J. Am. Chem. Soc. **1991**, *113*, 8628-8633

Theoretical Studies of the Ring-Opening Reactions of Bicycloalkyl Radicals: Electrocyclic and Degenerate Rearrangements in the Bicyclo[3.1.0]hex-3-en-2-yl Radical

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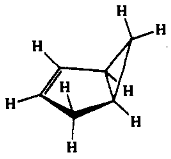
Received May 1, 1991

Abstract: Ab initio MCSCF calculations have been performed on the ring-opening and circumambulatory degenerate rearrangements in the bicyclo[3.1.0]hex-3-en-2-yl radical (**3**). The thermal ring opening of **3** to give cyclohexadienyl radical **5** is calculated to be a symmetry-forbidden electrocyclic process that takes place via a highly unsymmetric transition state lying about 16 kcal/mol above **3**. The degenerate 1,4-migration of the methylene group in **3** is predicted to be a two-step process, involving the formation of the cyclopentadienylmethyl radical (**6**) as the stable intermediate, rather than a pericyclic suprafacial 1,4-sigmatropic rearrangement. The calculated potential energy barrier for the first step (i.e., the ring opening **3** → **6**) of this degenerate rearrangement is 12.1 kcal/mol, while the second step of (i.e., the cyclization **6** → **3**) is predicted to be about 6 kcal/mol lower. The lower activation energy calculated for the **3** → **6** ring opening mode, as compared with that calculated for the alternative **3** → **5** ring-opening mode, is attributed to the fact that the SOMO in **3** can overlap to some extent with the exocyclic cyclopropane bonds, while this orbital is orthogonal to the inter-ring bond.

I. Introduction

Radical species containing small, strained bicycloalkyl structures are interesting because the rigid framework of carbon atoms can lead to unusual and even unprecedented chemical behavior.[1] The rearrangement of bicyclic cyclopropylallyl radicals does serve as an interesting example. While 1-cyclopropylallyl radicals (**1**) are less prone to undergo rearrangement by β-scission than their saturated analogues (**2**) (see Scheme I), some bicyclic cyclopropylallyls such as bicyclo[3.1.0]hex-3-en-2-yl radical (**3**) undergo rearrangements that can be formally regarded as pericyclic reactions.[2] Thus, the thermolysis of bicyclo[3.1.0]hex-2-ene (**4**) in the presence of di-*tert*-butyl peroxide in chlorobenzene at 130 °C affords benzene via an electrocyclic reaction involving cleavage of the inter-ring bond in **3** to give cyclohexadienyl radical (**5**).[3]



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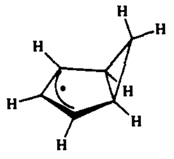

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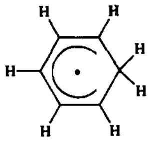

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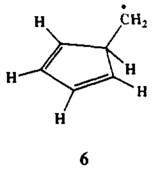
ESR studies of **3** in an adamantane matrix show that the **3** → **5** rearrangement has $\Delta G^{\ddagger} = 14.5$ kcal/mol at −50 °C.[4] Deuterium-substituted radicals such as **3a** were found to give cyclohexadienyl radicals (**5a**, **5b**, and **5c**) in which the deuterium atom was statistically distributed over the pentadienyl moiety.[4] This result implies the circumambulation of the methylene bridge about the five-membered ring in **3a**. Such a degenerate rearrangement (e.g., **3a** → **3b**) involves cleavage of the exocyclic cyclopropane bonds in **3** (see Scheme II) and must have a barrier of activation smaller than that for the electrocyclic ring-opening reaction **3a** → **5a**, namely, $\Delta G^{\ddagger} < 14.5$ kcal/mol at −50 °C. As noted by Beckwith and Ingold,[2] it seems probable that this formal suprafacial 1,4-sigmatropic rearrangement is not truly pericyclic but involves a ring-opened intermediate such as cyclopentadienylmethyl radical (**6**). However, this hypothetical two-step mechanism for the 1,4-migration of the methylene group in **3** has not been experimentally established due to the failure to detect by ESR the putative intermediate **6** during the rearrangement.



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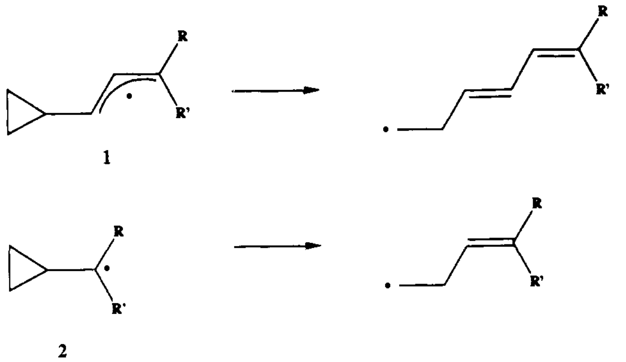
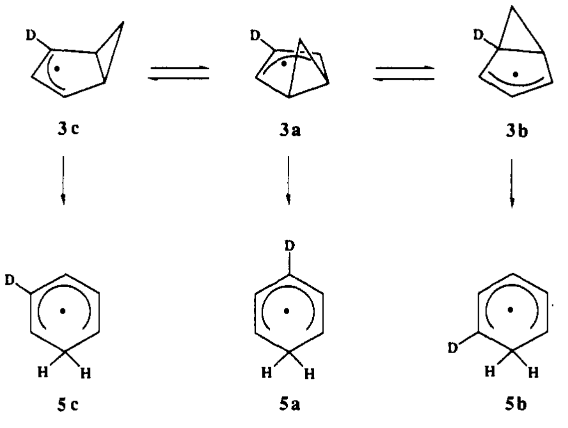
Scheme I



