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Ring Expansion in Methylcyclopentadiene Radicals. Quantum Chemical and Kinetics Calculations

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Ring expansion processes in 1-, 2-, and 5-methylenecyclopentadiene radicals and isomerizations among the three isomers were studied by the Becke three-parameter hybrid method with Lee−Yang−Parr correlation functional approximation (B3LYP). Structure, energy, and frequency calculations were carried out with the Dunning correlation consistent polarized double ξ (cc-pVDZ) and augmented aug-cc-pVDZ basis sets. The potential energy surfaces for ring expansion in methylenecyclopentadiene radicals consist of several intermediates and transition states. The process that takes place by insertion of the methylene group into the cyclopentadiene ring in the three isomers occurs via two principal mechanisms. One mechanism is associated with cleavage of the five-membered ring of the cyclopentadiene ring. In the second mechanism, the transition states of the first stage consist of a newly formed three-membered ring fused to the original cyclopentadiene ring. In all the three isomers of methylenecyclopentadiene, the reaction pathways leading to ring expansion include intermediates that via additional transition states lead to the production of the cyclohexadienyl radical. The latter, by a very fast H-atom ejection produces benzene. The structure and energetics of the various pathways are shown. The isomerization processes 1-methylenecyclopentadiene ⇔ 5-methylenecyclopentadiene and 2-methylenecyclopentadiene ⇔ 1-methylenecyclopentadiene involve a single 1,2-H atom shift and proceeds in one step without intermediates. The ring expansion in 1-methylenecyclopentadiene proceeds much faster via isomerization to 5-methylenecyclopentadiene than via direct formation of cyclohexadienyl.

I. Introduction

Dimerization of propargyl radicals is considered a major step in the aliphatic → aromatic conversion in combustion chemistry. However, the expansion of a five-membered ring to form benzene is also an important pathway.[1,2] Such a conversion is known to take place in methylcyclopentadiene and in its nitrogen analogue methylpyrrole when the latter are elevated to high temperatures.[3] It has been found that one of the major components of post-shock mixtures of heated methylcyclopentadiene is benzene, whereas pyridine is a major reaction product in the decomposition of *N*-methylpyrrole. Analysis of shock-heated mixtures of methylcyclopentadiene revealed also the presence of higher aromatics.[4]

Quantum chemical calculations on ring expansion in the methylpyrrole system clearly show that that ring expansion of the five-membered ring takes place via the methylenepyrrole radical rather than from methylpyrrole itself.[5] Under combustion conditions, the radical is obtained by an H-atom ejection or H-atom abstraction from the methyl group in methylpyrrole. The structure of the transition state describing ring expansion from the molecule methylpyrrole is such that the C−H bond in the methyl group is practically broken and the energy level of the transition state corresponds to C−H bond rupture followed by ring expansion in the radical.

We are not aware of any quantum chemical calculation on ring expansion in the various isomers of methylcyclopentadiene, neither from the molecule nor from radicals, that are obtained by H-atom ejection from the methyl group in the molecule. We are aware, however, of quantum chemical calculations of fulvene → benzene isomerization.[6] These calculations were performed using B3LYP for optimization and CCSD(T), G2M, and other methods for energetics, including both carbene and biradical structures. Bachrach has calculated the barriers for 1,5 sigmatropic hydrogen shifts in methylcyclopentadiene, pyrrole, and phosphole.[7]

The purpose of this investigation is to study the mechanism of ring expansion in methylenecyclopentadiene radicals and to determine the energetics and other parameters in the process. Methylcyclopentadiene and its corresponding free radicals have three isomers depending upon the location of the methyl group with respect to the SP^3 carbon in the molecule. We are interested to know the isomerization rates and mechanism of ring expansion in the three isomers of methylenecyclopentadiene. They can yield the cyclohexadienyl radical by direct ring expansion, or alternatively, they can first isomerize and undergo ring expansion from the radical with the lowest barrier for this process.

II. Computational Details

We used the Becke three-parameter hybrid method[8] with Lee−Yang−Parr correlation functional approximation with unrestricted open shell wave functions (uB3LYP)[9] and the Dunning correlation consistent polarized valence double ξ (cc-pVDZ) basis set.[10] Optimization of the ground-state geometry of the radical species was done using the Berny geometry optimization algorithm.[11] For determining transition state structures, we used the combined synchronous transit-guided quasi-

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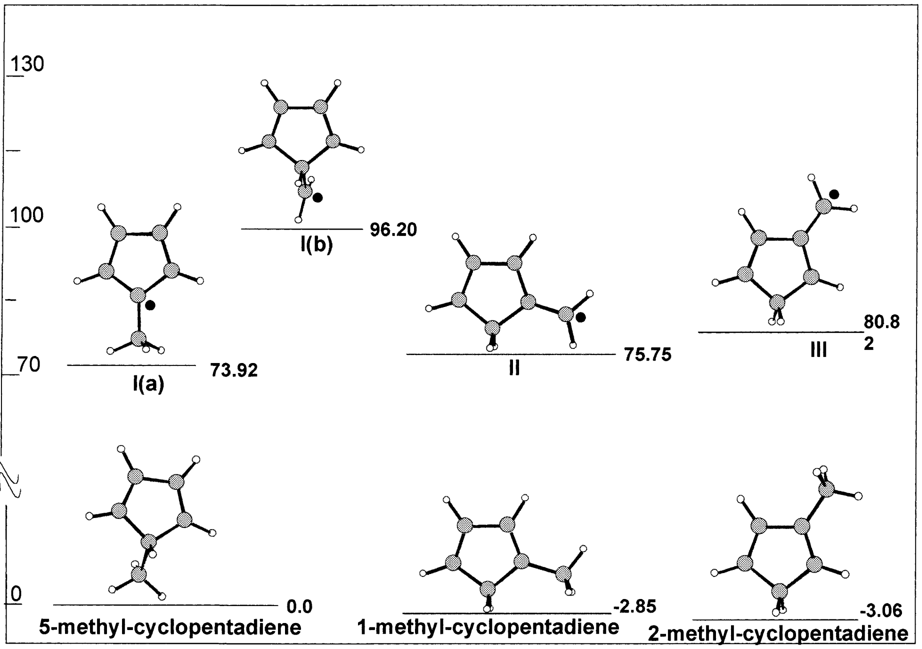


Figure 1. Energy levels of 5-, 1-, and 2-methylcyclopentadiene and of the four radicals: 5-methylcyclopentadienyl, I(a); 5-methylenecyclopentadiene, I(b); 1-methylenecyclopentadiene, II; 2-methylenecyclopentadiene, III. Relative energies (kcal/mol) are calculated at the QCISD(T)//B3LYP/cc-pVDZ level of theory.

Newton (STQN) method.[12] Higher level calculations were made using these geometries. The bond orders of the methylenecyclopentadienes and methylcyclopentadienyl were calculated using the "atom in molecules" method (AIM) that analyzed the distribution of the double and single bonds in the radicals.[13-15]

All the calculations were performed without symmetry restrictions. Vibrational analyses were done at the same level of theory to characterize the optimized structures as local minima or transition states. Calculated vibrational frequencies and entropies (at uB3LYP level) were used to evaluate preexponential factors of the reactions under consideration. All the calculated frequencies, the zero point energies and the thermal energies are of harmonic oscillators. The calculations of the intrinsic reaction coordinate (IRC), to check whether the transition states under consideration connect the expected reactants and products, were done at the uB3LYP level of theory with the same basis set as was used for the stationary point optimization.

There is a large volume of information on quantum chemical calculations of free radicals[16-21] that are the main subject of this investigation. Jursic has shown that the structure and energetics of many free radicals were successfully reproduced by hybrid density functional theory (DFT) methods.[20,21]

As all the species in this investigation are radicals, we checked also the effect of additional diffuse functions on the energetics of several species. We used the geometry and second derivatives that were obtained with the cc-pVDZ basis set and performed further optimization using augmented basis set (aug-cc-pVDZ).[22,23] The vibrational analysis was carried out also with this augmented basis set for calculating ZPE. As will be shown later, the reaction energetics calculated by using these two basis sets were very close and the differences did not exceed 1 kcal/mol.

