Three transition structures have been located for each nucleophile. Methyllithium is calculated to favor 1,2-addition over 1,4-addition via either a four-membered or a six-membered cyclic transition structure. In the case of methylcopper, a cyclic, six-membered structure is found to be markedly preferred over the other two addition modes. These results confirm the notion that the reactions of the "hard" alkyllithium nucleophiles are charge-controlled, whereas the alkylcopper reactions are controlled by orbital interactions. Our calculations also show that conjugate addition of methylcopper to acrolein proceeds to yield directly the metal enolate, rather than the α-cuprio ketone, in agreement with recent experimental observations.

The Walk Rearrangement in Bicyclo[2.1.0]pent-2-ene. An MCSCF Study

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Abstract: The walk rearrangement in bicyclo[2.1.0]pent-2-ene has been examined by ab initio calculations at Hartree–Fock, Møller–Plesset, and multiconfigurational levels of theory. At the multiconfigurational level of theory, it is found that the Woodward–Hoffman allowed reaction, occurring with inversion at the migrating carbon, is a concerted process, while that occurring with retension proceeds via a biradical intermediate. The difference in activation energies for the two reaction pathways is predicted to be at least 8 kcal/mol, favoring the Woodward–Hoffmann allowed reaction. The activation energy calculated at the MP2/6-31G* level for the reaction occurring with inversion agrees well with the value that can be estimated from experimental data. Calculations using spin contaminated unrestricted Hartree–Fock wave functions are found to give deviating results.

The migration of a divalent group, such as O, S, NR, or CR_2, which is part of a three-membered ring in a bicyclic molecule, is commonly referred to as a "walk" rearrangement.[1] The rearrangement can formally be characterized according to the Woodward–Hoffmann (W–H) rules as being a $(1, n)$-sigmatropic rearrangement.[2] Of the neutral hydrocarbon systems,[3] derivatives of the three smallest homologs, bicyclo[2.1.0]pent-2-ene, bicyclo[4.1.0]hepta-2,4-diene, and bicyclo[6.1.0]nona-2,4,6-triene, have been studied experimentally.[1a] These rearrangements can be denoted as (1,3)-, (1,5)-, and (1,7)-sigmatropic shifts. For reactions occurring in a concerted manner, i.e., without any intermediates along the reaction pathway, the W–H rules predict that the (1,3)- and (1,7)-migration should occur with inversion of the cyclopropane ring, while the (1,5)-migration should occur with retention of configuration. The walk rearrangement in the parent bicyclo[2.1.0]pent-2-ene system is not observed since the ring-opening reaction forming cyclopentadiene occurs at lower temperature. For the larger homologs the ring-open and -closed forms are in equilibrium, with the ring-open form favored in the parent systems. For systems with electron-withdrawing groups at the top position of the cyclopropane ring, such as cyano or esters, the walk rearrangement can compete with ring-opening reactions. For suitably substituted compounds belonging to the above three systems, it is found that the walk rearrangement occurs exclusively with inversion of configuration at the top carbon. For the bicyclo[4.1.0]hepta-2,4-diene system this is opposite to the prediction based on the W–H rules and is indeed one of the few known exceptions.

Recently Skancke, Yamashita, and Morokuma (SYM) reported ab initio calculations on the ring opening and walk rearrangements

of the parent bicyclo[2.1.0]pent-2-ene.[4] Their conclusion was that the walk rearrangement occurs with inversion but via a biradical intermediate which was estimated to be 6 kcal/mol below the transition state leading to it. The barrier for rotation of the migrating CH_2 group in the intermediate was calculated to be 3 kcal/mol. The calculated activation energy for the walk rearrangement at the partial fourth-order Møller–Plesset level (MP4(SDQ)/6-31G*) was 41 kcal/mol (the value at the MP2/6-31G* level was 51 kcal/mol) compared to a value of 40 kcal/mol that can be estimated from experimental data.[5] In all cases they used spin unrestricted Hartree–Fock and Møller–Plesset wave functions (UHF and UMP) which for ground-state molecules are identical with spin restricted wave functions (RHF and RMP).

