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Ab Initio Calculations on the β-Cleavage Reactions of Polycyclic Radicals. Why Does Cubylcarbinyl React Much Faster than Either Homocubyl or 1-Bicyclo[1.1.1]pentyl?

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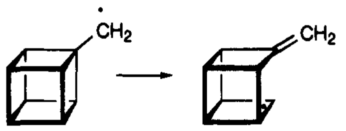
Abstract: In order to understand the very different rates of β-scission reactions in cubylcarbinyl (**1**) and homocubyl (**3**) radicals, *ab initio* calculations have been performed on these and other polycyclic radicals in which the scissile bond is part of a four-membered ring. The finding of a Bell−Evans−Polanyi relationship between the calculated values of ΔH and E_a for the β-cleavage reactions of **1**, **3**, bicyclo[2.2.0]hexylcarbinyl (**7**), bicyclo[1.1.1]pentylcarbinyl (**9**), and basketyl (**11**) radicals with $r^2 = 0.997$ indicates that the rates of these reactions parallel their exothermicities. However, this parallel is not found in the β-scission reaction of either 1-bicyclo[1.1.1]pentyl (**13**) or 2-bicyclo-[1.1.1]pentyl (**15**) radicals. Despite the high exothermicities calculated for both reactions, the activation energies are also computed to be very high. Population analyses support the hypothesis that the transition states for β-cleavage in **13** and **15** are destabilized by strong antibonding interactions between the two AOs to which the SOMO is largely confined. Comparison of the transition state geometries calculated for the eight β-scission reactions studied indicates that only the transition states for β-cleavage in **13** and **15** are substantially destabilized by overlap between the AOs of the SOMO.

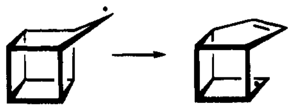
Eaton and Yip have found that cubylcarbinyl radical (**1**) undergoes a cascade of cleavage reactions, the first of which is breaking one of the three equivalent C−C bonds, β to the radical center, to form **2**.[1,2] Eaton, Newcomb, and co-workers measured the rate of this reaction by competitive trapping of **1** with phenylselenol.[3] The rate constant at room temperature was found to be 2.9×10^{10} s^{-1}, making this reaction one of the fastest radical rearrangements known.[3] From the temperature dependence of the rate constant, $E_a = 3.7$ kcal/mol was obtained for this reaction.



1 **2**

In marked contrast, Della, Walton, and their co-workers have found that, even at 220 °C, homocubyl radical (**3**) gives no indication of undergoing scission of one of the four equivalent C−C bonds, β to the radical center, to form **4**.[4] Assuming an Arrhenius preexponential factor of 10^{13} s^{-1}, $E_a > 14.9$ kcal/mol was obtained for this transformation.[5]

Della, Walton, *et al.* discussed two possible explanations for the striking difference between the ease of the β-scission reactions in **1** and **3**.[4] First, they noted that transformation of **1** to **2** results in cleavage of a C−C bond that is common to two four-membered rings. Scission of such a bond relieves more strain than does rearrangement of **3** to **4**, which breaks a bond that is common to one four-membered and one five-membered ring.



3 **4**

However, the MINDO/3 calculations performed by these authors found that rearrangement of **1** to **2** liberates only 7.1 kcal/mol more energy than rearrangement of **3** to **4**. This difference is significantly less than either the difference of 10 kcal/mol between the MINDO/3 E_as for these two reactions or the difference of about 11 kcal/mol between the experimental E_as for these rearrangements. If greater strain relief were wholly responsible for the much faster rearrangement of **1** to **2**, the difference between the enthalpies of these two reactions would have to be at least as large as the difference between their activation energies.

Second, Della, Walton, *et al.* considered the possibility that the transition state for C−C bond scission in **3** is destabilized, relative to the transition state for the same process in **1**. These authors pointed out that in the transition state leading to **4** there is more overlap between the two terminal AOs of the SOMO (i.e., the two AOs in the transition state in which the odd electron appears) than in the transition state leading to **2**. Since these two AOs have an antibonding relationship in the SOMO, overlap between them is destabilizing. Therefore, the larger overlap between these AOs in the transition state leading to **4** could be responsible for the higher E_a for formation of **4** from **3**.

Della, Walton, *et al.* looked for evidence of this type of destabilization in the MINDO/3 structure of **4**. They reported,

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[1] Eaton, P. E.; Yip, Y. C. *J. Am. Chem. Soc.* **1991**, *113*, 7692.

[2] EPR studies of this reaction are consistent with the mechanism that was proposed: Della, E. W.; Head, N. J.; Mallon, P.; Walton, J. C. *J. Am. Chem. Soc.* **1992**, *114*, 10730.