Scheme II



Besides the question concerning the possible intermediacy of **6** in the circumambulatory rearrangement of **3**, another important question remains unanswered: Why is the activation energy for this rearrangement smaller than that for the electrocyclic ring opening of **3**? While the degenerate rearrangement of **3** is (of necessity) thermoneutral, the ring opening of **3** to **5** must be exothermic because it leads to a substantial relief of ring strain and the formation of a conjugated pentadienyl system. Conse-

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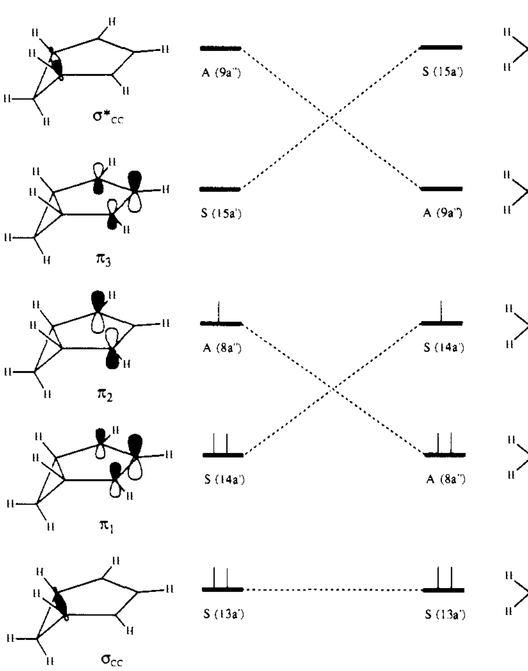

Figure 1. Molecular orbital correlation diagram for the disrotatory interconversion between bicyclo[3.1.0]hex-3-en-2-yl and cyclohexadienyl radicals.

quently, one would expect a lower energy of activation for the latter rearrangement as compared with the former (Hammond's postulate). This is an area where accurate quantum mechanical calculations should clearly be of major value in providing a response to such questions. To our knowledge, no theoretical study has been devoted yet to the rearrangement reactions of **3**.

As a part of a comprehensive theoretical study of the thermal rearrangement reactions in bicycloalkyl radicals, here we report the first ab initio molecular orbital (MO) investigation of the $C_6H_7^•$ potential energy surface associated to both the electrocyclic ring-opening reaction and the degenerate circumambulatory rearrangement of **3**.

II. Elementary Theoretical Considerations

The first step in the present investigation was to determine the geometrical requirements of the transition structures for the two different ring-opening modes of **3**, involving cleavage of either the inter-ring bond or one exocyclic cyclopropane bond, respectively, as well as the characteristics of the electronic wave function describing these processes.

In principle, during the ring opening of **3** into **5** the methine hydrogens adjacent to the inter-ring CC bond might move in either a disrotatory or conrotatory fashion. However, owing to the severe geometrical constraint in **3**, only the disrotatory motion can take place. Figure 1 shows the correlation diagram for the MOs most directly involved in the disrotatory conversion of **3** into **5**. For **3** these are the orbitals associated with the CC bond that is broken (σ_{CC} and σ^*_{CC}) and the three π orbitals (π_1, π_2, and π_3) of the allyl moiety, while for **5** these are the five π orbitals (π_1, π_2, π_3, π_4, and π_5) of the pentadienyl moiety. Each of these orbitals is classified by symmetry labels (S, symmetrical; A, antisymmetrical) relating to the symmetry plane that is maintained during the conventional disrotatory process, namely, the plane bisecting the central CC bond in **3**. Alternative symmetry labels appropriate to the irreducible representations (a′ or a″) of the common point group C_s are also included. Assuming that the equilibrium geometry of **3** has C_s molecular symmetry, its ground-state electron configuration can be written in short form as

$$...(13a')^2(14a')^2(8a'')^1 \qquad (1)$$

As regards **5**, it is reasonable to assume that its equilibrium geometry has C_{2v} symmetry. Then the ground-state electron configuration is found to be

$$...(1b_1)^2(1a_2)^2(2b_1)^1 \qquad (2)$$

If C_{2v} molecular geometry is retained but the individual MOs are classified according to the lower symmetry point group C_s then the ground-state electron configuration of **5** is written

$$...(13a')^2(8a'')^2(14a')^1 \qquad (3)$$

From configurations 1 and 3 it follows that the ground states of **3** ($^2A''$) and **5** ($^2A'$) belong to different symmetry classes of the common point group C_s, and in order to conserve the orbital symmetry, the disrotatory thermal reaction would thus always have to give an electronically excited state of the product. Therefore, if it is assumed that the rearrangement proceeds through a pathway conserving the symmetry plane bisecting the inter-ring CC bond, it becomes apparent that the thermal interconversion between **3** and **5** is both orbital-symmetry forbidden and state-symmetry forbidden. This suggests that the thermal electrocyclic conversion of **3** into **5** is a nonadiabatic reaction. However, this prediction seems to be in direct contradiction with the fact that the ESR spectrum of **5** is observed at temperatures above −60 °C in adamantane as matrix. For this reason, it is unlikely that the reaction gives an electronically excited state of the product.