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(5) The activation energy for the walk rearrangement in bicyclo[2.1.0]-pent-2-ene is estimated as follows. A lower bound of 28 kcal/mol for the activation energy ($\Delta G^{\ddagger}$) can be determined from the parent system since the activation energy for the ring-opening reaction is 24.9 kcal/mol, and none of the product expected from a walk rearrangement is observed (assuming a 1% detection limit, which corresponds to 3 kcal/mol at the reaction temperature).[6] The activation energy for the walk rearrangement in the substituted system 5-cyano-1,5-dimethylbicyclo[2.1.0]pent-2-ene is 21.9 kcal/mol.[7] To correct for the effects of a cyano and a methyl group, we utilize data taken from the interconversion of cis and trans isomers of cyclopropanes. For this presumably similar reaction the stabilizing effect of a cyano group is found to be 8.9 ± 1.0 kcal/mol, while that of a CH_3 group is 2.0 kcal/mol.[8] Assuming similar effects for the walk rearrangement we have $\Delta G^{\ddagger}_{est} \simeq 21.9 + 8.9 + 2.0 \simeq 35$ kcal/mol. To make comparison with the calculated values in Table VI, we have to correct for the entropic contribution to $\Delta G^{\ddagger}$ and for vibrational contributions to $\Delta H^{\ddagger}$. $\Delta S^{\ddagger}$ for the reaction is probably slightly positive (the calculated value using the CAS1/STO-3G frequencies is 5.8 cal/mol·K, and the experimental value for cis–trans isomerization in 1,2-dicyanocyclopropane is 6.6 cal/mol·K) and $\Delta H^{\ddagger}$ is consequently $\simeq 2$ kcal/mol higher than $\Delta G^{\ddagger}$. The correction for zero-point energy differences is typically 2–3 kcal/mol (the calculated value here is 3.4 kcal/mol), thus the final estimate of $\Delta H^{\ddagger}$ to be directly compared to the calculated values is $\simeq 40$ kcal/mol. To estimate the energy difference between reaction occurring with inversion and retention we note that in 5-cyano-1,5-dimethylbicyclo[2.1.0]pent-2-ene only the reaction taking place with inversion is observed, thus the final difference in this compound must be >3 kcal/mol (again assuming a 1% detection limit).[7] Since the cyano and methyl groups probably stabilize preferentially the reaction occurring with retention, the 3 kcal/mol lower bound should also hold for the parent bicyclo[2.1.0]pent-2-ene.

Chart I

1   **2**   **3**

There are two things in the work of SYM that we find surprising. In connection with other work,[9] we have calculated the transition structure for the walk rearrangement corresponding to inversion of configuration in bicyclo[2.1.0]pent-2-ene using an RHF wave function and found that it occurs in a concerted manner, i.e., without an intermediate. The activation energy at the RMP2/6-31G* level was calculated to be 35 kcal/mol in contrast to the 51 kcal/mol at the UMP/6-31G* level reported by SYM. Furthermore if the reaction occurs via an intermediate which lies in a potential well of 6 kcal/mol with a barrier for rotation of only 3 kcal/mol, as concluded by SYM, it becomes difficult to explain why the walk rearrangement of substituted systems give products exclusively with inversion at C_5, as is experimentally observed. In order to clarify these apparently divergent conclusions, we wish here to report additional calculations at a number of different levels of theory.

Calculations

Configuration interaction (CI) and multiconfigurational self-consistent field (MCSCF) calculations were carried out with the GAMESS program,[10] and second-order Møller–Plesset (MP2) calculations were done using the Gaussian-82 program package.[11] For structure 2 spin restricted wave functions are of the usual RHF type,[12] while for structure 3 they are of the spin restricted open shell (ROHF) type.[13] Spin unrestricted wave functions were calculated using the procedure of Pople and Nesbet.[14] A description of the basis sets used can be found in ref 28. The MCSCF calculations were of the complete active space (CASSCF) type.[15] Two different sizes of the active space were used, which are denoted CAS1 and CAS2. The CAS1 consists of four electrons in four orbitals (i.e., the orbitals which are composed mainly of the interacting carbon p-orbitals), for a total of 12 configurations of A′ symmetry and eight configurations of A″ symmetry. The CAS2 has eight electrons distributed in eight orbitals for a total of 900 configurations of A′ symmetry and 864 configurations of A″ symmetry. The corresponding CI methods are labeled CI1 and CI2. Stationary points on the potential energy surface (PES) were characterized by diagonalizing the mass-weighted force constant matrix to obtain harmonic vibrational frequencies. The force constants were calculated using an analytical method at the HF level and by finite differences of the analytical first derivatives at the MCSCF level. Single-point calculations at the CAS2/STO-3G and CAS1/3-21G levels were done at the CAS1/STO-3G optimized geometries for structures 2 and 3, while the RHF/3-21G geometry was used for 1. Semiempirical calculations were done using the AMPAC program.[16]

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Figure 1. Orbital interaction diagram for structures 2 and 3.