[3] Choi, S. Y.; Eaton, P. E.; Newcomb, M.; Yip, Y. C. *J. Am. Chem. Soc.* **1992**, *114*, 6326.

[4] Binmore, G. T.; Della, E. W.; Elsey, G. M.; Head, N. J.; Walton, J. C. *J. Am. Chem. Soc.* **1994**, *116*, 2759.

[5] In subsequent experiments at 200 °C in which much lower concentrations of radical trapping reagent were used, a significant fraction of **3** went on to unidentified olefinic products, presumably via **4** (Spitz, U.; McCabe, D.; Eaton, P. E., unpublished results). Therefore, 14.9 kcal/mol is more likely to be an upper than a lower limit to E_a for the rearrangement of **3** to **4**. We thank Professor Eaton for communicating his results to us.

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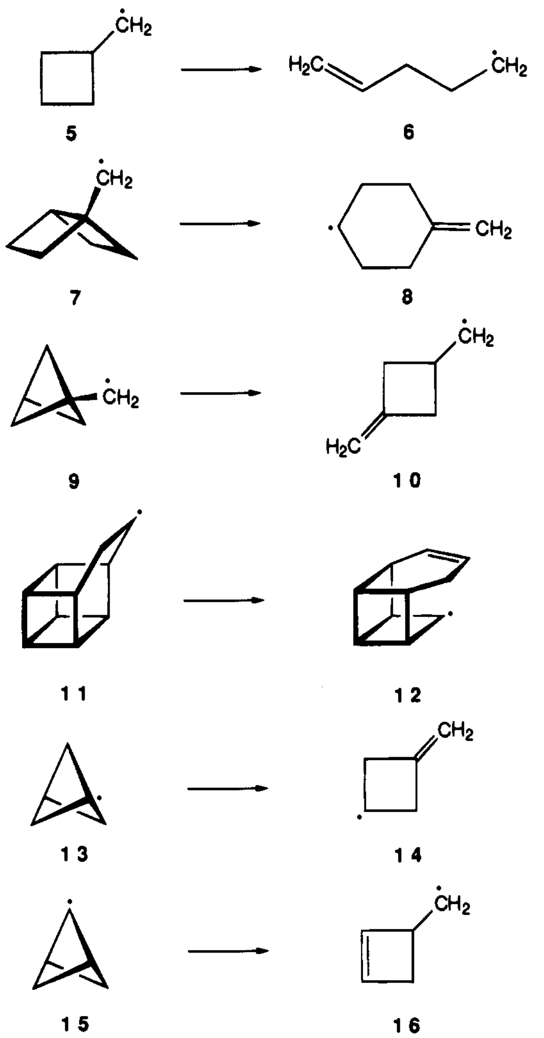
Table 1. Calculated UHF and PUMP2/6-31G* Energy Differences (kcal/mol) between Reactants and Products (ΔE), Reactants and Transition States (ΔE^{TS}), and the UHF/6-31G* Vibrational Corrections Necessary To Transform these Energy Differences into ΔH^{298} and E_a^{298} Also Given Is the Distance (R) in Each Transition State between the Two Carbons Bearing the AOs to Which the SOMO Is Largely Localized

reaction	ΔE (UHF)	ΔE(PUMP2)	$\Delta H^{298} - \Delta E$	ΔE^{TS}(UHF)	ΔE^{TS}(PUMP2)	$E_a^{298} - \Delta E^{TS}$	R (Å)
1 → **2**	−23.2	−22.6	1.1	7.7	4.0	−0.6	2.928
3 → **4**	−7.5	−6.6	0.0[a]	17.4	14.3	−1.3[b]	2.592
5 → **6**	−3.4	1.6	−0.6	17.9	15.6	−1.1	2.945
7 → **8**	−29.3	−24.5	0.7	6.2	2.9	−0.5	2.912
9 → **10**	−20.0	−11.3	−0.7	12.4	10.5	−0.9	3.000
11 → **12**	−8.1	−4.5	0.5	18.7	16.2	−0.9	2.809
13 → **14**	−30.4	−20.0	−2.1	25.8	28.0	−1.8	1.905
15 → **16**	−24.6	−18.7	−1.9	21.3	20.7	−1.7	2.220

[a] $\Delta H^{493} - \Delta E = -0.3$ kcal/mol. [b] $E_a^{493} - \Delta E^{TS} = -1.1$ kcal/mol.