Perturbation by not fully concerted changes in the geometrical parameters during the reaction can lead to a complete annulment of the symmetry of **3**, and consequently, this would allow an interaction between the aforementioned configurations of the unperturbed system, which should force the correlation between the ground states. On the basis of this hypothesis, it appears that in order to locate a true transition structure on the potential energy surface for the conversion of **3** into **5**, it is necessary to destroy the initial molecular symmetry along the reaction path, by performing adequate distortions of the geometrical parameters in the sense of not allowing a synchronous change of their values from the reactant to the product. Concerning the electronic wave function, we note that in order to account for the change in the MO configuration along the pathway, it should at least include the configurational interaction between the crossing pair of configurations (i.e., 1 and 3). An obvious choice is a multiconfiguration self-consistent-field (MCSCF) wave function of the "complete active space" (CAS) class,[5,6] hereafter designated CASSCF.

Regarding the ring-opening mode of **3** involving cleavage of an exocyclic cyclopropane bond, it is worth noting that the symmetry plane of **3** is not maintained during this bond-breaking process. As a consequence, it should not be difficult to locate the corresponding transition structure on the reaction pathway obtained using the conventional reaction coordinate method (e.g., using the length of the breaking bond in **3** as the reaction coordinate) starting at the equilibrium geometry of **3**. However, the electronic wave function must describe the electronic changes that take place at the transition structure. These consist in starting the formation of a new π bond in the five-membered ring by coupling the formerly unpaired electron in **3** with one of the two electrons of the CC bond being broken while the other electron is localized on the methylene group. Obviously, such an electronic rearrangement cannot be adquately described by a restricted single-configuration wave function. Again, a CASSCF wave function seems to be the best choice.

III. Computational Details

The equilibrium geometries of **3**, **5**, and **6** as well as the transition structures for the ring opening of **3** involving cleavage of either the inter-ring bond (designed TS1) or one exocyclic cyclopropane bond (designed TS2), were initially optimized by using the spin-unrestricted Hartree–Fock (UHF)[7] version of the AM1 (UAM1) semiempirical SCF

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Table I. Expectation Values of S^2 and Occupation Numbers of the Relevant Natural Orbitals of the UHF/3-21G Wave Function of Bicyclo[3.1.0]hex-3-en-2-yl (**3**), Cyclohexadienyl (**5**), and Cyclopentadienylmethyl (**6**) Radicals and the Transition Structures for the Ring Opening of **3** To Give **5** (TS1) or **6** (TS2)[a]

		$\langle S^2 \rangle$		occupation no. for natural orbitals				
species	state	BA[b]	AA[c]	ϕ_i	ϕ_j	ϕ_o	ϕ_k	ϕ_l
3	$^2A''$	0.976	0.762	1.9970	1.8932	1.0000	0.1068	0.0030
TS1	^2A	1.258	0.915	1.9205	1.8158	1.0000	0.1842	0.0795
5	$^2B_1$	1.224	0.896	1.9315	1.8282	1.0000	0.1718	0.0685
TS2	^2A	1.224	0.898	1.9248	1.8343	1.0000	0.1657	0.0752
6	^2A	1.308	0.922	1.9390	1.7649	1.0000	0.2351	0.0610

[a] All calculations at the UHF/3-21G-optimized geometries. [b] Before annihilation of the quartet-state component. [c] After annihilation of the quartet-state component.

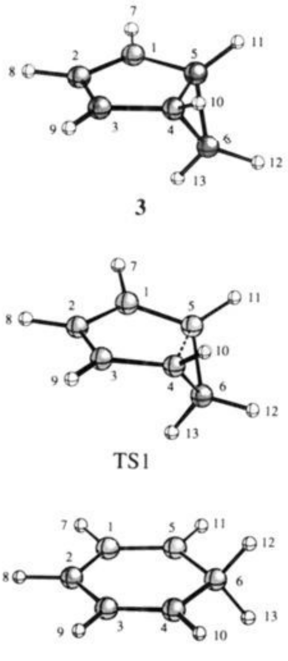
Table II. Selected Geometrical Parameters[a] of the CASSCF/3-21G-Optimized Equilibrium Structures of Bicyclo[3.1.0]hex-3-en-2-yl (**3**) and Cyclohexadienyl (**5**) Radicals and the Transition Structure of the Ring Opening of **3** To Give **5** (TS1)

	3	TS1	**5**
molecular symmetry	C_s	C_1	C_{2v}
bond lengths, Å			
C_1C_2	1.398	1.448	1.425
C_2C_3	1.398	1.362	1.425
C_1C_5	1.497	1.418	1.364
C_3C_4	1.497	1.487	1.364
C_4C_5	1.527	1.975	2.523
C_6C_4	1.524	1.489	1.515
C_6C_5	1.524	1.518	1.515
bond angles, deg			
$H_{10}C_4C_3$	120.4	123.4	120.5
$H_{11}C_5C_1$	120.4	121.6	120.5
$C_6C_5C_1$	114.9	119.1	122.3
$C_6C_4C_3$	114.9	114.1	122.3
dihedral angles, deg			
$H_{10}C_4C_3C_2$	143.5	132.0	180.0
$H_{11}C_5C_1C_2$	143.5	151.8	180.0
$C_6C_4C_3C_2$	62.7	49.2	0.0
$C_6C_5C_1C_2$	62.7	33.0	0.0
plane–plane angles, deg			
$(C_4C_6C_5)(C_1C_2C_3)$	109.3	109.5	180.0
$(H_{10}C_4C_6)(C_2C_3C_4)$	54.8	48.8	0.0
$(H_{11}C_5C_6)(C_2C_1C_5)$	54.8	31.4	0.0

[a] Atom numbering as in Figure 2.