Results and Discussion

The walk rearrangement in the parent bicyclo[2.1.0]pent-2-ene system is degenerate (reactant and product are identical), and consequently the C_s symmetric optimized structures 2 and 3 corresponding to the reaction occurring with inversion or retention at C_5 are stationary points on the potential energy surface (PES).[17]

The symmetries of the frontier orbitals of structures 2 and 3 can be derived by considering them as linear combinations of an allyl system and the p-orbital on the migrating carbon, as shown in Figure 1. For structure 2 the orbital symmetries are a′, a″, a″, and a′. With four electrons both the lowest closed shell configuration $(a′)^2(a″)^2$ and the biradical configuration $(a′)^2(a″)^1(a″)^1$ have overall A′ symmetry. For structure 3, however, the biradical configuration $(a′)^2(a′)^1(a″)^1$ will be of A″ symmetry, while the closed shell configuration will have A′ symmetry. A priori we cannot know which configuration is lowest in energy, but, as shown below, the A″ configuration is significantly more stable than the A′ configuration.

The distinction between a concerted (one-step) and a nonconcerted reaction (occurring via an intermediate) can be made by determining whether structures 2 and 3 are maxima or minima on the PES. Computationally this can be done by optimizing the structures constrained to C_s symmetry and evaluating the vibrational frequencies at the optimized geometries. A minimum will have all real frequencies, while a transition structure will have exactly one imaginary frequency. Previously we have optimized structures 2 and 3 at the RHF level of theory using the minimal STO-3G basis.[9] At this level it was found that structure 2 was a transition structure with one imaginary frequency ($\nu_i = 825i$ cm^{-1}) corresponding to the motion expected for a migration of the CH_2 group. The same result is obtained at the RHF/3-21G level ($\nu_i = 536i$ cm^{-1}). For structure 3 it was found that the lowest energy RHF/STO-3G wave function (corresponding to the configuration $(a′)^2(a′)^2$) had only C_1 symmetry even though the nuclear framework has C_s symmetry. This is an example of a so-called symmetry broken wave function[18] and usually indicates that the level of theory is insufficient for even a qualitative description of the wave function. Indeed when the more flexible UHF wave function is used, the wave function obtained has A″ symmetry. At the UHF/STO-3G level, structure 2 is a transition structure ($\nu_i = 331i$ cm^{-1}) for the rotation of the migrating CH_2 group, while structure 3 is a minimum on the PES (lowest frequency is 143 cm^{-1}). These UHF wave functions are, however, very heavily contaminated with higher spin states as seen from the $\langle S^2 \rangle$ values of 1.36–1.37 ($\langle S^2 \rangle = 0$ for a singlet wave function). The values after annihilation of the triplet state are 2.34–2.41 indicating that significant amounts of spin states other than the triplet are mixed into the singlet state. In contrast to these results, SYM report that at the UHF/3-21G level structure 2 is a min-

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Table I. Number of Imaginary Vibrational Frequencies and Corresponding Motion in Structures **2** and **3** at Different Levels of Theory

level	2	3
RHF/STO-3G	1 (migration)	
UHF/STO-3G	1 (rotation)	0
RHF/3-21G	1 (migration)	
UHF/3-21G[a]	0	1 (rotation)
CAS1/STO-3G	1 (migration)	0
RHF/AM1	1 (migration)	
UHF/AM1	1 (rotation)	0

[a] Reference 4.

imum and **3** is a transition structure for rotation of the CH_2 group ($\nu_i = 134i$ cm^{-1}). Although SYM do not report the $\langle S^2 \rangle$ value for these UHF wave functions, our calculations show that they are 1.25 and 1.75 after annihilation of the triplet state, i.e., the more flexible basis set gives a slightly less contaminated wave function, especially the contamination by spin states higher than the triplet is reduced. The UHF method thus predicts that the reaction is nonconcerted, although different basis sets disagree on whether **2** or **3** is the actual minimum on the PES. The semiempirical method AM1[19] gives results similar to those obtained with the STO-3G basis, thus, at the RHF/AM1 level, structure **2** is a transition structure for migration, while at the UHF/AM1 level it is a transition structure for rotation of the CH_2 group, and structure **3** is a minimum on the PES.