Each optimized B3LYP structure was recalculated at a single-point quadratic CI including single and double substitutions with a triple contribution to the energy, QCISD(T).[24] All of the reported relative energies include zero-point energy correction (ZPE).

The DFT and QCISD(T) computations were carried out using the Gaussian-98 program package[25] and were done on a DEC Alpha XP1000 1/667 professional workstation.

III. Results

1. Structure and Energetics of Methylenecyclopentadiene and Methylcyclopentadienyl Radicals. Figure 1 shows the energy levels of the four radicals that can be formed as a result of H-atom elimination from the three isomers of methylcyclopentadiene (three different positions of the methyl group). As can be seen in the figure, the energy level of 5-methylenecyclopentadiene {I(b)} has the highest energy level. This results from lack of resonance stabilization of this radical as compared to 1- and 2-methylenecyclopentadiene (II and III) (Figure 2). As 5-methylcyclopentadienyl {I(a)} does have resonance stabilization, its formation from 5-methylcyclopentadiene requires about 23 kcal/mol less than the formation of 5-methylenecyclopentadiene (1a) does. Because the ring expansion can take place only by insertion of a methylene group into the ring, a transition from I(a) to I(b) must take place before the process of ring expansion can occur.

Figure 2 shows the bond orders in the four different radicals (the bond distances in the species are given in other figures). The radical I(b) does not have resonance stabilization because C(5) already has four bonds and it cannot form a double bond with C(6). In view of the fact that C(5)−C(6) must remain a single bond, the electron density on C(6) cannot be shared with the ring. This limitation does not exist in the other three radicals. Radical I(a) has two resonance structures. This reflects itself by the distribution of the bond lengths and the bond orders in the radicals. C(3)−C(4), which is a double bond in both resonance structures, has a bond order close to 2, i.e., 1.78. C(1)−C(5) and C(1)−C(2), on the other hand, have bond orders between 1.4 and 1.6, because the bonds alternate between single and double bonds in two resonance structures. The remaining bonds in this radical that are single bonds in the two resonance structures show a bond order close to unity, i.e., 1.09−1.17.

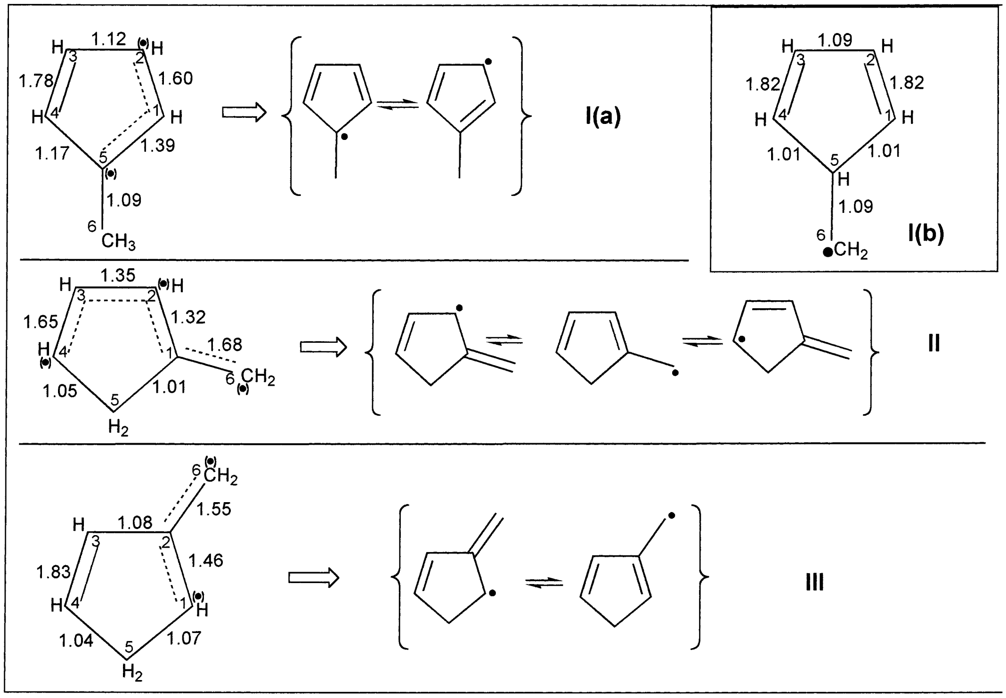
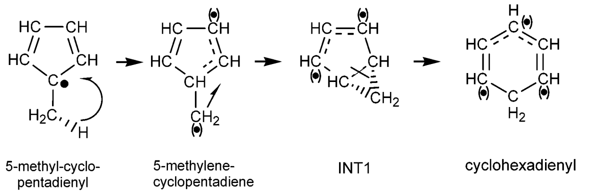


Figure 2. Bond orders and free electron density distribution in the four radicals obtained from methylcyclopentadiene radicals by H-atom ejection. The symbol (●) denotes partially distributed free electron density. The resonance structures of each radical are shown in brackets.

SCHEME 1



Radical II has three resonance structures. C(1)−C(5) and C(4)−C(5) are single bonds in all the three resonance structures, and their calculated bond orders are 1.01 and 1.05, respectively. The bonds C(1)−C(2) and C(2)−C(3) appear as double bonds in one out of the three structures. Their bond orders are thus 1.32 and 1.35, respectively. C(3)−C(4) and C(1)−C(6), on the other hand, appear each in two structures out of the three. Their bond orders increase to the values 1.65 and 1.68, respectively.

Radical III has only two resonance structures. The bond C(3)−C(4) is a double bond in both structures and its order is close to 2, i.e, 1.83. C(1)−C(2) and C(2)−C(6) alternate between double and single bonds and their bond orders are 1.46 and 1.55, respectively.

2. Ring Expansion. *A. 5-Methylcyclopentadienenyl.* Scheme 1 describes the general pathway of 5-methylcyclopentadienyl → cyclohexadienyl ring expansion and the potential energy surface is shown in Figure 3. The figure contains selected structural parameters of the species on the surface and the location of the high electron density.

The energetics, both at the uB3LYP/cc-pVDZ and uQCISD(T)/cc-pVDZ//uB3LYP/cc-pVDZ levels of theory and the uB3LYP/aug-cc-pVDZ and uQCISD(T)/cc-pVDZ//uB3LYP/aug-cc-pVDZ levels of theory are shown in Table 1. As can be seen, the results of the calculations are almost the same with and without the addition of diffuse functions in the form of the augmented basis set.

Starting with the 5-methylcyclopentadienyl radical, the surface contains three transition states and two intermediates. This can be seen in Figure 3. The first stage in the process is the formation of 5-methylenecyclopentadiene from 5-methylcyclopentadienyl via transition state TS1. It is a 1,2-H-atom shift from C(6) to C(5) and the electron density shift from C(5) and C(2) to C(6). The energy barrier of this stage is 49.16 kcal/mol at the uQCISD(T)//uB3LYP/cc-pVDZ level of the theory, and it is the highest barrier on the surface.

The next step in the process is the production of a three-membered ring C(5)C(6)C(1) via transition state TS2. A highly symmetrical bicyclic intermediate INT1 with C(3)−C(6) as the axis of symmetry is formed. It is symmetrical in both bond length and spin density distribution. The electron density that was located completely on C(6) in 5-methylenecyclopentadiene is evenly distributed between C(2) and C(4) in INT1. In view of the high symmetry and thus resonance stabilization in INT1, it is more stable than 5-methylenecyclopentadiene by some 6 kcal/mol.

The transition from 5-methylenecyclopentadiene to INT1 that occurs via transition state TS2 has a barrier of ~9 kcal/mol. The transition state is characterized by a small movement of the methylene group toward C(1). The geometrical parameters and electron distributions are very similar to the ones in 5-methylenecyclopentadiene. The reaction coordinate of the transition state TS2 is C(6)C(5)C(1) angle bend that brings C(6) closer to C(1), together with a rotation of the methylene group C(6)H(6)H(7) with respect to the ring plane (Figure 3).