MO method[8] as implemented in the AMPAC program[9] and then further optimized within the framework of the UHF method with the 3-21G split-valence basis set[10] employing analytical gradient procedures.[11,12] All these ab initio UHF calculations were performed with a locally modified version[13] of the GAUSSIAN 80 system of programs.[14] Finally, the resulting structures were reoptimized employing the CASSCF approach.

The CAS was selected following the procedure recently suggested by Pulay and Hamilton,[15] based on the fractional occupation of the natural orbitals of the UHF wave function (designated UNOs). Table I lists the occupation numbers of the relevant UNOs of **3**, TS1, **5**, TS2, and **6**, computed from the UHF/3-21G wave function, along with the expectation values of the spin-squared operator S^2. In the case of TS1, **5**, TS2, and **6** the fractional occupancies of the UNOs indicate that there are five active orbitals, hereafter referred as to ϕ_i, ϕ_j, ϕ_o, ϕ_k, and ϕ_l, where ϕ_o is the MO describing the unpaired electron. As expected, for TS1 and TS2 ϕ_j and ϕ_k are the bonding and antibonding MOs of the CC bond being broken. Regarding **5** and **6**, ϕ_j and ϕ_k are the highest doubly occupied and the lowest unoccupied π MOs, respectively. Finally, for TS1, **5**, TS2, and **6** the remaining active orbitals (i.e., ϕ_i and ϕ_l) are the lowest occupied and the highest unoccupied π MOs, respectively. Distribution of the five reacting electrons within the five active orbitals with all possible couplings leads to a MCSCF wave function for TS1, **5**, TS2, and **6** formed as a linear combination of 75 doublet spin-adapted configuration state functions (CSFs). In the case of **3** there are only three UNOs showing significant fractional occupancy (i.e., ϕ_j, ϕ_o, and ϕ_k), which correspond to the three π orbitals of the allyl moiety. Distribution of the three π electrons within these three active orbitals with all possible couplings leads to a MCSCF wave function for **3** formed as a linear combination of 8 doublet spin-adapted CSFs.



3

TS1

5

Figure 2. Computer plots of the CASSCF/3-21G-optimized equilibrium structures of bicyclo[3.1.0]hex-3-en-2-yl (**3**) and cyclohexadienyl (**5**) radicals and of the transition structure for the ring opening of **3** to give **5** (TS1).

All CASSCF calculations were carried out by using the GAMESS system of programs,[16] which includes a Newton–Raphson orbital optimization procedure for MCSCF wave functions.[17] Molecular geometries were optimized with the 3-21G basis set either by the Murtagh–Sargent[11] (equilibrium structures) or the Schlegel[12] (transition structures) multiparameter search routines, employing analytically calculated forces. Cartesian coordinates of all CASSCF/3-21G-optimized structures of this investigation are available as supplementary material. The harmonic vibrational frequencies of these structures were calculated with the 3-21G basis set, both to characterize these stationary points as minima (representing equilibrium structures) or saddle points (representing transition structures) and to evaluate zero-point vibrational energy (ZPVE) corrections to the relative energies, by diagonalizing the mass-weighted Cartesian force constant matrix, computed numerically by finite differences of analytical gradients.[18] The displacement Cartesian coordinates

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Table III. Calculated Total Energies (Hartrees) and Zero-Point Vibrational Energies (kcal/mol) of Bicyclo[3.1.0]hex-3-en-2-yl (**3**) and Cyclohexadienyl (**5**) Radicals and the Transition Structure for the Ring Opening of **3** To Give **5** (TS1)[a,b]

species	state	CASSCF/3-21G	CASSCF/6-31G*	ZPVE
3[c]	$^2A''$	−229.94993 (0.0)	−231.24110 (0.0)	72.7
TS1	^2A	−229.92639 (14.8)	−231.21273 (17.8)	70.9
5	$^2B_1$	−230.00223 (−32.8)	−231.28709 (−28.9)	72.2

[a] All calculations at the CASSCF/3-21G-optimized geometries. [b] The quantities in parentheses are the relative energies in kcal/mol. [c] Taking as active orbitals the bonding and antibonding MOs associated with the C_4C_5 bond, in addition to the three π MOs.

of the normal coordinates associated with the imaginary frequencies of the transition structures are available as supplementary material.

In order to obtain reliable relative energies, additional CASSCF single-point calculations were performed with the split-valence plus d-polarization 6-31G* basis set.[19] To compare the energy of structure **3** with those of TS1, **5**, TS2, and **6**, two different single-point CASSCF/6-31G* energy computations were performed for **3**. In these calculations both the MCSCF expansion and nature of the orbitals were defined by analytical continuation from TS1 and TS2. Hence, in addition to the three active MOs indicated by the fractional occupancy of the UNOs (i.e., ϕ_j, ϕ_o, and ϕ_k), the bonding and antibonding MOs of the CC bond undergoing cleavage were taken as the active orbitals ϕ_i and ϕ_l of **3** in each case.