To treat both closed shell and biradical states on an equal footing and obtain pure spin functions, one has to use the multiconfigurational self-consistent field (MCSCF) method. In the present case we have used MCSCF wave functions of the complete active space (CASSCF) type.[15] For the optimization and characterization of stationary points on the PES, we have used an active space with four electrons distributed in all possible ways in four orbitals, denoted CAS1, using the minimal STO-3G basis. This configurational space should be sufficient for a correct description of both biradical and closed shell species of interest here. As shown below, the larger CAS2 (eight electrons in eight orbitals) gives virtually identical electronic structures. The minimal STO-3G basis set has been found to favor biradical states in other MCSCF studies,[20] but geometries are usually very close to those obtained with better basis sets.[20-22] The CAS1/STO-3G calculations show that structure **2** is a transition structure with an imaginary frequency of 479i cm^{-1}. The atomic displacements for this frequency correspond to those expected for migration of the CH_2 group. The lowest energy wave function for structure **3** has A″ symmetry and represents a minimum on the PES (lowest frequency is 110 cm^{-1}, corresponding to rotation of the CH_2 group and presumably leading to ring closure to **1**[23]). The A′ symmetric wave function is 60–80 kcal/mol higher in energy, depending on the geometry used. Since structure **3** is a minimum on the PES, there must be a transition structure leading to it with C_1 symmetry (actually two equivalent structures). Various attempts to locate this TS were unsuccessful; the PES in this region is very flat with several eigenvalues of the hessian being less than 0.1. From the magnitude of the lowest frequency of structure **3** (110 cm^{-1}), it is likely that the minimum on the PES is very shallow. These results are summerized in Table I.

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(23) Note that since the energy of **3**, which is a minimum, is higher than the energy of **2** (Table VI), which is a transition structure, it is unlikely that there exists a transition structure corresponding to a rotation of the CH_2 group, connecting two equivalent structures **3**.
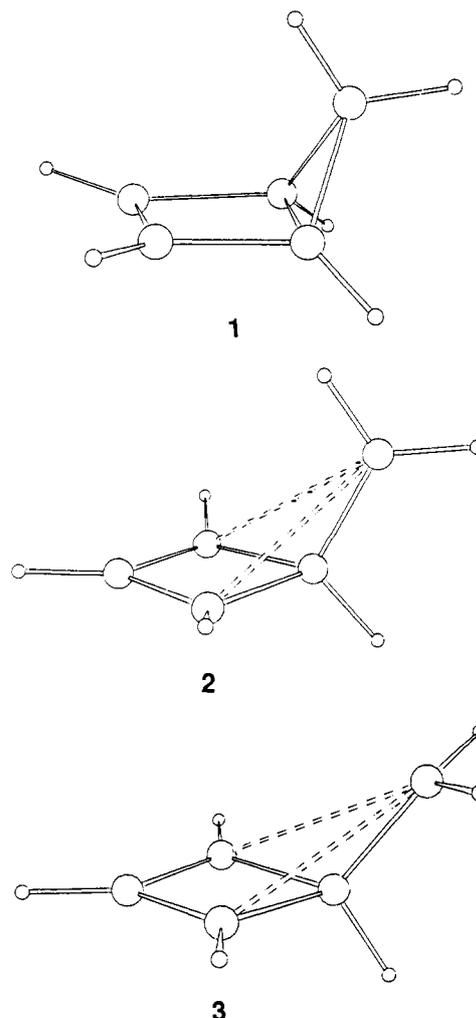
Figure 2. Optimized geometries for structures **1** (RHF/3-21G), **2**, and **3** (CAS1/STO-3G).

Table II. Selected Structural Parameters from Figure 2[a]

str	level	C_1-C_5	C_1-C_2	C_2-C_3	C_2-C_5	$\angle C_3C_1C_5$
2	RHF/STO-3G	1.444	1.515	1.390	2.167	94.7
	RHF/3-21G	1.447	1.532	1.398	2.237	98.4
	UHF/STO-3G	1.517	1.544	1.414	2.602	126.3
	UHF/3-21G[b]	1.495	1.557	1.409	2.530	120.0
	CAS1/STO-3G	1.506	1.541	1.410	2.542	118.9
	RHF/AM1	1.432	1.538	1.409	2.338	107.7
	UHF/AM1	1.456	1.536	1.415	2.528	125.4
3	ROHF/STO-3G	1.522	1.538	1.381	2.622	128.8
	UHF/STO-3G	1.521	1.544	1.414	2.618	128.3
	UHF/3-21G	1.498	1.561	1.409	2.581	124.3
	CAS1/STO-3G	1.522	1.542	1.408	2.622	129.8
	UHF/AM1	1.452	1.534	1.415	2.548	128.4

[a] Bond lengths in Å, angle in deg. [b] Reference 4.

The optimized geometries of **1**, **2**, and **3** are shown in Figure 2, and selected bond lengths and angles are shown in Table II. The only major difference between the structures optimized at the different levels is the smaller angle $C_3C_1C_5$ obtained at the RHF level for **2** as compared to the CAS1 and UHF values. The AM1 method gives results similar to those at the ab initio levels, except that the C_1-C_5 bond length is calculated to be slightly shorter.