Scheme 1



"An examination of the calculated structure ... did not provide corroboration for the explanation presented above for the slow rate of ring opening of [**3**]...." Therefore, they concluded, "Since the semiempirical results do not support the expectation based on frontier orbital theory, an *ab initio* study including full allowance for electron correlation is obviously desirable."[4]

Herein we report the results of such a study. We find that the difference between the exothermicities of the β-cleavage reactions of **1** and **3** accounts for most, if not all, of the difference between the activation energies for these two reactions. The greater interaction between the terminal AOs of the SOMO in the β-scission reaction of **3** may play a small role in making the E_a for this reaction higher than that for the analogous reaction of **1**, but this second effect appears to be the major factor responsible for the kinetic stability toward β-cleavage of some other polycyclic radicals, most notably 1-bicyclo[1.1.1]pentyl (**13**).

Computational Methodology

The geometries of **1**−**4** were optimized with UHF wave functions, using the 6-31G* basis set.[6] The transition states connecting **1** to **2** and **3** to **4** were located at the same level of theory. UHF/6-31G* vibrational analyses confirmed that **1**−**4** are energy minima and that the other two stationary points are indeed transition states. All the UHF/6-31G* and subsequent post-Hartree−Fock calculations were carried out using the Gaussian 92 suite of *ab initio* programs.[7]

For comparison with the β-scission reactions of **1** and **3**, several other radical reactions that open four-membered rings were also studied computationally. These included the β-cleavage reactions shown in Scheme 1: cyclobutylcarbinyl (**5**) → 4-penten-1-yl (**6**), bicyclo[2.2.0]hexylcarbinyl (**7**) → 4-methylenecyclohex-1-yl (**8**), bicyclo[1.1.1]pentylcarbinyl (**9**) → 3-methylenecyclobutylcarbinyl (**10**). These reactions are obviously more closely related to the β-scission reaction in **1** than in **3**.

In order to understand more completely the factors that cause C−C bond cleavage in **3** to be slower than in **1**, calculations were also performed on the three additional β-scission reactions shown in Scheme 1: 9-basketyl (**11**) → **12**, 1-bicyclo[1.1.1]pentyl (**13**) → 3-methylenecyclobut-1-yl (**14**) and 2-bicyclo[1.1.1]pentyl (**15**) → 2-cyclobutenylcarbinyl (**16**). The geometries of all the reactants and products were optimized and the transition states located at the UHF/6-31G* level. The geometries of **1**−**16** and the transition states connecting them are available as supporting information,[8] and the relative UHF energies of reactants, products, and transition states are given in Table 1.

Single point calculations that included electron correlation were performed at the UMP2/6-31G* level, using the UHF/6-31G* geometries. MP2[9] energies after spin projection (PUMP2)[10] are generally more reliable than those calculated without projection of higher spin contaminants.[11] Therefore, the PUMP2, rather than the UMP2 relative energies of **1**−**16** and the transition states connecting them are reported in Table 1.

In order to test the effect of including electron correlation in optimizing the geometries of the reactants and locating the transition states, the geometries of cubylcarbinyl (**1**) and bicyclopentyl (**13**) radicals were reoptimized and the transition state for β scission in each radical was relocated at the UMP2 level of theory. These UMP2/6-31G* geometries are also available as supporting information.[8] The PUMP2 energy difference between the transition state and reactant [ΔE^{TS}(PUMP2)] increased from 4.0 to 4.3 kcal/mol in the case of **1**

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[6] Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213.

[7] Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, W. P. M.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A.; Gaussian, Inc.: Pittsburgh, PA, 1992.

[8] Ordering information is given on any current masthead page.

[9] Moller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618. Pople, J. A.; Binkley, J. S.; Seeger, R. *Int. J. Quantum Chem. Symp.* **1976**, *10*, 1.

[10] Schlegel, H. B. *J. Chem. Phys.* **1986**, *84*, 4530.

[11] Hammons, J. H.; Coolidge, M. B.; Borden, W. T. *J. Phys. Chem.* **1990**, *94*, 5468. Hrovat, D. A.; Borden, W. T. *J. Phys. Chem.* **1994**, *98*, 10460.

and from 28.0 to 29.7 kcal/mol in the case of **13**. Since these reactions have, respectively, the second lowest and the highest values of ΔE^{TS} in Table 1, the finding that relocation of reactant and transition state geometries at the UMP2 level increased the values of ΔE^{TS}(PUMP2) by less than 10% in both cases provides good evidence that the UHF geometries are adequate for the single-point PUMP2 calculations.

Results and Discussion

The UHF and PUMP2/6-31G* energy differences between the reactants and products (ΔE) and reactants and transition states (ΔE^{TS}) are given in Table 1. Also given in Table 1 are the corrections for differences in zero-point energies and heat capacities that are necessary to transform ΔE and ΔE^{TS} into ΔH and E_a at 298 K.