IV. Results and Discussion

Electrocyclic Ring Opening. The most relevant geometrical parameters of the CASSCF/3-21G-optimized transition structure TS1 are given in Table II, along with those of the equilibrium structures computed at the same level of theory for **3** and **5**. Figure 2 contains drawings illustrating the numbering scheme used to describe the geometrical parameters. The total and relative energies calculated with the CASSCF wave function (including the 75 doublet spin-adapted CSFs) using the 3-21G and 6-31G* basis sets are summarized in Table III. The ZPVE computed at the CASSCF/3-21G level are also given in Table III.

As can be seen from Table II, at the transition structure the CC bond undergoing cleavage has stretched to 1.975 Å. This is slightly shorter than the value of 2.066 Å obtained for the corresponding CC bond in the transition structure (calculated at the same level of theory) for the related ring-opening reaction of cyclopropyl radical (**7**) to give allyl radical (**8**).[20] The interesting feature here is that the transition structure for the formal electrocyclic rearrangement of **3** to **5** is highly unsymmetrical. In particular, note the differences in the lengths of the bonds that in **3** and **5** are equal (e.g., C_1C_2 and C_1C_3, C_1C_5 and C_3C_4, C_6C_4 and C_6C_5). These geometrical features are similar to those noted in the transition structure (calculated at the same level of theory) for the ring opening of bicyclo[1.1.1]but-2-yl radical (**9**) to give cyclobutenyl radical (**10**).[21] In both ring-opening reactions there is a nonsymmetric change of the geometrical parameters in passing from the reactant to the product. As noted in section II, these nonsymmetric geometrical changes along the minimum energy reaction path allow the correlation between the electronic ground states of the reactant and the product, which belong to different symmetry classes of the common molecular point group.

7 **8**

9 **10**

The potential energy barrier for the formation of **5** from **3** via TS1 is 14.8 kcal/mol at the CASSCF/3-21G level and becomes 13.0 kcal/mol after including the ZPVE correction. When using the single-point CASSCF/6-31G* energies plus the ZPVE correction, an energy of activation at 0 K of 16.0 kcal/mol is predicted. The experimental $\Delta G^\ddagger$ at −50 °C is 14.5 kcal/mol.[4] From the harmonic frequencies and moments of inertia the absolute entropies of **3** and TS1 were computed by standard methods.[22] These led to an activation entropy ($\Delta S^\ddagger$) of 0.3 cal/mol at −50 °C. From this theoretical $\Delta S^\ddagger$ and the experimental $\Delta G^\ddagger$ an activation enthalpy ($\Delta H^\ddagger$) of 14.6 kcal/mol at −50 °C can be estimated. Consequently, the activation energy of 16.0 kcal/mol at 0 K calculated at the highest level of theory of this investigation is in reasonable agreement with the estimated value of $\Delta H^\ddagger$ at −50 °C. At this point it is worth mentioning that the starting UAM1 calculations predicted a $\Delta H^\ddagger$ of 14.7 kcal/mol at 25 °C. For the sake of comparison, we note that from the CASSCF/6-31G*-calculated energies plus the ZPVE correction an energy barrier of 21.9 kcal/mol was predicted[20] for the related electrocyclic ring-opening reaction **7** → **8**, in excellent agreement with the experimental activation energies ranging from 19.1 to 22 kcal/mol.[23-25]

The energy of reaction for the isomerization of **3** to **5** is calculated at the CASSCF/3-21G + ZPVE correction level to be −33.3 kcal/mol. The inclusion of d-polarization functions reduces this large exothermicity to −29.4 kcal/mol. While no experimental thermochemical data are available for this reaction, it is worth mentioning that although the CASSCF/6-31G* calculations describe satisfactorily the difference in electron correlation energy between the radical **3** and the transition structure TS1, this theoretical model is not adequate to account for the overall change in correlation energy that occurs in going from **3** to **5**. Better energies of reaction can only be obtained by including dynamical correlation effects in addition to the nondynamical ones accounted for in the CASSCF treatment, for example, when CI including all singly and doubly excited configurations (CISD) relative to the zeroth-order CASSCF wave function is performed.[26] Such sophisticated multireference CISD computations are beyond the scope of the present investigation. In this regard it is worth noting that for the related **7** → **8** ring opening the energy of reaction calculated at the CASSCF/6-31G* + ZPVE correction level is −35.5 kcal/mol,[20] which is 12.7 kcal/mol lower than the enthalpy of reaction of −22.8 ± 4.9 kcal/mol estimated from thermochemical data.[20] The computed energy of reaction for the **3** → **5** ring opening is then probably too negative by 13 kcal/mol.

Circumambulatory Degenerate Rearrangement. A detailed search of the potential energy surface failed to reveal any suprafacial 1,4-sigmatropic path for the methylene group migration in **3** or any direct path involving a single transition structure. On the other hand, it was identified a true transition structure (TS2) for the interconversion between **3** and **6**. Our calculations therefore imply that the degenerate 1,4-migration of the methylene group in **3** is a two-step process involving **6** as the stable intermediate, in agreement with the mechanism suggested by Beckwith and Ingold.[2] The most relevant geometrical parameters of the CASSCF/3-21G-optimized transition structure TS2 are given in Table IV, along with those of the three different structures (**6a**, **6b**, and **6c**) calculated at the same level of theory for **6**. For the sake of comparison, the corresponding values of these geometrical parameters for **3** are also given in the first column of Table IV. Figure 3 contains drawings illustrating the numbering scheme used to describe the geometrical parameters. The total and relative energies calculated at the CASSCF level of theory (including the