The electronic structures of **2** and **3** are of some interest in connection with substituent effects on the two different pathways. Of special interest here is the amount of biradical character that these structures have. Although the biradical character is a commonly used concept in physical organic chemistry there is no unique way of defining it from first principles. An often used quantity is based on the square of the coefficient of the HF

Table III. Total Energies and Configurational Coefficients[a] Using Different Orbitals with the STO-3G Basis

str	level	$-E_{total}$	C_{2200}	C_{2020}	C_{2110}	C_{1111}
2	CI1/RHF	190.355 95	0.80	0.53	0.03	0.12
	CI1/α-UHF	190.248 18	0.19	0.11	0.84	0.47
	CI1/β-UHF	190.223 76	0.20	0.15	0.80	0.52
	CAS1/RHF	190.385 25	0.77	0.55	0.03	0.13
	CAS1/α-UHF	190.385 25	0.18	0.02	0.83	0.51
	CAS1/β-UHF	190.385 25	0.18	0.02	0.83	0.52
3	CI1/ROHF	190.368 35	–	–	0.96	0.25
	CI1/α-UHF	190.216 87	–	–	0.82	0.47
	CI1/β-UHF	190.264 97	–	–	0.87	0.45
	CAS1/ROHF	190.382 20	–	–	0.95	0.27
	CAS1/α-UHF	190.382 20	–	–	0.82	0.44
	CAS1/β-UHF	190.382 20	–	–	0.85	0.44

[a] Subscripts on configurational coefficients refer to the electron occupation. A dash indicates that the coefficient is identically zero due to symmetry.

Table IV. Occupation Numbers for the MCSCF Natural Orbitals[a]

str	level	η_1	η_2	η_3	η_4	η_5	η_6	η_7	η_8
1	CAS1/STO-3G	–	–	1.98	1.87	0.13	0.02	–	–
	CAS2/STO-3G	1.99	1.98	1.96	1.88	0.13	0.04	0.02	0.01
	CAS1/3-21G	–	–	1.99	1.91	0.10	0.01	–	–
2	CAS1/STO-3G	–	–	1.86	1.30	0.70	0.14	–	–
	CAS2/STO-3G	1.98	1.97	1.87	1.31	0.69	0.13	0.03	0.02
	CAS1/3-21G	–	–	1.90	1.45	0.55	0.10	–	–
3	CAS1/STO-3G	–	–	1.86	1.00	1.00	0.14	–	–
	CAS2/STO-3G	1.98	1.97	1.87	1.00	1.00	0.13	0.03	0.02
	CAS1/3-21G	–	–	1.89	1.00	1.00	0.11	–	–

[a] A dash indicates that the occupation number is identically 2 or 0 due to the constraints on the wave function.

configuration in a CI or MCSCF expansion.[22,24] For a simple two configurational wave function

$$\psi_{TC} = C_1(core)(HOMO)^2(LUMO)^0 + C_2(core)(HOMO)^0(LUMO)^2 \quad (1)$$

a biradical index (BR1) can be defined as $2(1-C_1^2)$. This will be zero when the wave function is the HF wave function and one for an equal mixture of the two configurations. The same expression is normally used for wave functions with more than two configurations. For an open shell species described by a spin restricted open shell (ROHF) wave function, (core)(SOMO)^1·(SOMO)^1, where SOMO stands for singly occupied molecular orbital, the corresponding index is directly the square of the Hartree–Fock configuration, C_{HF}^2. SYM reported that the CAS1/3-21G wave function for structure **2** has the dominant configuration (core)(13a')^2(5a'')^1(6a'')^1 with a coefficient of 0.86. This would indicate that **2** has a biradical character of 74%. The configurational coefficients in a CASSCF wave function, however, are not unique.[25] They depend on the coefficients obtained from the starting CI calculation, which in turn depend on how the molecular orbitals were generated. Table III shows the configurational coefficients for the CAS1 wave functions for **2** and **3** obtained with different orbitals (RHF, ROHF, and UHF). The UHF orbitals are already heavily polarized with the highest occupied molecular orbital (HOMO) for the α spin localized on the migrating carbon, while the HOMO for the β spin consist of the antisymmetric combination of the p-orbitals on carbons 2 and 4. Thus the UHF orbitals already show significant biradical character and the dominance of the configuration (core)(13a')^2(5a'')^1(6a'')^1 is not an indication of biradical character when UHF orbitals are used. When spin restricted orbitals (RHF or ROHF) are used, however, the coefficient of the HF configuration in a CI expansion provides a well-defined quantity for discussing biradical character, as does the occupation number of the MCSCF natural orbitals.[26]