As expected, the *β*-cleavage of **1** is calculated to be more exothermic than the *β*-cleavage of **3**. However, the calculated difference between these two enthalpies, which amounts to 14.6 kcal/mol in the UHF/6-31G* calculations and 14.9 kcal/mol with inclusion of electron correlation at the PUMP2 level, is much larger than the 7.1 kcal/mol computed by MINDO/3.

The energy barrier to ring opening of **1** is 7.7 kcal/mol at the UHF level and 4.0 kcal/mol at PUMP2. These values decrease by 0.9 kcal/mol after UHF corrections for zero-point energy differences. Correction for differences in heat capacities at 298 K and addition of $RT = 0.6$ kcal/mol to convert $\Delta H^{\ddagger}$ to E_a adds 0.3 kcal/mol. The PUMP2 value of $E_a = 3.4$ kcal/mol is in excellent agreement with the value of $E_a = 3.7$ kcal/mol, measured by Eaton, Newcomb, *et al.*[3]

The barrier to ring opening of **3**, found by the PUMP2/6-31G* calculations, is 14.3 kcal/mol, which, after correction for zero-point energy and heat capacity differences and addition of *RT*, becomes 13.0 kcal/mol at 298 K and 13.2 kcal/mol at 493 K. This PUMP2/6-31G* value is ≈2 kcal/mol below the experimental lower limit of $E_a > 14.9$ kcal/mol, estimated by Della, Walton, *et al.*[4] from their failure to observe *β*-cleavage in **3** at 493 K. However, the actual E_a may be somewhat smaller than their estimated value.[5]

The differences between the calculated values at 298 K of E_a for **1** → **2** and **3** → **4** at the UHF and PUMP2/6-31G* level are respectively 9.0 and 9.6 kcal/mol. These differences between the values of E_a calculated for the two *β*-scission reactions are comparable to the MINDO/3 difference of 10.0 kcal/mol.[4] However, whereas the MINDO/3 difference between the two E_as is roughly 40% greater than the MINDO/3 difference between the ΔHs, the *ab initio* differences between the two activation energies are, in contrast, 40% less than the *ab initio* differences between the exothermicities of these two reactions. Therefore, unlike the MINDO/3 results, our *ab initio* calculations allow the possibility that the large difference between the rates of these two *β*-scission reactions is due to the difference between the amount of strain that is relieved by each of them.

In order to test whether the smaller exothermicity of **3** → **4**, compared to **1** → **2**, is really responsible for the slower rate of the latter reaction, the values of ΔH and E_a were calculated for the reactions **5** → **6**, **7** → **8**, and **9** → **10**, all of which are closely related to *β*-scission in **1**. The results are given in Table 1.

At the UHF (PUMP2) level the ring opening of **5** is computed to have $\Delta H = -4.0$ (1.0) kcal/mol and to have an E_a at 298 K of 16.8 (14.5) kcal/mol. MINDO/3 predicts this reaction to be more endothermic ($\Delta H = 5.2$ kcal/mol) and to have a higher E_a (23.4 kcal/mol).[4] The experimentally determined $E_a = 12.2$ kcal/mol[12] is much closer to the PUMP2 than to the MINDO/3 result.

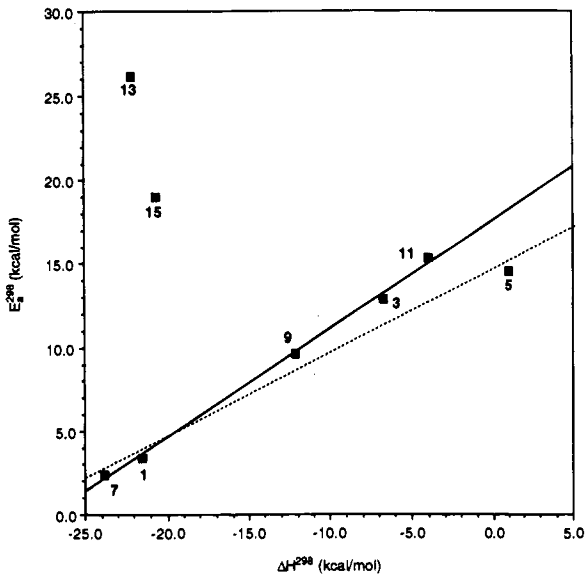

Figure 1. Plot of the PUMP2/6-31G* values of E_a for *β*-scission versus the PUMP2/6-31G* values of ΔH for these reactions. The broken line represents eq 1, which provides a least-squares fit with $r^2 = 0.982$ to the points for *β*-cleavage in **1**, **5**, **7**, and **9**, and the solid line is a plot of eq 2, which provides a least-squares fit with $r^2 = 0.997$ to the points for this reaction in **1**, **3**, **7**, **9**, and **11**.