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Table IV. Selected Geometrical Parameters[a] of the CASSCF/3-21G-Optimized Equilibrium Structures of Bicyclo[3.1.0]hex-3-en-2-yl (**3**) Radical, Pseudobisected (**6a**), Bisected (**6b**), and Pseudoeclipsed (**6c**) Conformations of Cyclopentadienylmethyl Radical, and the Transition Structure for the Ring Opening of **3** To Give **6a** (TS2)

	3	TS2	**6a**	**6b**	**6c**
molecular symmetry	C_s	C_1	C_1	C_s	C_s
bond lengths, Å					
C_1C_2	1.398	1.368	1.348	1.348	1.348
C_2C_3	1.398	1.443	1.487	1.487	1.487
C_1C_5	1.497	1.508	1.527	1.531	1.528
C_3C_4	1.497	1.412	1.348	1.348	1.348
C_4C_5	1.527	1.511	1.534	1.531	1.528
C_6C_4	1.524	1.944	2.513	2.518	2.523
C_6C_5	1.524	1.508	1.511	1.508	1.510
bond angles, deg					
$H_{10}C_4C_3$	120.4	126.9	127.1	127.1	126.9
$H_{11}C_5C_1$	120.4	117.7	110.9	110.4	109.8
$H_{12}C_6H_{13}$	115.7	120.1	118.0	119.3	117.6
dihedral angles, deg					
$H_{10}C_4C_3H_9$	37.4	16.0	−0.3	0.3	0.0
$H_{11}C_5C_1H_7$	37.4	44.0	62.7	63.1	64.1
$H_{12}C_6C_5H_{11}$	5.3	26.3	35.2	0.0	79.3
$H_{13}C_6C_5H_{11}$	−139.8	−146.0	−168.0	180.0	−79.3
plane−plane angles, deg					
$(C_4C_6C_5)(C_1C_2C_3)$	109.3	107.8	117.9	118.7	119.9
bond−plane angles, deg					
$(C_5C_6)(H_{12}C_6H_{13})$	30.1	6.7	−19.9	0.0	−18.2

[a] Atom numbering as in Figure 3.

Table V. Calculated Total Energies (Hartrees) and Zero-Point Vibrational Energies (kcal/mol) of Bicyclo[3.1.0]hex-3-en-2-yl (**3**) Radical, Pseudobisected (**6a**), Bisected (**6b**), and Pseudoeclipsed (**6c**) Conformations of Cyclopentadienylmethyl Radical, and the Transition Structure for the Ring Opening of **3** To Give **6a** (TS1)[a,b]

species	state	CASSCF/3-21G	CASSCF/6-31G*	ZPVE
3[c]	$^2A''$	−229.94968 (0.0)	−231.24087 (0.0)	72.7
TS2	^2A	−229.93497 (9.2)	−231.21806 (14.3)	70.5
6a	^2A	−229.96114 (−7.2)	−231.24412 (−2.0)	70.6
6b	$^2A''$	−229.96081 (−7.0)	−231.24353 (−1.7)	69.9
6c	$^2A'$	−229.95924 (−6.0)	−231.24308 (−1.4)	70.4

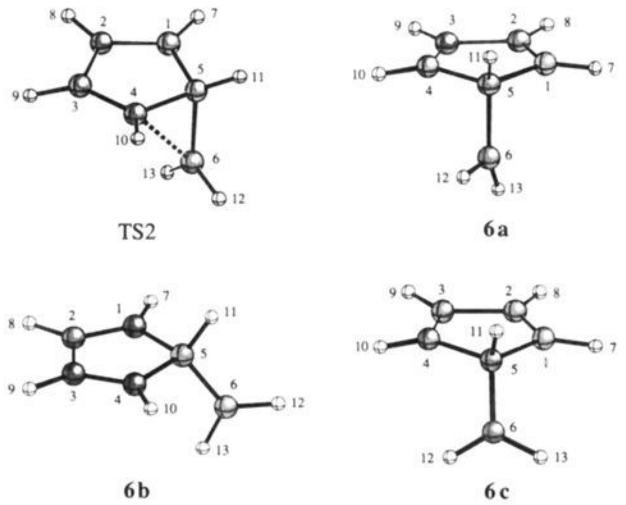
[a] All calculations at the CASSCF/3-21G-optimized geometries. [b] The quantities in parentheses are the relative energies in kcal/mol. [c] Taking as active orbitals the bonding and antibonding MOs associated with the C_4C_6 bond, in addition to the three π MOs.

75 doublet spin-adapted CSFs) with the 3-21G and 6-31G* basis sets and the corresponding ZPVE (computed at the CASSCF/3-21G level) are listed in Table V.

It can be seen from Table IV that at the transition structure the CC bond undergoing cleavage has stretched to 1.944 Å. This is slightly longer than the value of 1.858 Å obtained for the corresponding CC bond in the transition structure (calculated at the same level of theory) for the related ring-opening reaction of cyclopropylmethyl radical (**11**) to give homoallyl radical (**12**).[27]

11 **12**

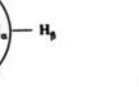
In going from the reactant **3** to the transition structure, the interesting geometrical changes here are that the dihedral angle $H_{10}C_4C_3H_9$ decreases 21.4° while the C_1C_2 and C_3C_4 bond lengths decrease 0.030 and 0.085 Å, respectively, and the C_2C_3 bond length lengthens 0.045 Å. These results indicate that the two CC double bonds of **6** become notably formed at the transition structure. Another point of particular interest is that in TS2 the angle between the C_5C_6 bond and the $H_{12}C_6H_{13}$ plane (hereafter referred to as δ), which expresses the degree of planarity of the radical center in **6**, is 6.7°. This result reveals that at the transition structure the forming radical center (C_6) is nearly planar.