The intermediate INT1 forms a cyclohexadienyl radical via transition state TS3. The main process in obtaining this transition state is C(1)−C(5) bond rupture and expansion of the two fused (three- and five-membered) rings into one six-membered benzene ring. The reaction coordinate is a C(1)−C(5) bond stretch combined with a C(1)C(6)C(5) angle bend (Figure 3). The energy barrier of this stage is rather low, 18.27 kcal/mol. The low energy that is required to break the C(1)−C(5) bond is the result of the large amount of strain energy that is released in the process.

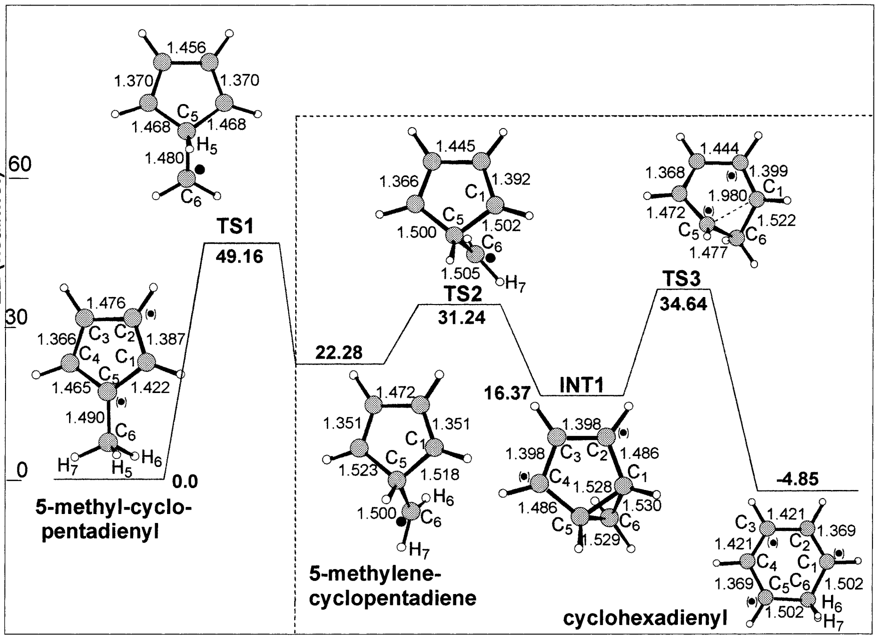


Figure 3. Reaction pathway for 5-methylcyclopentadienyl ring expansion. Relative energies (kcal/mol) are calculated at the QCISD(T)//B3LYP/cc-pVDZ level of theory. The broken frame separates the species that belong to the 5-methylenecyclopentadiene → cyclohexadienyl process. Bond distances are given in Å units.

TABLE 1: Total Energies E_{total} (au), Zero Point Energies, Relative Energies ΔE,[a] Imaginary Frequencies,[b] Entropies,[c] and Spin Contamination for All the Species on the Ring Expansion Surface of 5-Methylcyclopentadienyl (I(a), Figure 1), Calculated at the uB3LYP/cc-pVDZ and uQCISD(T)/cc-pVDZ//uB3LYP/cc-pVDZ Levels of Theory and uB3LYP/aug-cc-pVDZ* and uQCISD(T)/cc-pVDZ//UB3LYP/aug-cc-pVDZ*

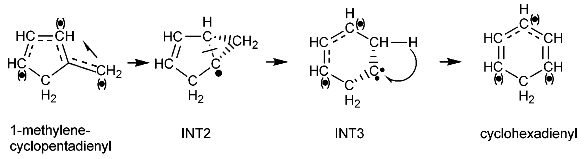
		UB3LYP						uQCISD(T)	
species	basis set	E_{total}	ΔE^a	ZPE	S^c	ν^b	$\langle S^2\rangle$	E_{total}	ΔE
I(a)	cc-pVDZ	−232.798034	0.00	66.58	77.23		0.7760	−232.114374	0.0
I(a)	aug-cc-pVDZ	−232.811001	0.00	66.46	77.09		0.7654	−232.114319	0.0
TS1	cc-pVDZ	−232.719884	46.61	64.15	73.94	(i-1565)	0.7607	−232.032156	49.16
TS1	aug-cc-pVDZ	−232.734579	45.52	64.02	73.96	(i-1544)	0.7600	−232.032079	49.19
I(b)	cc-pVDZ	−232.756370	25.71	66.15	78.04		0.7541	−232.078185	22.28
I(b)	aug-cc-pVDZ	−232.770234	24.82	66.00	78.60		0.7542	−232.078077	22.28
TS2	cc-pVDZ	−232.746353	32.04	66.19	72.10	(i-503)	0.7901	−232.063963	31.24
TS2	aug-cc-pVDZ	−232.760533	31.38	66.17	72.11	(i-489)	0.7876	−232.063801	31.41
INT1	cc-pVDZ	−232.770926	18.15	67.73	71.61		0.7757	−232.090116	16.37
INT1	aug-cc-pVDZ	−232.784138	18.09	67.69	71.68		0.7746	−232.089993	16.49
TS3	cc-pVDZ	−232.742660	35.05	66.69	71.65	(i-714)	0.7810	−232.059354	34.64
TS3	aug-cc-pVDZ	−232.757090	34.20	66.73	71.63	(i-701)	0.7790	−232.059266	34.82
cyclohexadienyl	cc-pVDZ	−232.806946	−4.23	67.94	73.18		0.7885	−232.119936	−4.85
cyclohexadienyl	aug-cc-pVDZ	−232.819924	−4.26	67.80	73.36		0.7863	−232.119875	−2.15

[a] Relative energies in kcal/mol. $\Delta E = \Delta E_{total} + \Delta(\text{ZPE})$. [b] Imaginary frequencies in cm^{-1}. [c] Entropies in cal/(K·mol).

The final product cyclohexadienyl radical is planar. Among the six C−C bonds in the molecule two, C(1)−C(2) and C(4)−C(5), are double bonds, having lengths of 1.369 Å; two, C(1)−C(6) and C(5)−C(6), are single bonds; and the remaining two, C(2)−C(3) and C(3)−C(4), have lengths of 1.421 Å, which is practically the same as the bond length in benzene (∼1.40 Å). The electron density is almost evenly distributed among C(1), C(3), and C(5). The C(6)−H(6) and C(6)−H(7) bonds are 1.114 Å as compared to 1.093 Å in the intermediate and 1.091 Å in 5-methylenecyclopentadiene. The increased bond lengths indicate a weakening of these two bonds that facilitates the ejection of one hydrogen atom and the formation of benzene.

B. 1-Methylenecyclopentadiene. The process of ring expansion in 1-methylenecyclopentadiene to the cyclohexadienyl radical proceeds via two principle pathways. One is somewhat similar to the process of the ring expansion in 5-methylenecyclopentadiene in the sense that the expansion occurs without cleavage of the five-membered ring. The second pathway proceeds via cyclopentadiene ring cleavage.

SCHEME 2



a. Ring Expansion without Ring Cleavage. Scheme 2 describes the first pathway and the potential energy surface is shown in Figure 4.