Table V. Biradical Indexes for Structures **1**, **2**, and **3** at Different Levels of Theory[a]

level	**1** BR1	**1** BR2	**2** BR1	**2** BR2	**3** BR1	**3** BR2
[4e,4o]/STO-3G	0.06	0.13	0.73	0.70	0.91	1.00
[8e,8o]/STO-3G	0.15	0.13	0.77	0.69	0.91	1.00
[4e,4o]/3-21G	0.03	0.09	0.52	0.55	0.94	1.00

[a] BR1 is defined as $2(1-C_{HF}^2)$ for structures **1** and **2** and as C_{HF}^2 for structure **3** using the CI configurational coefficients and RHF (ROHF) orbitals. BR2 is defined as $2-\eta_H$ from the CAS wave functions, see text for discussion.

Table VI. Total and Relative Energies for Structures **1**, **2**, and **3**

level	$E_{total}(\mathbf{1})^a$	$\Delta E^{\ddagger b}$	$\Delta\Delta E^{\ddagger b}$
RHF/STO-3G	–190.37800	85.5	–68.2
RHF/3-21G	–191.62165	45.0	–51.9
RHF/6-31G*//RHF/3-21G	–192.70891	48.5	
RHF/6-31G*//CAS1/STO-3G		61.4	
RMP2/6-31G*//RHF/3-21G	–193.34986	34.8	
RMP2/6-31G*//CAS1/STO-3G		41.1	
UHF/STO-3G	–190.37800	7.3	0.2
UHF/3-21G[c]	–190.62165	4.7	2.7
UMP2/6-31G*//UHF/3-21G[c]	–193.34986	51.1	
CI1/STO-3G[d]	–190.39902	27.0	–7.8
CI2/STO-3G[d]	–190.43780	39.6	–5.7
CI1/3-21G[d]	–191.62949	16.2	–2.1
CAS1/STO-3G[d]	–190.43329	30.1	1.9
CAS2/STO-3G[d]	–190.47266	26.9	1.4
CAS1/3-21G[d]	–191.66118	17.6	7.7
RHF/AM1		98.4	42.9
UHF/AM1	98.4	4.5	–0.8
CI1/AM1//UHF/AM1	89.4	15.8	–0.8
estimated exp.[5]	$\cong$40.	>3	

[a] Total energies are given in Hartrees for ab initio methods and in kcal/mol for semiempirical methods (heat of formation). Relative energies are given in kcal/mol. [b] $\Delta E^{\ddagger}$ = activation energy for reaction occurring with inversion = $E(\mathbf{2}) - E(\mathbf{1})$. $\Delta\Delta E^{\ddagger}$ is the energy difference between **3** and **2** = $E(\mathbf{3}) - E(\mathbf{2})$. Note that all spin restricted calculations for **3** are of the ROHF type. [c] Taken from ref 4. [d] Using the RHF/3-21G optimized geometry for structure **1** and CAS1/STO-3G optimized geometries for structures **2** and **3**. CI configurations are built from RHF (**1** and **2**) or ROHF (**3**) orbitals.

A definition of biradical character based on MCSCF natural orbitals could be BR2 = $2 - \eta_H$, where η_H is the occupation number of the natural orbital corresponding to the HOMO.[27] Table IV shows the occupation number of the natural orbitals for the CAS1 and CAS2 wave functions, and the corresponding biradical indexes are shown in Table V. There is no significant difference between the two definitions, but the definition based on η_H appears less sensitive to the size of the configuration space and is independent of the choice of starting orbitals. The results indicate that structure **3** is an almost pure biradical, while structure **2** has approximately 50% biradical character. By these definitions structure **1** has 5–10% biradical character. The minimal STO-3G basis overestimates the biradical character, which has been found in other cases as well.[20]

The radical character of structure **2** is in qualitative agreement with the experimental observation that a cyano group at C_5 lowers the activation energy for the walk rearrangement. At the HF/3-21G level the stabilizing effect of a cyano group on the CH_2 radical has been calculated to be 11 kcal/mol, while the effect on ethane is 2 kcal/mol,[28] thus the stabilization expected for **2** based on 50% biradical character is 6.5 kcal/mol.[29] This value may be compared with an experimental value of 8.9 $\pm$ 1.0 kcal/mol found for the stabilizing effect of a cyano group in the

(24) (a) Osamura, Y.; Kato, S.; Morukuma, K.; Feller, D.; Davidson, E. R.; Borden, W. T. *J. Am. Chem. Soc.* **1984**, *106*, 3362. (b) Hayes, E. F.; Siu, A. K. Q. *J. Am. Chem. Soc.* **1973**, *95*, 2090.

(25) This is due to the energy invariance with respect to orbital rotation within the active space of a CASSCF wave function.