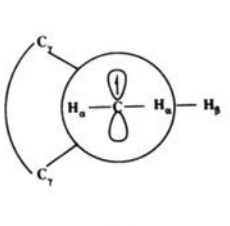
TS2 **6a** **6b** **6c**

Figure 3. Computer plots of the CASSCF/3-21G-optimized equilibrium structures of pseudobisected (**6a**), bisected (**6b**), and pseudoeclipsed (**6c**) conformations of cyclopentadienylmethyl radical and the transition structure for the ring opening of bicyclo[3.1.0]hex-3-en-2-yl radical to give **6a** (TS2).

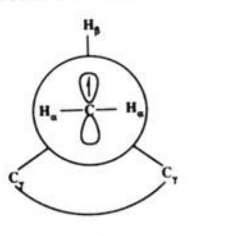
A geometry reoptimization of the TS2 structure, slightly modified according to the nuclear displacement indicated by the normal mode of imaginary frequency associated with the C_6C_4 bond stretching, led to the potential energy minimum **6a**, which turned out to be the lowest energy conformation of **6**. An interesting geometrical feature of **6a** is the considerable nonplanarity (δ = −19.9°) of the radical center, which is larger than that in TS2 (δ = 6.7°) and of opposite sign. This result is in clear contrast with that found for cyclopropenylmethyl radical (**13**). In fact, recent ab initio CASSCF/3-21G calculations[21] predicted two equilibrium geometries for **13**, which correspond to the conformations usually referred to as bisected (**14**) and eclipsed (**15**), possessing a planar radical center. The lowest energy conformation of **13** was predicted to be the bisected form **14**. This result was in line with ESR studies[28] showing that cyclobutenylmethyl and cyclopentenylmethyl radicals also prefer the bisected conformation **14**. Within the C_s molecular symmetry constraint, two additional stationary points were found for **6**, which correspond to the bisected (**6b**) and pseudoeclipsed (i.e., has a nonplanar radical center) (**6c**) conformations. At the CASSCF/6-31G* level the **6b** and **6c** forms are calculated to lie 0.3 and 0.6 kcal/mol above **6a**, respectively. Additional CASSCF calculations with the 3-21G basis set showed a relatively free rotation about the C_5C_6 bond.



13



14



15

The salient feature of the computed results for **6** was that while the harmonic vibrational analysis of **6c** proved this structure to be a true potential energy minimum, that of **6b** showed an imaginary frequency (300i cm^{-1}). The normal mode associated with this frequency corresponds to a nuclear displacement of a″ symmetry which leads to the pseudobisected conformation **6a**. This

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[27] Olivella, S.; Solé, A., to be published.

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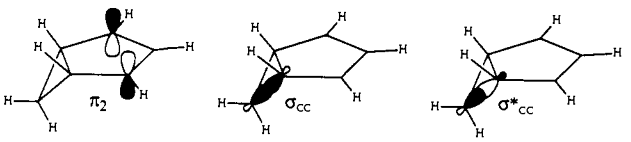

Figure 4. Qualitative drawings of the SOMO (π_2) and the bonding (σ_{CC}) and antibonding (σ^*_{CC}) MOs of one of the two exocyclic cyclopropane bonds of bicyclo[3.1.0]hex-3-en-2-yl radical.

structural distortion of **6b** is ascribed to a second-order Jahn–Teller effect.[29] In fact, at the single-configuration ROHF level of theory with the 3-21G basis set, a relatively small energy gap was found between the singly occupied MO (SOMO) and the lowest unoccupied MO (LUMO), which are of the symmetry classes a″ and a′, respectively. Consequently, a structural distortion in **6b** belonging to the a″ symmetry class, like the normal mode of the imaginary frequency, allows intermixing between these orbitals and leads to a second-order change in the energy of the SOMO, which results in a small energy lowering of **6b**. In the case of the bisected conformation of radical **13**, the SOMO–LUMO energy gap, calculated at the ROHF/3-21G level, is 0.9 eV larger than that for **6b**. Moreover, both MOs belong to the same symmetry class a″, so that a second-order Jahn–Teller distortion of the a″ symmetry class leading to a pyramidal radical center in **13** is precluded. Another interesting feature, related to the computed nonplanarity of the radical center and the sign change of the δ angle in **6a**, is that the H_{12} and H_{13} hydrogens have undergone inversion from their arrangement in **3**. Hence the **3** → **6a** rearrangement proceeds with inversion at the C_6 center rather than retention.

The potential energy barrier for the formation of **6a** from **3** via TS2 is 9.2 kcal/mol at the CASSCF/3-21G level and becomes 7.0 kcal/mol after including the ZPVE correction. When using the single-point CASSCF/6-31G* energies plus the ZPVE correction, an energy activation at 0 K of 12.1 kcal/mol is predicted. While no experimental value is available, the present result is in keeping with the experimental fact indicated in section I, namely, the degenerate rearrangement **3a** → **3b** must have a barrier of activation smaller than the electrocyclic ring opening reaction **3a** → **5a** (e.g., $\Delta G^{*} < 14.5$ kcal/mol at −50 °C). Furthermore, the reliability of our theoretical procedure in computing the barrier height for the **3** → **6a** rearrangement can be assessed from the activation energy predicted in the case of the related ring opening of **11** to give **12**. In fact, at the CASSCF/6-31G* + ZPVE correction level this activation energy is computed to be 7.1 kcal/mol,[27] in excellent agreement with the recommended experimental value of 7.26 kcal/mol.[30]