The energetics is shown in Table 2. There are three transition states on the surface, TS4, TS5, and TS6, and two intermediates, INT2 and INT3. The reaction coordinates represented by TS4 and TS5 are similar to the ones in TS2 and TS3 for 5-methylcyclopentadienyl expansion (Figure 3). Note that to form the three-membered ring, C(6) must form a bond with C(2), rather than C(5), because the latter, which is an SP^3 carbon, has already four bonds. There are, however, substantial differences in the

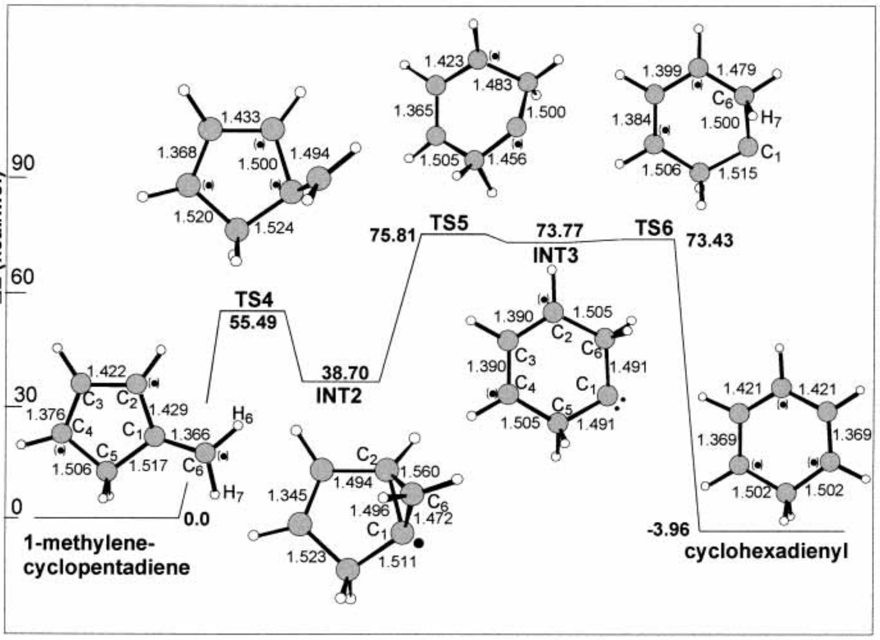


Figure 4. Reaction pathway for 1-methylenecyclopentadiene ring expansion via the closed-ring mechanism. Relative energies (kcal/mol) are calculated at the QCISD(T)//B3LYP/cc-pVDZ level of theory. Bond distances are given in Å units.

TABLE 2: Total Energies E_{total} (au), Zero Point Energies, Relative Energies ΔE,[a] Imaginary Frequencies,[b] Entropies,[c] and Spin Contamination for the All Species on the Ring Expansion Surfaces of 1-Methylenecyclopentadiene (II, Figure 1), Calculated at the uB3LYP/cc-pVDZ and uQCISD(T)/cc-pVDZ//uB3LYP/cc-pVDZ Levels of Theory

	uB3LYP						uQCISD(T)	
species	E_{total}	ΔE^{a}	ZPE	S^{c}	ν^{b}	$\langle S^2\rangle$	E_{total}	ΔE
II	−232.797961	0.00	67.09	74.09		0.7925	−232.112277	0.0
				Pathway without Ring Cleavage				
TS4	−232.705929	56.61	65.95	72.54	(i-297)	0.8091	−232.022037	55.49
INT2	−232.731849	36.28	67.87	72.20		0.7590	−232.051680	38.70
TS5	−232.676869	74.47	65.57	72.82	(i-327)	0.9191	−231.989046	75.81
INT3	−232.679695	71.88	64.76	79.21		1.1034	−231.991000	73.77
TS6	−232.676748	73.12	64.15	74.38	(i-640)	0.7756	−232.990566	73.43
				Pathway with Ring Cleavage				
TS7	−232.708546	53.05	64.03	77.16	(i-682)	0.7877	−232.019403	55.22
INT4	−232.748563	29.18	65.27	81.20		0.7901	−232.056273	33.32
TS8	−232.703494	57.65	65.46	74.60	(i-602)	0.8045	−232.013085	60.61
INT5	−232.747464	32.77	68.17	73.60		0.7671	−232.066794	29.62
TS9	−232.683957	68.87	64.42	73.90	(i-1596)	0.7810	−231.995289	70.74
cyclohexadienyl	−232.806946	−4.79	67.94	73.18		0.7885	−232.119936	−3.96

[a] Relative energies in kcal/mol. $\Delta E = \Delta E_{\mathrm{total}} + \Delta(\mathrm{ZPE})$. [b] Imaginary frequencies in cm^{-1}. [c] Entropies in cal/(K·mol).

geometry, electron distribution, and energetics of the processes in 5-methylenecyclopentadiene and 1-methylenecyclopentadiene. In addition, whereas transition state TS3 (Figure 3) leads directly to the formation of the cyclohexadienyl radical, TS5 leads to an intermediate INT3 (Figure 4) that forms the cyclohexadienyl radical via an additional transition state, TS6.

Figure 4 shows the bond length distribution in all the species on the surface. As can be seen in 1-methylenecyclopentadiene, the C(1)−C(6) bond has a length close to a double bond (bond order of 1.68) and thus the methylene group C(1)H(6)H(7) has only a partial free radical character and the electron density is evenly distributed among C(6), C(2), and C(4). These findings are in contrast with the distribution in 5-methylenecyclopentadiene, because in the latter C(5) has four bonds that prevent conjugation between the methylene group and the ring. The conjugation between the methylene group and the ring in 1-methylenecyclopentadiene expresses itself also by resonance stabilization of the radical. Indeed, 1-methylenecyclopentadiene is more stable than 5-methylenecyclopentadiene by some 20 kcal/mol (Figure 1). On the other hand, the picture is reversed when the intermediates INT1 (Figure 3) and INT2 (Figure 4) are concerned. INT2 has no resonance stabilization whereas, as has been mentioned before, INT1 is resonance stabilized. INT2 is less stable than 1-methylenecyclopentadiene by ∼39 kcal/mol, whereas INT1 is more stable than 5-methylenecyclopentadiene by some 6 kcal/mol. The high instability of INT2 relative to 1-methylenecyclopentadiene causes a high barrier of ∼55 kcal/mol for the process 1-methylenecyclopentadiene → TS4 → INT2, whereas the barrier of 5-methylenecyclopentadiene → TS2 → INT1 is only ∼9 kcal/mol. Note that the barrier of the reverse processes (INT → TS) is almost the same for the two radicals.

INT2, via transition state TS5, produces an intermediate INT3, which is a radical that has also a carbene structure on C(1). It is a nonplanar species with a dihedral angle of $\tau\{C(4)C(5)C(1)C(6)\} = 13.39°$. The reaction coordinate of this

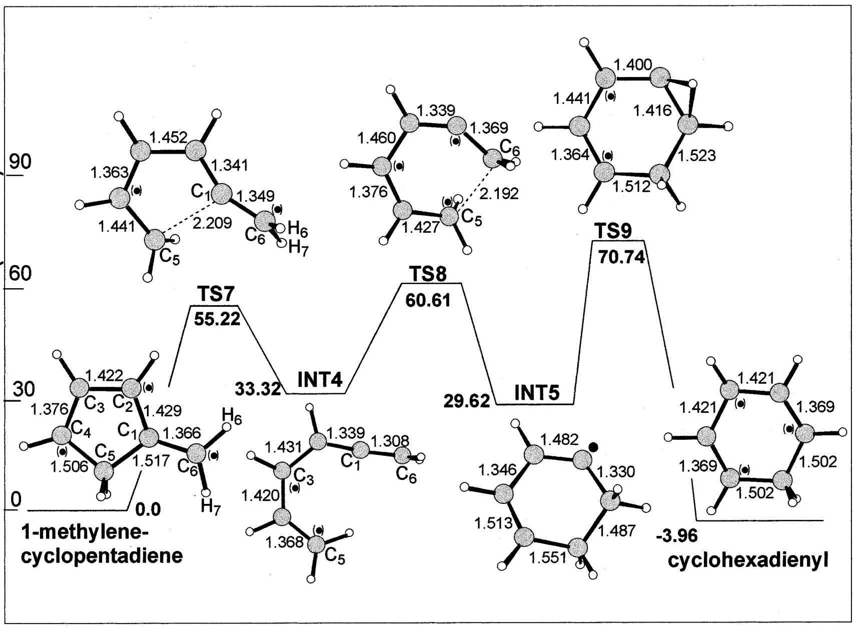
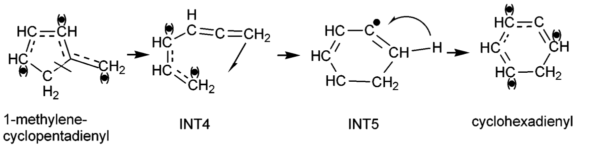


Figure 5. Reaction pathway for 1-methylenecyclopentadiene ring expansion via the open-ring mechanism. Relative energies (kcal/mol) are calculated at the QCISD(T)//B3LYP/cc-pVDZ level of theory. Bond distances are given in Å units.