To the best of our knowledge, the *β*-cleavage reaction, **7** → **8**, has not been studied experimentally. Our calculations find that this reaction is even more exothermic than **1** → **2** and predict that it has an even lower E_a. Although both reactions result in the transformation of a bicyclo[2.2.0]hexylcarbinyl radical into a 4-methylenecyclohexyl radical, greater exothermicity is predicted for **7** → **8** than for **1** → **2** because the rigid skeleton of **2** allows less complete geometrical relaxation than that permitted by the more flexible skeleton of **8**.

The rate of the *β*-cleavage of **9** to form **10** has been measured by Della, Walton, and co-workers, and $E_a = 7.1 \pm 1.2$ kcal/mol was obtained.[13] These investigators also performed UHF/6-31G* calculations on this reaction, and our UHF/6-31G* results are identical to theirs. However, Della, Walton, and co-workers corrected only for zero-point energy differences; whereas, the corrections in Table 1 also include the effect of heat capacity differences and 0.6 kcal/mol for the conversion of $\Delta H^{\ddagger}$ to E_a at 298 K. These differences account for the small difference between our UHF/6-31G* value of $E_a^{298} = 11.5$ kcal/mol and their value of $\Delta H_0^{\ddagger} = 11.2$ kcal/mol.[13] Our PUMP2/6-31G* value of $E_a^{298} = 9.6$ kcal/mol is closer than the UHF/6-31G* value to the E_a actually measured for *β*-scission in **9**.

The values in Table 1 of E_a for the *β*-scission reactions of the four carbinyl radicals—**1**, **5**, **7**, and **9**—appear to be linearly related to the values of ΔH, as would be expected from the principle of Bell[14] and Evans and Polanyi.[15] As the calculated exothermicities decrease, the calculated activation energies increase. A least-squares fit between the UHF/6-31G* values of E_a and ΔH gives $r^2 = 0.898$, but a much better fit is obtained using the PUMP2/6-31G* values. The equation

$$E_a = 14.5 \text{ kcal/mol} + 0.50\Delta H \qquad (1)$$

fits the PUMP2 energies with $r^2 = 0.982$. The fit of the calculated energies for *β*-scission in **1**, **5**, **7**, and **9** to this equation is shown by the broken line in Figure 1.

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[12] Walton, J. C. *J. Chem. Soc., Perkin Trans. 2* **1991**, 173.

[13] Della, E. W.; Schiesser, C. H.; Taylor, D. K.; Walton, J. C. *J. Chem. Soc., Perkin Trans. 2* **1991**, 1329.

[14] Bell, R. P. *Proc. Roy. Soc. London, A* **1936**, *154*, 414. **1938**, *34*,

[15] Evans, M. G.; Polanyi, M. *Trans. Faraday Soc.* **1936**, *32*, 1340. Evans, M. G.; Polanyi, M. *Trans. Faraday Soc.* **1938**, *34*, 11.

Also plotted in Figure 1 are the calculated values of ΔH and E_a in Table 1 for β-scission in **3** and **11**. The points for **3** and **11** both lie slightly above the broken line that fits the points for **1**, **5**, **7**, and **9**. In apparent disagreement with experiment,[4,5] β-scission is calculated to have a higher E_a in 9-basketyl (**11**) than in 9-homocubyl (**3**). The PUMP2 value of $E_a = 15.3$ kcal/mol for β-cleavage in **11** is 1.8 kcal/mol higher than the experimentally derived value of $E_a = 13.5$ kcal/mol[4] and 2.1 kcal/mol higher than the computed value of $E_a^{493} = 13.2$ kcal/mol in **3**.

As noted above, the PUMP2 value of $E_a^{493} = 13.2$ kcal/mol for β-cleavage in **3** is probably too low by 1−2 kcal/mol.[4,5] To the extent that E_a for β-scission in **3** is underestimated by our PUMP2/6-31G* calculations,[16] the point for **3** in Figure 1 will be even farther above the line for **1**, **5**, **7**, and **9**. However, the calculated value of $E_a^{298} = 13.0$ kcal/mol for **3** is only 1.8 kcal/mol above the broken line in Figure 1, which is slightly less than the 2.8 kcal/mol by which the point calculated for **11** → **12** lies above the broken line.