Regarding the energy of reaction for the rearrangement of **3** to **6a**, at the CASSCF/6-31G* + ZPVE correction level, it is predicted to be −4.1 kcal/mol. While no experimental thermochemical data are available for this reaction, we recall again that the CASSCF/6-31G* model probably underestimates the energy of **6a** with respect to that of **3**, due to the expected differences in the dynamical correlation energy of these structures. Thus, it is worth mentioning that for the related **11** → **12** rearrangement the energy of reaction calculated at the CASSCF/6-31G* + ZPVE correction level is −12.8 kcal/mol,[27] which is 9.7 kcal/mol lower than the value of −3.15 kcal/mol estimated from thermochemical data.[31] The computed energy of reaction for the **3** → **6a** rearrangement is then probably too negative by 10 kcal/mol. With this correction, the radical **6a** is predicted to lie about 6 kcal/mol above **3**. On the basis of this prediction, it can be concluded that the potential energy barrier for the second step of the degenerate 1,4-migration of the methylene group in **3** (i.e., the cyclization **6a** → **3**) must be about 6 kcal/mol lower than for the first step (i.e., the ring opening **3** → **6a**), implying that the latter step is the rate determining step for the overall rearrangement. This conclusion accounts for the aforementioned observation that the ESR spectrum of the radical intermediate **6** could not be detected during the degenerate 1,4-migration of the methylene group in **3**.

At this point it is of interest to inquire why the ring opening of **3** to give **6** predominates (occurs more rapidly) over the ring opening to afford **6**. The trivial answer is that the potential energy barrier for the **3** → **6** rearrangement is lower. But why is this? The simplest explanation is based on the stereoelectronics of the radical ring-opening reactions. It has been pointed out that ring opening by cleavage of a β,γ C–C bond with respect to the radical center (i.e., β scission) readily occurs in cycloalkyl radicals if the SOMO can assume an eclipsed conformation with respect to the $\gamma\beta$ bond; namely, there is a strong overlap between the SOMO and the orbitals of the bond about to break.[2] This stereoelectronic explanation accounts for the relatively reluctant ring opening of **7** to give **8** and the rapid β scission of **11** to give **12**. Despite its favorable energetics the ring-opening mode **3** → **5** involves a considerable potential barrier due to the fact that the SOMO of **3** (π_2) is orthogonal to both the bonding (σ_{CC}) and antibonding (σ^*_{CC}) MOs of the C_4C_5 inter-ring bond (see Figure 1). In clear contrast, π_2 can overlap to some extent with the MOs of the exocyclic cyclopropane bonds in **3** (e.g., the σ_{CC} and σ^*_{CC} MOs of Figure 4), and so the **3** → **6** ring-opening mode is preferred, even though its disfavorable energetics would suggest the contrary.

V. Conclusions

The following conclusions can be drawn from the ab initio CASSCF calculations reported here:

(1) The thermal ring opening of **3** to give **5** is a symmetry-forbidden electrocyclic process that takes place via a highly unsymmetric transition structure lying about 16 kcal/mol above **3**. This allows the mixing of the SOMO (a″ symmetry) and the highest doubly occupied MO (a′ symmetry) of **5** and the coupling between the crossing states ($^2A''$ and $^2A'$), resulting in an adiabatic reaction on the ground-state potential energy surface.

(2) The degenerate 1,4-migration of the methylene group in **3** is a two-step process, involving the radical **6** as the stable intermediate, rather than a pericyclic suprafacial 1,4-sigmatropic rearrangement. The potential energy barrier for the second step of this degenerate rearrangement (i.e., the cyclization **6** → **3**) is predicted to be about 6 kcal/mol lower than that for the first step (i.e., the ring opening **3** → **6**), implying that the latter step is the rate-determining step for the overall rearrangement. This accounts for the failure to detect by ESR the intermediate **6** during the rearrangement.

(3) The lower activation energy (12.1 kcal/mol) calculated for the **3** → **6** ring-opening mode, as compared with that calculated (16.0 kcal/mol) for the alternative **3** → **5** ring-opening mode, is attributed to the fact that the SOMO in **3** can overlap to some extent with the exocyclic cyclopropane bonds, while this orbital is orthogonal to the inter-ring bond.

Acknowledgment. This work was supported by the Spanish CICYT (Grant PB86-0270). The preliminary AM1 calculations were carried out by one of us (S.O.) in Professor Dewar's research group at the University of Texas in Austin during his stay in the summer of 1988, which was partially supported by the Catalonian CIRIT. The ab initio calculations were carried out with IBM 4381 and ALLIANT FX/80 computers at the University of Barcelona. We are indebted to Dr. Michael W. Schmidt (North Dakota State University) for providing us a copy of his greatly extended version of the GAMES system of programs.

Registry No. 3, 55394-12-2; **5**, 12169-67-4; **6**, 136202-28-3.

Supplementary Material Available: Tables of Cartesian coordinates (in angstroms) of the optimized equilibrium structures of 3, 5, 6a, 6b, and 6c and of the transition structures TS1 and TS2 (calculated at the CASSCF/3-21G level of theory) and the displacement Cartesian coordinates of the normal coordinates associated with the imaginary frequencies of TS1 and TS2 (5 pages). Ordering information is given on any current masthead page.

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