SCHEME 3



step that is similar to INT1 → TS3 is a C(1)−C(2) bond stretch combined with a C(1)C(6)C(2) angle bend (Figure 4). This results in a C(1)−C(2) bond rupture and combining of the bicyclic five-membered and three-membered rings to a six-membered ring. To transfer the intermediate INT3 into the cyclohexadienyl radical, an H-atom shift from C(6) to C(1) must take place. This shift takes place via transition state TS6. The TS5−INT3−TS6 section of the surface is very shallow and the shift takes place with practically no barrier. From the kinetics viewpoint, the last section of the process of ring expansion can be described by the path INT2 → TS6 → cyclohexadienyl radical.

The highest energy barrier on the potential energy surface for the 1-methylenecyclopentadiene ring expansion, which is the location of TS5 is 75.81 kcal/mol at the uQCISD(T) level of theory.

We tried to establish an additional reaction path avoiding a carbene structure intermediate by shifting an H atom prior to the formation of the six-membered ring. We did indeed find such a pathway, but with a considerably higher barrier, 88.29 kcal/mol at the uQCISD(T)//uB3LYP/cc-pVDZ level of theory namely, ∼12 kcal/mol higher than the previously described pathway. Because this pathway represents a considerably slower process, we will not discus its potential surface.

b. Ring Expansion with Ring Cleavage. Scheme 3 describes the pathway for ring expansion in 1-methylenecyclopentadiene with ring cleavage.

The potential energy surface is shown in Figure 5. The five-membered ring is opened and the methylene group is then combined with C(5) that was previously a member of the five-membered ring, to form the six-membered ring. Table 2 shows the energetics and other parameters on the surface. The surface contains three transition states TS7, TS8, and TS9 and two intermediates, INT4 and INT5.

Because C(1)−C(5) is a single bond and C(1)−C(2) has a bond order of 1.32 (Figure 2), C(1)−C(5) is broken preferentially. C(1)−C(5) is extended from 1.517 Å in 1-methylenecyclopentadiene to 2.209 Å in the transition state TS7 with the barrier of 55.22 kcal/mol. C(1)−C(5) in TS7 is practically a broken bond. The atom movement in the normal mode of the imaginary frequency indicates that the reaction coordinate is composed of two processes, C(1)−C(5) stretching and a rotation of the methylene group H(6)C(6)H(7), with respect to the ring plane.

The intermediate INT4 has an open ring structure. The electron density is higher on C(3) than on C(5). INT4 closes to a six-membered ring in INT5 via transition state TS8 (Figure 5). The transition state TS8 is still an open ring structure, but the angle C(6)C(1)C(2), which is close to 180° in INT4 bends to 140.2° in TS8, thus decreasing the distance between C(5) and C(6) from 3.228 to 2.192 Å toward the formation of a new C(5)−C(6) bond.

Similar to INT3, the formation of the cyclohexadienyl radical from INT5 still requires a 1,2-H-atom shift. This takes place via transition state TS9 with a barrier of 41.12 kcal/mol at the uQCISD(T)//uB3LYP/cc-pVDZ level of theory. Note the big difference between the structure and stability of INT3 in the two fused-ring pathways (Figure 4) and INT5 in the open-ring pathway (Figure 5). Whereas INT3 is a carbene and as such is very unstable, INT5 is a stable radical. The difference between their stability is ∼44 kcal/mol.

In summary, the highest energy level on the two fused ring pathway (Figure 4) is 75.81 kcal/mol (TS5), whereas the highest level on the open ring pathway (Figure 5) is 70.74 kcal/mol (TS9) at the uQCISD(T)//uB3LYP//cc-pVDZ level of theory. The difference is not dramatic and the two pathways proceed in parallel.

C. Ring Expansion in 2-Methylenecyclopentadiene. Scheme 4 describes the ring expansion in 2-methylenecyclopentadiene.

Figure 6 shows its potential energy surface. We found only one pathway for this process, which is a closed ring pathway. There are three transition states on the surface, TS10, TS11,

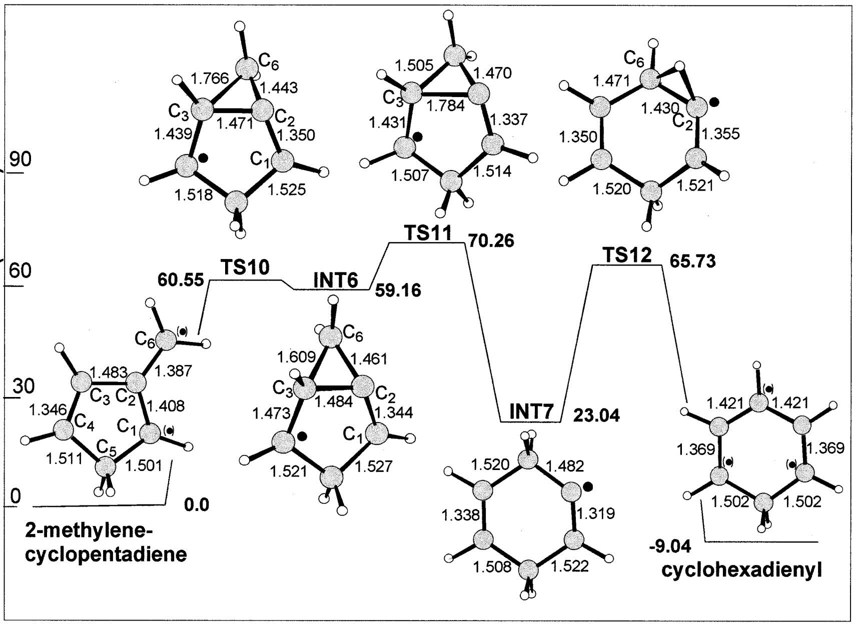


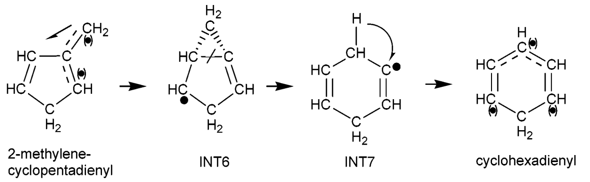
Figure 6. Reaction pathway for 2-methylenecyclopentadiene ring expansion. Relative energies (kcal/mol) are calculated at the QCISD(T)//B3LYP/cc-pVDZ level of theory. Bond distances are given in Å units.

TABLE 3: Total Energies E_{total} (au), Zero Point Energies, Relative Energies ΔE,[a] Imaginary Frequencies,[b] Entropies,[c] and Spin Contamination for All the Species on the Ring Expansion Surface of 2-Methylenecyclopentadiene (III, Figure 1), Calculated at the B3LYP/cc-pVDZ and QCISD(T)/cc-pVDZ//B3LYP/cc-pVDZ Levels of Theory

	B3LYP						QCISD(T)	
species	E_{total}	ΔE^{a}	ZPE	S^{c}	ν^{b}	$\langle S^2\rangle$	E_{total}	ΔE
III	−232.788014	0.00	66.83	74.09		0.7866	−232.103756	0.0
TS10	−232.687306	61.78	65.41	72.73	(i-455)	0.7646	−232.004995	60.55
INT6	−232.688697	61.67	66.18	73.86		0.7560	−232.008449	59.16
TS11	−232.674234	76.54	65.73	73.16	(i-730)	0.7912	−231.990037	70.26
INT7	−232.748542	23.54	68.06	74.14		0.7595	−232.068994	23.04
TS12	−232.681045	64.86	64.57	73.09	(i-1856)	0.7634	−231.995407	65.73
cyclohexadienyl	−232.806946	−10.77	67.94	73.18		0.7885	−232.119936	−9.04

[a] Relative energies in kcal/mol. $\Delta E = \Delta E_{\mathrm{total}} + \Delta(\mathrm{ZPE})$. [b] Imaginary frequencies in cm^{-1}. [c] Entropies in cal/(K·mol).

