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Ab Initio Theoretical Studies on the Ring-Opening Modes of the Oxiranyl-, Aziridinyl-, Oxaziridinyl-, and Thiaranylmethyl Radical Systems

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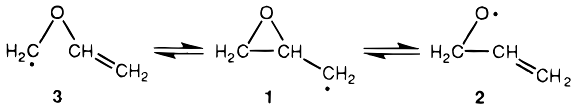
Ab initio theoretical studies have been carried out on the oxiranyl-, aziridinyl-, oxaziridinyl-, and thiaranylmethyl radical systems and on the various possible conformations of the ring-opened heteroallylic radical systems derived by ring opening of the first three systems. Previous theoretical studies on the ring opening of the oxiranylmethyl radical indicated that there is an overwhelming thermodynamic preference for the formation of the allyloxy radical over the formation of the (vinyloxy)methyl radical. The results of the present theoretical studies on the potential energy surfaces for ring opening also indicate a strong kinetic preference for allyloxy radical formation over the formation of the (vinyloxy)methyl radical. The results of the present calculations on the aziridinylmethyl radical indicates that it kinetically prefers to ring open by cleavage of the C−N bond, but thermodynamically by cleavage of the C−C bond. The results of the calculations on the C_2H_4NO radical system indicate that ring opening of the oxaziridinylmethyl radical by C−O bond cleavage is both thermodynamically and kinetically favored over C−N bond cleavage. Calculations on the thiaranylmethyl radical suggest that it does not represent a minimum-energy structure on the C_3H_5S potential energy surface.

Introduction

Experimentally, the ring opening of substituted oxiranylmethyl radicals occurs with the exclusive formation of the corresponding allyloxy radical by C−O bond cleavage of the oxirane ring (eq 1),[1] except when aryl



(1)

	3	1	2
UHG/6-31G*	10.2-10.8	14.4	0.0-0.1
UMP2/6-31G*	0.0-1.0	0.6	4.2
QCISD(T)/6-31G*	1.9-2.8	5.4	0.0-0.4

substituted at C_3 of the oxiranylmethyl radical system.[2] Spectroscopic studies[3] have provided an upper limit for the rate of ring opening of the oxiranylmethyl radical of $\sim 10^8$ s^{-1}, while the competitive fragmentation of the oxiranylmethyl portion versus the that of the cyclopropylmethyl portion in the cyclopropyloxiranylmethyl radical has provided an upper limit for the rate of ring opening of the oxiranylmethyl radical of $\sim 10^{10}$ s^{-1}.[4] The latter number is approximately 2 orders of magnitude greater than that observed for ring opening of the cyclopropylmethyl radical of 1.2×10^8 s^{-1}.[5]

The experimental results derived from the formation of both **1** and **2** by the photoinduced, homolytic decomposition of allyl 4-nitrobenzenesulfenate, which leads directly to the formation of the allyloxy radical, and 4,5-epoxy-2-methyl-2-pentyl 4-nitrobenzenesulfenate, which results in the formation of the oxiranylmethyl radical after β scission of the initially formed 4,5-epoxy-2-methyl-2-pentyloxy radical, reveal that the formation of the products can only be rationalized as being formed via the allyloxy radical.[6] No evidence was obtained, indicating that the intermediate oxiranylmethyl radical **1** was trapped by coupling with the 4-nitrobenzenethiyl radical or underwent dimerization.[6] This is consistent with the kinetic data reported in refs 3 and 4 in which ring opening occurs more rapidly than does coupling,[7] the rate of which should be diffusion controlled under the dilute (0.01 M) reaction conditions employed in the author's studies.[6]

The results of earlier high-level *ab initio* MO calculations carried out in the author's laboratories have indicated that the formation of the allyloxy radical is highly thermodynamically favored.[6] It was concluded by the author that the greater electronegativity of the oxygen atom, and the relatively small stabilization afforded an adjacent radical center by a nonbonded pair of electrons on an oxygen atom (calculated to be ~ 5.3 kcal mol^{-1}),[8] favored the formation of the allyloxy radical over the vinyloxymethyl radical.[6]

It then became of interest to consider the ring opening of other heterocyclopropylmethyl radical systems in order to determine the kinetically and thermodynamically favored modes of ring opening. In this context, high-level

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[3] Laurie, D.; Nonhebel, D. C.; Suckling, C. J.; Walton, J. C. *Tetrahedron* **1993**, *49,* 5869.