Figure 1 can be interpreted as indicating that some effect destabilizes the transition states for β-scission in **3** and **11** by 2−3 kcal/mol, relative to the transition states for β-scission in **1**, **5**, **7**, and **9**. However, if the point for **5** is not used in establishing the correlation between E_a and ΔH that is represented by the broken line in Figure 1, the points for **3** and **11** fall on the same line as the points for **1**, **7**, and **9**.

There are two arguments for omitting the point for **5** from the correlation between E_a and ΔH. First, **1**, **3**, **7**, **9**, and **11** are all polycyclic radicals, whereas **5** is monocyclic. The transition state for β-cleavage in **5** is, therefore, less constrained than the transition states for this reaction in **1**, **3**, **7**, **9**, and **11**. Second, the reaction **5** → **6** is *endothermic* at the PUMP2 level of theory, unlike all the other β-scission reactions in Table 1, which are exothermic.

If the point for β-scission in **5** is not included in the correlation of ΔH with E_a, the equation

$$E_a = 17.5\ \text{kcal/mol} + 0.65\Delta H \qquad (2)$$

fits the points calculated for β-scission in **1**, **3**, **7**, **9**, and **11** with $r^2 = 0.997$. The goodness of the fit is shown by the solid line in Figure 1.

This excellent correlation between the PUMP2/6-31G* values of E_a and ΔH for **3** → **4**, **11** → **12**, and the β-scission reactions of **1**, **7**, and **9** suggests that there is nothing unusual about the transition state for β-scission in either **3** or **11**. Of course, to the extent that the experimental E_a for **3** → **4** actually is higher than the 13.0 kcal/mol that we compute, the transition state for this reaction is destabilized, relative to those for the β-scission reactions of **1**, **7**, **9**, and **11**.[16] However, our PUMP2/6-31G* calculations fail to detect any significant destabilization of the transition state for β-cleavage in **3**.

Although we find no evidence for strong destabilization of the transition state for β-cleavage of **3**, it seemed likely to us that interaction between the two orbitals where the SOMO is largely localized might destabilize the transition state for β-cleavage of 1-bicyclo[1.1.1]pentyl radical (**13**). The enforced proximity of C-1 to C-3 in **13** should result in a considerable destabilizing interaction in the transition state between the AOs of the SOMO,[4] which are largely localized at these two carbons. This effect could be responsible for the amazing stability of **13** toward β-scission.[17,18]

Despite the fact that this reaction of **13** should be highly exothermic, we are unaware of any report that β-cleavage has been observed in the parent radical. 3-Phenyl-1-bicyclo[1.1.1]pentyl radical does undergo this reaction.[17] However, despite the presence of the radical stabilizing substituent at C-3, $E_a > 20$ kcal/mol has been measured for this reaction, and $E_a > 25$ kcal/mol has been calculated for β-scission in the unsubstituted radical (**13**).[19]

If interaction between the AOs of the SOMO significantly raised the energy of the transition state for β-cleavage in **13**, the E_a for this reaction should be higher than that predicted from ΔH, using eq 2. Therefore, the point for this reaction in Figure 1 should lie well above the solid line, and this is, in fact, the case.

Our calculations on the β-cleavage reaction of **13** to form **14** confirm the expectation that this reaction is highly exothermic. In fact, as shown in Table 1, after vibrational corrections this reaction is slightly more exothermic even than **1** → **2**. However, despite the exothermicity of this reaction of **13**, it has the highest calculated E_a in Table 1. Consequently, in Figure 1, the point for the β-cleavage reaction of **13** does, indeed, lie very far above the solid line that represents the correlation in eq 2.

It might be argued that β-cleavage in **13** differs from all the other β-scission reactions on which we have performed calculations, because **13** does not contain a cyclobutylcarbinyl moiety. However, the isomeric 2-bicyclo[1.1.1]pentyl radical (**15**) does contain such a moiety, and like the cleavage of **13** to **14**, that of **15** to **16** is calculated to be highly exothermic.[20] Moreover, as in the cleavage of **13** to **14**, that of **15** to **16** is calculated to have a high E_a;[21] in fact, only the E_a for **13** → **14** in Table 1 is higher. Consequently, the point for **15** → **16** also lies very far above the solid line in Figure 1.

We believe that the explanation of the very high E_as for β-cleavage in **13** and **15** is that, as suggested by Della, Walton,

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[16] Our PUMP2/6-31G* calculations give values of E_a for β-cleavage in **5**, **9**, and **11** that are uniformly *higher* by about 2 kcal/mol than those measured experimentally. Since, compared to experiment,[4,5] the PUMP2 value of E_a for **3** → **4** appears to be 1−2 kcal/mol too low, it may be that the transition state for this reaction is slightly destabilized, but in a way that is not mirrored in our calculations.