(26) Morokuma, K.; Borden, W. T.; Hrovat, D. A. *J. Am. Chem. Soc.* **1988**, *110*, 4474.

(27) Other definitions are possible, e.g., η_{LUMO} or a sum of occupation numbers for all orbitals that are unoccupied in the HF wave function.

(28) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular* Orbital Theory; Wiley-Interscience: 1986.

(29) We note that the stabilization of a cyano group at the 5 position was calculated to be 7 kcal/mol by SYM for structure **2** at the UHF/3-21G level.

interconversion of *cis-* and *trans-*1,2-dicyanocyclopropane.[8] Note also that the present results indicate that the W–H forbidden reaction should be stabilized more than the allowed pathway by a radical stabilizing substituent.[30]

The total and relative energies of structures **1**, **2**, and **3** at various levels of theory are shown in Table VI.[31] Spin restricted wave functions for **2** are of the RHF type, while those for **3** are of the ROHF type. The calculated activation energy for the reaction proceeding with inversion, $\Delta E^\ddagger$, is too large at the RHF level, as is usually the case.[32] Inclusion of electron correlation at the MP2 level at the CAS1/STO-3G geometry brings the calculated activation energy very close to the value that can be estimated from experimental data.[5] The almost quantitative agreement is probably in part due to the fortuitous cancellation of errors by the combination of inclusion of electron correlation to only second order in the perturbation series and the use of a medium size basis set.[32] The activation energies at the UHF level are clearly much too low. This is due to the spin contamination which allows the incorporation of some (nondynamic) electron correlation into the UHF wave function. The activation energy calculated by CI or CASSCF methods is also too low. This is not unexpected since very little of the dynamical electron correlation is recovered by these methods, i.e., the number of electron pairs is different in structures **1** and **2**. The energy difference between structures **2** and **3** should be less affected by inclusion of dynamic electron correlation (beyond that included in the CAS1) than that between **1** and **2**, since **2** and **3** have approximately the same distribution of electrons not included in the CAS. At the RHF (ROHF) and CI levels, **3** is calculated to be too stable relative to **2** as compared to the MCSCF results. This is understandable since the ROHF orbitals for **3** are close to optimum, while the RHF orbitals for **2** are less so (Table III and IV). The energy difference between structures **2** and **3** at the UHF level is found to be small, 0.2 kcal/mol with the STO-3G basis and 2.7 kcal/mol with the 3-21G basis, favoring structure **2**. These values are similar to the CAS1 and CAS2 values, 1.9 and 1.4, found with the STO-3G basis, but this basis usually overestimates the stability of biradicals and indeed the better basis, 3-21G, favors structure **2** by 7.7 kcal/mol with the CAS1 wave function. The next improvement of the basis set that can be expected to give results different from the 3-21G would be addition of polarization functions on all carbons, i.e., a DZP type basis such as 6-31G*. Even at the CAS1 level such a basis set is currently too large to handle with the programs available to us. The semiempirical AM1 method gives results similar to those obtained with the 3-21G basis set, both at the HF and CI levels. The CI result is similar to what was found by Schoeller using the MINDO/2 method followed by a 2 × 2 CI, where structure **3** is 4 kcal/mol lower in energy than **2**.[33]

As mentioned above, SYM concluded that the C_s symmetric structure **2** was an intermediate, necessitating a transition structure with C_1 symmetry. This was located using an UHF wave function, and the relative energy of the C_1 TS and the C_s minimum was evaluated at the UMP2, UMP3, and UMP4(SDQ) levels with the 6-31G* basis set. At the UHF level, structure **2** was 12 kcal/mol lower in energy than the TS. At the correlated levels, however, structure **2** was higher in energy than the TS by 1–4 kcal/mol. This implies that **2** is actually a transition structure at the correlated levels and not a minimum as found at the UHF level. In an attempt to evaluate what changes could be expected at higher levels of theory, SYM reoptimized the structures at the UHF/6-31G* and UMP/3-21G levels and extrapolated these

results to obtain approximate MP2/6-31G* geometries. At this level of theory they concluded that structure **2** should be 6 kcal/mol lower in energy than the TS.