[4] Krosley, K. W.; Gleicher, G. J. *J. Phys. Org. Chem.* **1993**, *6,* 228.

[5] Bowry, V. W.; Lusztyk, J.; Ingold, K. U. *J. Am. Chem. Soc.* **1991**, *113,* 5687.

[6] Pasto, D. J.; Cottard, F.; Picconatto, C. *J. Org. Chem.* **1994**, *59,* 7172.

[7] Iodoepoxides have, however, been observed to be formed in the decomposition of allyl hypoiodites (Galatsis, P.; Millan, S. D. *Tetrahedron Lett.* **1991**, *32,* 7493. Rawal, V. H.; Iwasa, S. *Tetrahedron Lett.* **1992**, *33,* 4687. Suginome, H.; Wang, J. B.; *J. Chem. Soc., Chem. Commun.* **1990**, 1629.).

[8] Pasto, D. J.; Krasnansky, R.; Zercher, C. *J. Org. Chem.* **1987**, *52,* 3062.

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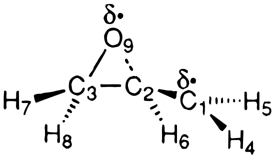
ab initio calculations have been carried out on the energy surfaces for ring opening of the oxiranyl-, aziridinyl-, oxaziridinyl-, and thiaranylmethyl radicals.

Extensive UHF *ab initio* calculations[9] utilizing the 6-31G*, 6-31+G*, 6-31++G**, and 6-311G(2d,p) basis sets on the oxiranylmethyl (**1**), allyloxy (**2**), and vinyloxymethyl (**3**) radicals indicated that there was very little difference in the relative energies of **1**−**3** at the different UHF basis-set levels, with **2** being lower in energy than **3** and **1** by ~10 and ~15 kcal mol^{-1}, respectively.[6] *However*, at the UMP2/6-31G* optimized level the relative energies differed significantly from those derived at the various UHF levels, with a reversal in the relative energies of **2** and **3**, and with **1** being predicted to be only slightly higher in energy than **3** (the relative energies are shown under the structures in eq 1). Calculations carried out at the QCISD(T)/6-31G* level on the 6-31G* geometry-optimized structures gave the same sequence in relative energies as those derived with the UHF procedures, but substantially compressed (see eq 1).[6] It was concluded that optimization at the UHF 6-31G* level, followed by single-point calculations at the QCISD(T)/6-31G* level, should be adequate for the calculational studies on other heterocyclopropylmethyl−heteroallyllic radical systems, the results of which are reported herein.

Results



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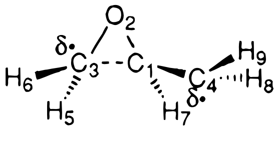

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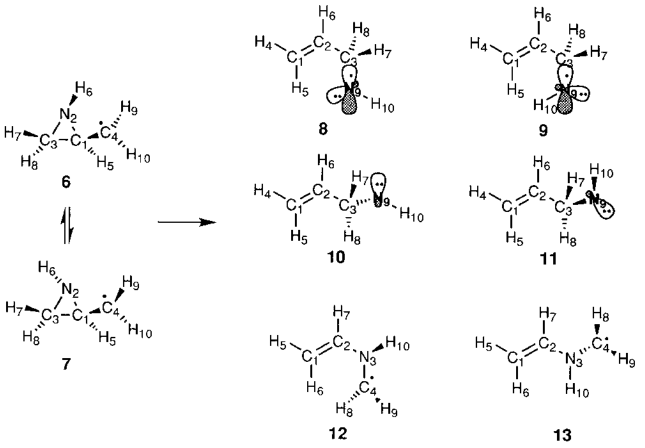
Table 1. QCISD(T)/6-31G* Total Energies and UHF $\langle S^2\rangle$ Values for the C$_3$H$_5$O Radical Species