[17] Della, E. W.; Pigou, P. E.; Schiesser, C. H.; Taylor, D. K. *J. Org. Chem.* **1991**, *56*, 4659.

[18] The stability of 1-bicyclo[1.1.1]pentyl radicals toward β-cleavage has allowed them to be used in radical additions to [1.1.1]propellanes to form bicyclo[1.1.1]pentane oligomers, also known as "staffanes": Kaszynski, P.; Friedli, A. C.; Michl, J. *J. Am. Chem. Soc.* **1992**, *114*, 601 and references therein.

[19] In ref 17 25.8 kcal/mol is given as the UHF/6-31G* activation energy for this reaction. However, this value is what we calculate, before vibrational corrections, for ΔE^{TS}.

[20] Although β-scission reactions in **9**, **13**, and **15** all result in the cleavage of the bicyclo[1.1.1]pentane skeleton to a cyclobutane, the PUMP2 exothermicity of the first of these reactions is 9−10 kcal/mol less than those of the last two. At least part of the reason appears to be that **9** is thermodynamically more stable than **13** and **15**. Calculations on the isomers of **9** in which the radical center is at C-1, as in **13**, or at C-2, as in **15**, find these two radicals to have nearly the same PUMP2 energy, which is >5 kcal/mol above that of **9**. It does not appear that the strained C−C bonds of the bicyclo[1.1.1]pentane skeleton significantly stabilize **9** by hyperconjugating with the primary radical center, since our MP2-PUMP2/6-31G* calculations find that the BDE of a methyl C−H in 1-methylbicyclo[1.1.1]pentane is lower by only 0.4 kcal/mol than the C−H BDE of ethane. Therefore, it appears that **13** and **15** are destabilized by the presence of a radical center in the highly strained bicyclo[1.1.1]pentane skeleton. Ring strain does, in fact, result in the radical center in both **13** and **15** adopting a pyramidal geometry, in contrast to the nearly planar geometry at this center in **9**.

[21] Experimentally, it has been found that bicyclo[1.1.1]pentane undergoes chlorination at 25 °C to give a mixture of 1- and 2-chlorobicyclo[1.1.1]pentanes. The presence of significant amounts of products, formed by rearrangement of the intermediate 2-bicyclo[1.1.1]pentyl radicals (**15**), was not reported: Wiberg, K. B.; Connor, D. S. *J. Am. Chem. Soc.* **1966**, *88*, 4437. Wiberg, K. B.; Williams, V. Z., Jr. *J. Org. Chem.* **1970**, *35*, 369. The latter paper did report formation of small amounts of 1-chloro-3-methylenecyclobutane, but the presence of this product has been attributed to an ionic rearrangement of 1-chlorobicyclo[1.1.1]pentane, rather than to β-cleavage in the free radical leading to it.[17]

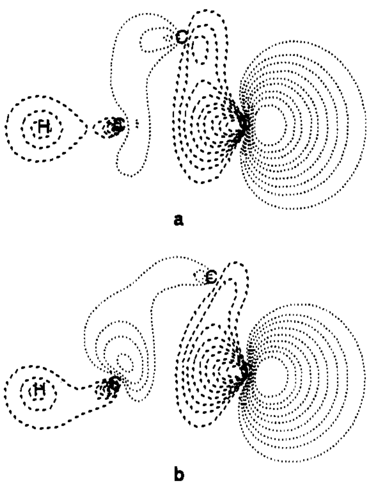

Figure 2. Contour plots of the singly occupied (SO)MO in (a) 1-bicyclo[1.1.1]pentyl radical (**13**) and (b) the transition state for β-cleavage of **13** to 3-methylenecyclobutyl radical (**14**). Contours are shown in the symmetry plane containing the two bridgehead carbons and the bridging carbon to which a σ bond is broken.

et al.,[4] the transition states for β-scission reactions are destabilized by overlap between the two AOs to which the SOMO is largely localized.[22] The increase in the antibonding interaction between these two AOs in going from **13** to the transition state for β-cleavage to **14** is readily seen in the contour plots in Figure 2 of the SOMO at these two geometries.

In the transition states for the β-scission reactions of **1**, **3**, and all the radicals shown in Scheme 1, there is an antibonding relationship between the two AOs to which the SOMO is largely localized. Therefore, the greater the spatial proximity of these two AOs in each transition state is, the more destabilizing the antibonding interaction between these AOs will be.