As seen in Table VI, the UHF wave functions give abnormally low energies as compared to RHF energies. This is a combination of two effects: the UHF method allows some electron correlation to be taken into account, thus lowering the energy, but the mixing in of higher spin states raises the energy. At the single determinant level the net effect is an energy lowering. At levels where electron correlation is explicitly taken into account, only the destabilization due to spin contamination remains (the MP procedure reduce the spin contamination only slightly[34]), and the energy is higher than the corresponding energy obtained using an RHF wave function as the reference.[35] The C_1 TS reported by SYM presumably has a lower $\langle S^2 \rangle$ value than structure **2** (the value was not reported), and thus a switch of the relative ordering of **2** and the TS when electron correlation is included is exactly what would be expected. Also, the MP2 procedure usually reduces the spin contamination slightly,[34] and indeed the C_1 TS geometry obtained by SYM at the UMP2/3-21G level is closer to C_s symmetry than at the UHF level. The straightforward test for whether spin contamination, and not nonideal geometries, is the cause of the switch in relative energies would be to perform calculations which project out the unwanted spin states from the UMP wave functions. However, the spin contamination of the UMP wave functions in these cases involves several spin states, and the correction for removal of all higher spin states is complicated.[36,37]

Conclusion

We have found that the walk rearrangement for the parent bicyclo[2.1.0]pent-2-ene occurring with inversion at C_5 (the Woodward–Hoffmann allowed reaction) has a transition structure with C_s symmetry and is thus concerted. The reaction corresponding to retention of configuration, on the other hand, occurs via an intermediate, also of C_s symmetry. The electronic structures of the two stationary points on the PES suggest that the former is approximately 50% biradical, while the latter is a pure biradical. At our best level of theory, CAS1/3-21G, the reaction occurring with inversion of configuration at C_5 is favored by more than 7.7 kcal/mol,[38] which agrees with experimental results for substituted systems where only inversion is observed. The use of spin contaminated UHF wave functions for studying this reaction is found to give deviating results, both for energies and for characterization of stationary points on the PES. Thus the results and conclusions drawn on the basis of spin contaminated UHF and UMP wave functions should be viewed with skepticism.

(30) That substituents should have a larger effect on the W–H forbidden reaction than the allowed one has been concluded by others as well, see, e.g.: (a) Carpenter, B. K. *Tetrahedron* **1978**, *34*, 1897. (b) Epiotis, N. D. *J. Am. Chem. Soc.* **1973**, *95*, 1191, 1200, 1206, 1214.

(31) We note that our CASSCF/3-21G energy for **1** is 6.5 kcal/mol higher than that reported by SYM at the RHF/3-21G optimized geometry. The origin of this discrepancy is unknown but could be due to the use of slightly different geometries or, as suggested by a referee, because two different orbitals are being correlated by SYM and us.

(32) (a) Jensen, F.; Houk, K. N. *J. Am. Chem. Soc.* **1987**, *109*, 3139. (b) Spellmeyer, D. C.; Houk, K. H. *J. Am. Chem. Soc.* **1988**, *110*, 3412.

(33) Schoeller, W. W. *J. Am. Chem. Soc.* **1975**, *97*, 1978.

(34) Schlegel, B. H. *J. Chem. Phys.* **1986**, *84*, 4530.

(35) See, e.g.: Schleyer, P. v. R.; Reed, A. E. *J. Am. Chem. Soc.* **1988**, *110*, 4453.

(36) (a) Lowdin, P.-O. *Phys. Rev.* **1955**, *97*, 1509. (b) Knowles, P. J.; Handy, N. C. *J. Chem. Phys.* **1988**, *88*, 6991.

(37) There has been recent interest in the problems associated with spin contamination of UMP wave functions and their convergence properties as compared to RMP and to spin projected UMP wave functions. For bonds stretched to less than approximately 1.5 times their equilibrium length (R_e), the RMP method is to be preferred over the corresponding UMP method. In these cases it has been shown that at the RMP4 level the perturbation series is close to being converged (residual error typical less than a few kcal/mol). For systems where bonds are stretched beyond 1.5R_e, single determinant methods are insufficient unless going to very high order in the perturbation series, and MCSCF methods are to be preferred. Typical transition structures for unimolecular reactions have bond lengths stretched to less than 1.5R_e and should be adequately described by RMP methods, as ref 32 also shows. For some references on the MP convergence, see ref 34, 36, and the following: (a) Knowles, P. J.; Handy, N. C. *J. Phys. Chem.* **1988**, *92*, 3097. (b) Schlegel, B. H. *J. Phys. Chem.* **1988**, *92*, 3075. (c) Gill, P. M. W.; Wong, M. W.; Nobes, R. H.; Radom, L. *Chem. Phys. Lett.* **1988**, *148*, 541. (d) Lepetit, M. B.; Pelissier, M.; Malrieu, J. P. *J. Chem. Phys.* **1988**, *89*, 998.

(38) Since the transition structure leading to **3** must be higher in energy than **3**, the 7.7 kcal/mol energy difference between **2** and **3** is a lower bound for the energy difference between reaction occurring with inversion or retention.