SCHEME 4



and TS12 and two intermediates INT6 and INT7. Several geometric parameters of the species on the surface are shown in Figure 6 and their energetics is given in Table 3. The pathway of ring expansion in 2-methylenecyclopentadiene contains the same steps that have been found in the closed ring pathway of 1-methylenecyclopentadiene ring expansion. Also, the reaction coordinates in these steps as they are reflected in the normal mode of the imaginary frequency are very much the same.

The first step on the 2-methylenecyclopentadiene surface is the formation of an intermediate INT6 with five- and three-membered rings fused together. This takes place via transition state TS10, where C(6) approaches C(3) toward the formation of a C(6)−C(3) bond in the intermediate. The intermediate INT6 is the less stable of all three intermediates that have bicyclic structures, namely, INT1, INT2, and INT6. We believe that this behavior is the result of the fact that carbon atom C(2) in INT6 is connected to C(1) by a double bond; namely, it has SP^2 hybridization. The fact that the two fused rings in INT6 are not in one plane distorts the SP^2 hybridization and decreases the stability of this intermediate. Thus, the energy level of INT6 relative to 2-methylenecyclopentadiene is ~59 kcal/mol whereas the level of INT2 relative to 1-methylenecyclopentadiene is ~39 kcal/mol.

The next step on the surface that proceeds via transition state TS11 is rupture of the C(2)−C(3) bond toward the formation of a six-membered ring, shown in Figure 6 as INT7. C(2)−C(3) that has a length of 1.484 Å in INT6 stretches to 1.784 Å in the transition state. As can be seen in Figure 6, the barrier of this process is only ~11 kcal/mol. It is interesting to compare this barrier to the barrier of the equivalent step in the closed ring pathway of 1-methylenecyclopentadiene, namely, INT2 → TS5 → INT3 (Figure 4), which is ~37 kcal/mol. The considerably higher barrier of the latter is the result of the high instability of INT3, which has a carbene structure. The equivalent step in 5-methylenecyclopentadiene, INT1 → TS3 → cyclohexadienyl radical, has also a lower barrier than the 37 kcal/mol in 1-methylenecyclopentadiene. The barrier height of the transition states for each one of these three processes is determined also by the extent of stretching of the bond that fuses the two rings, toward its rupture.

The final step on the surface of 2-methylenecyclopentadiene is a 1,2-H-atom shift from C(6) to C(2) in INT7 via transition state TS12 toward the formation of the cyclohexadienyl radical.

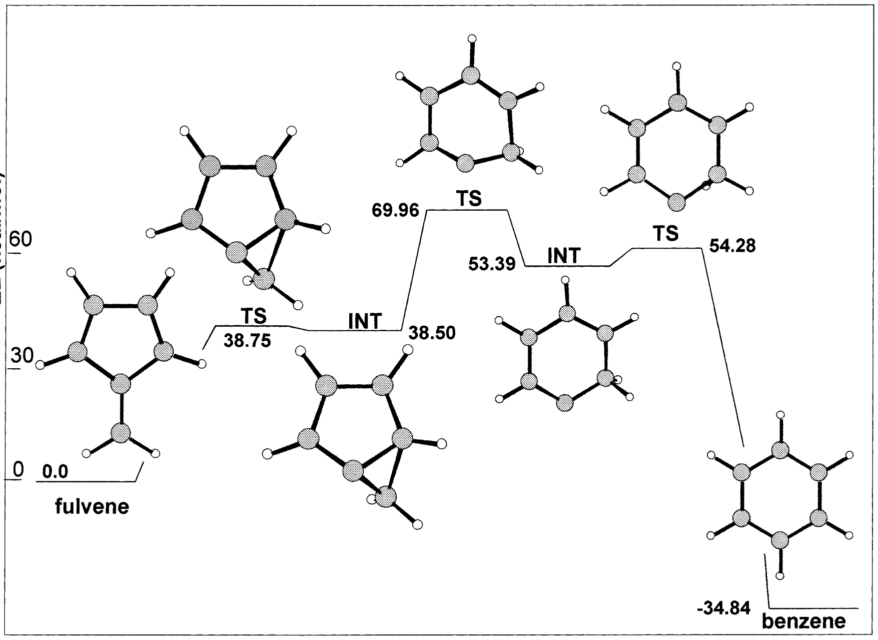


Figure 7. Reaction pathway for fulvene → benzene ring expansion. Relative energies (kcal/mol) are calculated at the QCISD(T)//B3LYP/cc-pVDZ level of theory.

The highest point on the surface relative to 2-methylenecyclopentadiene is that of TS11, which is 70.26 kcal/mol at the uQCISD(T)//uB3LYP//cc-pVDZ level of theory.

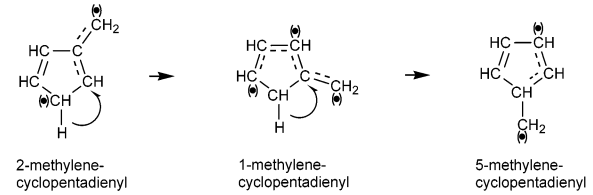
3. Ring Expansion in Fulvene. Both the 5-methylcyclopentadienyl radical and 5-methylenecyclopentadiene can eject an SP^3 hydrogen either from the methyl group or from the ring to form fulvene. We have calculated the barrier for H-atom ejection from the 5-methylenecyclopentadiene radical to form fulvene as ~32 kcal/mol. We have not calculated the barrier for 5-methylcyclopentadienyl, but it is probably of the same order of magnitude. The H-atom ejection path can take place in parallel to the ring expansion from these two radicals. Fulvene can now undergo ring expansion to form benzene. This process has been investigated in the past and potential energy surfaces of various reaction pathways have been established.[6] The pathway with the lowest barrier is characterized by the formation of both a bicyclic transition state and a bicyclic intermediate in the initial step. Rupture of the bond connecting the two rings with the formation of a six-membered ring and finally, 1,2-H-atom shift and formation of benzene complete the process.

We have recalculated the potential energy surface and confirmed the previous results. Figure 7 shows the surface with the pathways going from fulvene to benzene. It contains three transition states and two intermediates with the highest energy level on the surface being ~70 kcal/mol at the uQCISD(T)//uB3LYP//cc-pVDZ level of theory. This is in comparison with ~74 kcal/mol obtained at the G2M(rcc,MP2) level of theory.[6] We consider this agreement as quite satisfactory.

4. Isomerizations in 1- and 2-Methylenecyclopentadiene (H-Atom Shifts). As has been shown earlier, the ring expansion processes in 1- and 2-methylenecyclopentadiene proceed with much higher barriers than the process in 5-methylenecyclopentadiene. The question that arises is whether ring expansion from 1- and 2-methylenecyclopentadiene proceeds directly to the cyclohexadienyl radical or whether a faster route to ring expansion can take place via isomerization to the 5-methylene isomer.

We are not aware of any quantum chemical calculations of these isomerizations, which are practically 1,2-H-atom shifts.

SCHEME 5



We are aware however of experimental[26] and theoretical[7] studies on the isomerizations in the molecule methylcyclopentadiene. The energy barrier for the 5-methyl to 1-methyl isomerization was calculated as ~26 kcal/mol,[7] whereas ~24 kcal/mol was found experimentally.[26] We have therefore decided to calculate the rate constants for the interisomerizations of the methylenecyclopentadiene isomers and to carry out computer modeling to examine the rates for the possible pathways for ring expansion.

Scheme 5 describes the isomerization from 1- and 2-methylenecyclopentadiene to form 5-methylenecyclopentadiene.

The potential energy surface for the isomerization of 1-methylenecyclopentadiene to 5-methylenecyclopentadiene is shown in Figure 8 and for 2-methylenecyclopentadiene to 1-methylenecyclopentadiene is shown in Figure 9. The energetics and other parameters relevant to these surfaces are shown in Table 4. In both transition states TS13 (Figure 8) and TS14 (Figure 9) the reaction coordinates are 1,2-H atom shifts, accompanied by bond lengths redistribution in the ring. A major change in the transition states with respect to original radicals is the localization of the free electron density. Whereas, in both 1- and 2-methylenecyclopentadiene the electron density is distributed among several carbon atoms, the electron density in both transition states TS13 and TS14 is localized on the carbon atom of the methylene group.