The distances, R, in the transition states between the carbons on which these two AOs reside are given in Table 1. In the transition state for β-scission in **1** (R = 2.928 Å) these AOs overlap very little. Since the distance between these atoms increases on going from the reactant to the transition state, the antibonding MP2 overlap population between these two atoms actually decreases, going from −0.092 in **1** to −0.055 in the transition state.

In contrast, in the transition state for β-scission in **13** (R = 1.905 Å) the AOs of the SOMO overlap much more than in the transition state for this reaction in **1**. The antibonding MP2 overlap population between the two carbons on which these AOs reside increases from −0.448 in **13** to −0.509 in the transition state. The increase in antibonding between the two bridgehead carbons in the transition state for β-cleavage in **13** raises the energy of the transition state.

Most of the eight β-cleavage reactions on which we have performed calculations have $R > 2.90$ Å. For **11** → **12** R = 2.81 Å, and for **3** → **4**, R = 2.59 Å, but these C−C distances are probably still too large for the antibonding interaction between the AOs on these carbons to have a significant energetic impact. However, in the transition state for **15** → **16**, R = 2.20 Å, and in the transition state for **13** → **14**, R = 1.905 Å. At these last two values of R, interactions between AOs are significant,[24] and as shown in Figure 1, it is only these two transition states that have substantially higher E_as than those expected from eq 2.

The transition state with the smaller value of R should be more destabilized. Indeed, due to the difference between both the distance and angular orientation of the AOs of the SOMO in the two transition states, the increase in the magnitude of the antibonding overlap population between the two atoms to which the SOMO is localized is larger in **13** (0.06) than in **15** (0.02). Consequently, the point for β-scission in **13** is >8 kcal/mol farther above the solid line in Figure 1 than the point for β-scission in **15**.

Conclusions

Our PUMP2 calculations find that there is a very good Bell−Evans−Polanyi relationship (eq 2) between ΔH and E_a for the β-scission reactions of radicals **1**, **3**, **7**, **9**, and **11**. The existence of such a relationship implies that the much lower E_a for β-cleavage in **1**, compared to **3**, is almost entirely a consequence of the greater exothermicity of the former reaction.

In the β-cleavage reactions of these radicals, the antibonding interaction between the two AOs to which the SOMO is localized in the transition states has little effect on the transition state energies. The absence of significant destabilization of the transition states is due to the large distance, R, that separates the carbons that bear these AOs. However, in the transition states for β-cleavage in **13** and **15**, R is small enough that the transition states for these two reactions are destabilized. We believe this destabilization is the reason that, despite the large exothermicity associated with β-cleavage of the bicyclo[1.1.1]pentyl ring systems in **13** and **15**, large activation energies are computed for this reaction in these two radicals. We attribute the very unusual kinetic stability toward β-cleavage that has been found experimentally in **13**[17] to this effect, and our calculations predict that experiments on **15** will also find this radical to be unusually stable toward β-scission of a C−C bond.[21]

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Supporting Information Available: Tables of UHF/6-31G* optimized geometries and energies for radicals **1**−**16** and the transition states that connect them and UMP2/6-31G* geometries for **1** and **13** and the transition states for β-scission reactions of these two radicals (24 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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(22) Della, Walton, *et al.*[4] stated that they sought, but found no evidence for, this effect in the MINDO/3 structure of **4**, the β-cleavage product formed from **3**. They may have been misled by the fact that in **4** both of the AOs that form the π bond contribute to the SOMO in a fashion that has the same phase as the AO in which the odd electron is largely localized. The reason for this finding is that in **4** the dominant interaction between the singly occupied AO and the AOs of the π bond is through the pair of σ bonds that overlap effectively with them, rather than directly through space.[23] The dominance of the through-bond interactions between the singly occupied AO and the π bond results in the lower energy combination of these orbitals being that in which they are out of phase. This combination, therefore, is doubly occupied, leaving the odd electron in the higher energy in-phase combination.

(23) Reviews of through-bond coupling: Hoffmann, R. *Acc. Chem. Res.* **1971**, *4*, 1. Gleiter, R. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 696. Paddon-Row, M. N. *Acc. Chem. Res.* **1982**, *15*, 245. Gleiter, R.; Schäfer, W. *Acc. Chem. Res.* **1990**, *23*, 369.

(24) C−C distances of roughly 2.2 and 1.9 Å are those associated with the interallylic bonds in respectively the boat and chair transition states for the Cope rearrangement: Hrovat, D. A.; Morokuma, K.; Borden, W. T. *J. Am. Chem. Soc.* **1994**, *116*, 1072. Wiest, O.; Black, K. A.; Houk, K. N. *J. Am. Chem. Soc.* **1994**, *116*, 10336.