro*-3-(3-cyclopentenyl)succinic anhydride, 110511-23-4; *threo*-3-(3-cyclopentenyl)succinic anhydride, 110511-24-5; *threo*-3-(1-buten-3-yl)succinic anhydride, 110511-25-6; *erythro*-3-(1-buten-3-yl)succinic anhydride, 110511-30-3; maleic anhydride, 108-31-6; *cis*-2-butene, 590-18-1; *trans*-2-butene, 624-64-6; propene, 115-07-1; ethylene, 74-85-1; formaldehyde, 50-00-0; 1-pentene, 109-67-1; 3-buten-1-ol, 627-27-0.

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(26) Tietze, L. F.; Beifuss, U. *Angew Chem., Int. Ed. Engl.* **1985**, *24*, 1042.
(27) Tietze, L.-F.; Kiedrowski, G. V. *Tetrahedron Lett.* **1981**, *22*, 219.
(28) Brown, J. M. *J. Chem. Soc., B* **1969**, 868.