The energy barrier of the 1-methylenecyclopentadiene → 5-methylenecyclopentadiene isomerization is 40.27 kcal/mol at the QCISD(T)//B3LYP/cc-pVDZ level of the theory, whereas the barrier for isomerization of 2-methylenecyclopentadiene to 1-methylenecyclopentadiene via transition state TS14 is 30.65

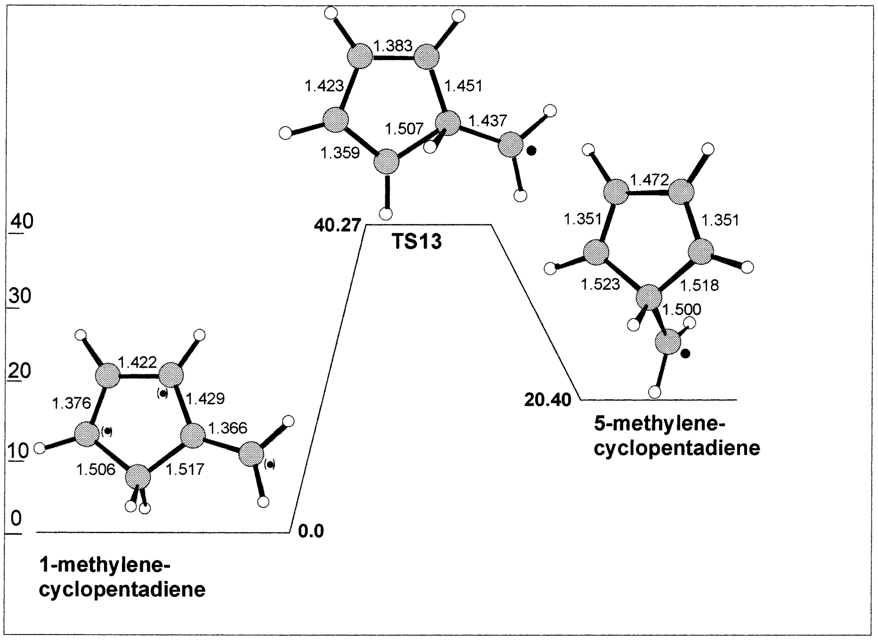


Figure 8. Reaction pathway for interisomerization 1-methylenecyclopentadiene → 5-methylenecyclopentadiene. Relative energies (kcal/mol) are calculated at the QCISD(T)//B3LYP/cc-pVDZ level of theory. Bond distances are given in Å units.

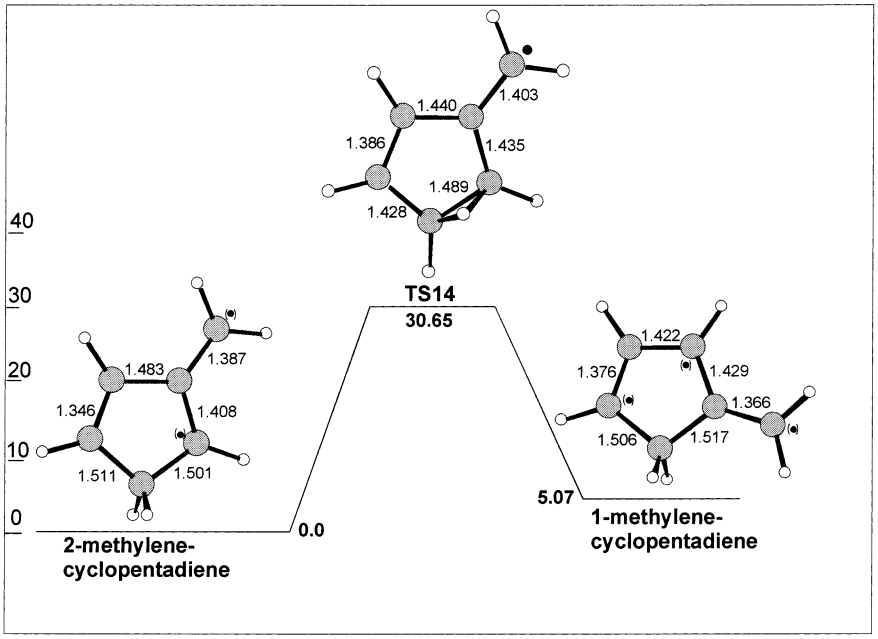


Figure 9. Reaction pathway for interisomerization 2-methylenecyclopentadiene → 1-methylenecyclopentadiene. Relative energies (kcal/mol) are calculated at the QCISD(T)//B3LYP/cc-pVDZ level of theory. Bond distances are given in Å units.

kcal/mol. This difference can be explained by the relatively large endothermicity of the 1- to 5-isomerization as compared to the 2- to 1-isomerization. Note that the back-reaction of 5-methylenecyclopentadiene → 1-methylenecyclopentadiene isomerization has a barrier of only 19.87 kcal/mol, whereas 1-methylenecyclopentadiene → 2-methylenecyclopentadiene has a barrier of 25.58 kcal/mol.

These results do not exclude the possibility that ring expansion of the 2- and 1-methylene isomers might be faster going via isomerization to the 5-methylene-isomer rather than going directly to the six-membered ring. The results of the rate constants and modeling calculations will be presented in the next section.

IV. Rate Constant Calculations

To evaluate the high-pressure limit, first-order rate constants from our quantum chemical calculations, the relation

$$k_\infty = \Gamma(T)\sigma(kT/h)\exp(\Delta S^{\#}/R)\exp(-\Delta H^{\#}/RT)$$

was used,[27,28] where h is Planck's constant, k is Boltzmann's factor, σ is the degeneracy of the reaction coordinate, $\Delta H^{\#}$ and $\Delta S^{\#}$ are the temperature dependent enthalpy and entropy of activation respectively and $\Gamma(T)$ is the tunneling correction. Because we deal with unimolecular reactions, $\Delta H^{\#} = \Delta E^{\#}$, where $\Delta E^{\#}$ is the energy difference between the transition state

TABLE 4: Total Energies E_{total} (au), Zero Point Energies, Relative Energies ΔE,[a] Imaginary Frequencies,[b] Entropies,[c] and Spin Contamination for All the Species on the Isomerization Surfaces of 1-Methylenecyclopentadiene (II, Figure 1) and 2-Methylenecyclopentadiene (III), Calculated at the B3LYP/cc-pVDZ and QCISD(T)/cc-pVDZ//B3LYP/cc-pVDZ Levels of Theory

	B3LYP						QCISD(T)	
species	E_{total}	ΔE^a	ZPE	S^c	ν^b	$\langle S^2\rangle$	E_{total}	ΔE
			1-Methylenecyclopentadiene → 5-Methylenecyclopentadiene					
II	−232.797961	0.00	67.09	74.09		0.7925	−232.112277	0.0
TS13	−232.730749	39.29	64.18	73.72	(i-1197)	0.7629	−232.043465	40.27
I(b)	−232.756370	25.16	66.15	78.04		0.7541	−232.078185	20.40
			2-Methylenecyclopentadiene → 1-Methylenecyclopentadiene					
III	−232.788014	0.00	66.83	74.09		0.7866	−232.103756	0.0
TS14	−232.740331	27.69	64.60	73.10	(i-1396)	0.7715	−232.051359	30.65
II	−232.797961	−5.98	67.09	74.09		0.7925	−232.112277	−5.07

[a] Relative energies in kcal/mol. $\Delta E = \Delta E_{\mathrm{total}} + \Delta(\mathrm{ZPE})$. [b] Imaginary frequencies in cm^{-1}. [c] Entropies in cal/(K·mol).

TABLE 5: Kinetic Parameters for Ring Expansion and Isomerization Reactions

		Arrhenius parameters		
reaction no.	reaction	A^a	$E_a{}^b$	$k(700\ \mathrm{K})^c$
R1	5-methylcyclopentadienyl → 5-methylenecyclopentadiene	3.0×10^{12}	50.4	3.9×10^{-4}
R2	5-methylenecyclopentadiene → cyclohexadienyl radical	1.4×10^{13}	17.4	3.6×10^{7}
R3	1-methylenecyclopentadiene → cyclohexadienyl radical	2.5×10^{13}	73.4	2.1×10^{-10}
R4	2-methylenecyclopentadiene → cyclohexadienyl radical	5.7×10^{12}	71.2	2.4×10^{-10}
R5	2-methylenecyclopentadiene → 1-methylenecyclopentadiene	3.7×10^{13}	31.5	3.8×10^{3}
R6	1-methylenecyclopentadiene → 5-methylenecyclopentadiene	7.4×10^{13}	42.0	4.0
R7	1-methylenecyclopentadiene → 5-methylenecyclopentadiene → cyclohexadienyl radical	3.8×10^{13}	40.8	5.6
R8	2-methylenecyclopentadiene → 1-methylenecyclopentadiene → 5-methylenecyclopentadiene → cyclohexadienyl radical			23.5[d]

[a] Preexponential factor in s^{-1}. [b] Activation energy in kcal/mol. [c] Rate constant (s^{-1}) at 700 K is taken from Figure 11. [d] The Arrhenius plot is not a straight line owing to multistage kinetics.

and the reactant. $\Delta E^{\#}$ is equal to $\Delta E^0_{\mathrm{total}} + \Delta E_{\mathrm{term}}$, where $\Delta E^0_{\mathrm{total}}$ is obtained by taking the difference between the total energies of the transition state and the reactant and ΔE_{term} is the difference between the thermal energies of these species.

The tunneling effects, in cases where H-atom shifts are important components of the reaction coordinate and the imaginary frequencies are high, were estimated using the Wigner's inverted harmonic model:[29]

$$\Gamma(T) = 1 + \frac{1}{24}\left(\frac{h\nu^{\#}}{kT}\right)^2 = 1 + \frac{1}{24}\left(\frac{hc\bar{\lambda}^{\#}}{kT}\right)^2$$

where $\bar{\lambda}^{\#}$ is the imaginary frequency of the reaction coordinate in cm^{-1}.[30,31]

The above relation for k_∞ was calculated for each step at several temperatures and the values were then plotted as log k vs $1/T$ to obtain the corresponding Arrhenius rate parameters.

In processes where the potential energy surface contains several intermediates, the overall unimolecular rate constant for the process must be calculated by solving a set of coupled differential rate equations that represent a series of consecutive unimolecular reactions. When the rate constants for all the steps are known, this can be calculated by constructing the corresponding reaction scheme and running computer modeling where all the steps on the surface including both the forward and the back-reactions are taken into account. The rate constants for the back-reactions are calculated from the constants of the forward reactions and the equilibrium constant of each individual step. The result of the computer modeling is the extent of product formation as a function of time from which a first-order rate constant is calculated using the relation: $k_{\mathrm{first}}t = -\ln(1 - [\mathrm{product}]_t/[\mathrm{product}]_0)$. We used values of $[\mathrm{product}]_t/[\mathrm{product}]_0$ at 2 ms. k_{first} was calculated for each path at several temperatures and the values were then plotted as log k vs $1/T$ to obtain the corresponding Arrhenius rate parameters. The values obtained are shown in Table 5 as reactions 1−6. Reactions 7 and 8 that correspond to consecutive isomerization and ring expansion are of the type A → B → C (R7) and A → B → C → D (R8). The overall rate constants for these two systems were also calculated using computer modeling in the same manner. The rate constant for reaction 7 obeys an Arrhenius rate expression (shown in Table 5) whereas the rate constant for reaction 7 that represents a more complicated path does not obey this relation.

As can be seen, the formations of cyclohexadienyl radicals from both 1-methylenecyclopentadiene and 2-methylenecyclopentadiene via isomerization to 5-methylenecyclopentadiene have much higher rate constants than the direct ring expansion. This can also be very well seen in Figures 10 and 11, where the unimolecular rate constants for ring expansion are plotted as an Arrhenius plot.

Kiefer et al.[4] have shown that a post shock analysis of a mixture of the three isomers of methylcyclopentadiene contained a considerable amount of aromatic compounds. They are clearly the result of ring expansion of the methylenecyclopentadiene radicals. The mixture also revealed the presence of minute quantities of 5-methylcyclopentadiene as compared the remaining 1-methyl and 2-methyl isomers. This verifies our finding that the 5-methylene isomer undergoes ring expansion much faster than the other two isomers.

V. Conclusions

The quantum chemical calculations presented in this article show that ring expansion in methylcyclopentadiene proceeds

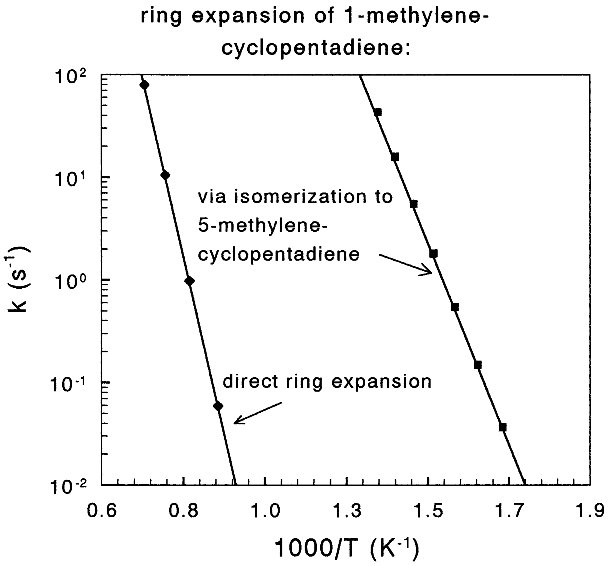


Figure 10. Arrhenius plot of the calculated rate constant of 1-methylenecyclopentadiene ring expansion via isomerization to 5-methylenecyclopentadiene and directly to the cyclohexadienyl radical.

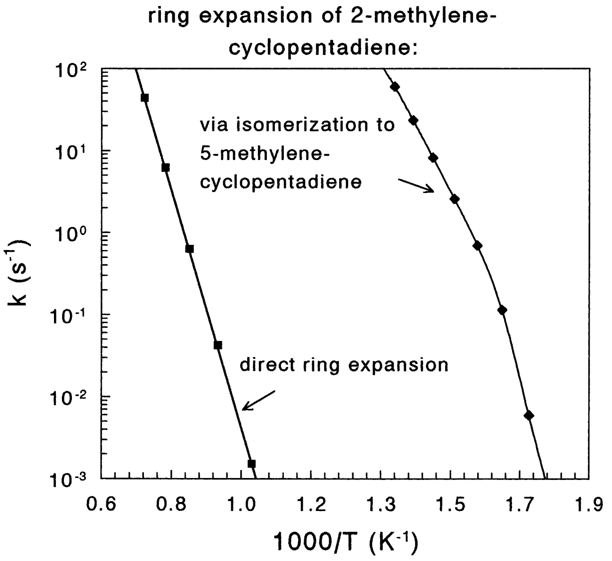


Figure 11. Arrhenius plot of the calculated rate constant of 2-methylenecyclopentadiene ring expansion via isomerization to 5-methylenecyclopentadiene and directly to the cyclohexadienyl radical.

via methylenecyclopentadiene radicals. Two different pathways were found for methylene group insertion into the cyclopentadiene ring. One pathway that was found for all three isomers of methylenecyclopentadiene takes place without cleavage of the five-membered ring. The second pathway, which was found only for the 1-methylenecyclopentadiene ring expansion proceeds via cyclopentadiene ring cleavage. All the pathways take place via stepwise mechanisms.

Because the energy barrier for ring expansion from 5-methylenecyclopentadiene is considerably lower than the barriers for the ring expansion from 1- and 2-methylenecyclopentadiene, and because the isomerizations of 2-methylenecyclopentadiene to 1-methylenecyclopentadiene and from 1-methylenecyclopentadiene to 5-methylenecyclopentadiene are fast, ring expansion from the 1-methylene and 2-methylene isomers takes place via the 5-methylene isomer.

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