structure	E_{tot} (Hartrees)	$\langle S^2\rangle$	E_{rel} (kcal mol^{-1})
1	−191.870 73	0.7676	5.40
syn-**2**	−191.879 33	0.7611	0.00
syn-**3**	−191.876 31	0.7844	1.89
4	−191.865 04	0.9184	8.97
5	−191.847 26	0.9802	20.12

The C$_3$H$_5$O Radical System. For comparison with the energy barriers for the different modes of ring opening of the aziridinyl-, oxaziridinyl-, and thiaranylmethyl radicals, calculations now have been carried out at the UHF 6-31G* level on the energy surfaces for the ring opening of the oxiranylmethyl radical by C−C and C−O bond cleavage. Transition structures **4** and **5** for C−O and C−C bond cleavage have been located. Frequency calculations on the two transition structures indicate the presence of one imaginary frequency in each structure, −785.86i and −754.36i cm^{-1}, respectively, corresponding to the appropriate motions for C−O or C−C bond cleavage. The calculated structural parameters for **4** and **5** are given in Tables 1 and 2 of the supporting information. The total energies and the UHF $\langle S^2\rangle$ values for the oxiranylmethyl, *syn*-allyloxy, and *syn*-vinyloxymethyl radicals (the conformations initially expected to be formed by the simple stretching and cleavage of the C−O and C−C bonds) and the transition structures **4** and **5** are given in Table 1. The $\langle S^2\rangle$ values for **1**, *syn*-**2**, and *syn*-**3** are all quite similar, being <0.80, indicating that the contaminations by higher spin states are relatively low and are of comparable magnitude. The $\langle S^2\rangle$ values for the transition structures **4** and **5**, however, are significantly higher, indicating significant spin-state contamination by higher-energy spin states, suggesting that the total energies of the transition structures **4** and **5** should be somewhat higher than those calculated at the UHF/6-31G* level and that the calculated geometries might be slightly in error from those of the pure doublet states. The calculated geometries, however, seem to be very reasonable. The extent of C−O bond cleavage in transition structure **4** is less than that for C−C bond cleavage in transition structure **5**. The calculated C−O distances in the oxiranylmethyl, transition structure **4**, and *syn*-allyloxy radicals are 1.412, 1.670, and 2.850 Å, while for C−C cleavage to form the *syn*-vinyloxymethyl radical the similar calculated C−C distances are 1.465, 1.814, and 2.325 Å. The differences in the changes of C−O versus C−C distances in going from the ground state oxiranylmethyl radical to the transition structures for C−O and C−C bond cleavage are in accord with an expected earlier transition state for the more exothermic C−O bond cleavage relative to that for C−C bond cleavage.

The C$_3$H$_6$N Radical System. Full geometry optimization calculations have been carried out on the *cis*- and *trans*-aziridinylmethyl radicals **6** and **7**, the allylaza radicals **8**−**11**, and the (vinylaza)methyl radicals **12** and **13**. (The *syn,syn*-conformation of the allylaza radical shown as structure **9** does not appear to represent a minimum-energy conformation on the energy surface of the C$_3$H$_6$N radical system.) The calculated structural parameters for **6**−**8** and **10**−**13** are provided in Tables 3−9 of the supporting information. Their total and relative energies and $\langle S^2\rangle$ values are given in Table 2.



The $\langle S^2\rangle$ values of the aziridinylmethyl radicals **6** and **7** and the allylaza radicals **8**, **10**, and **11** are very similar and significantly less than 0.80, indicating very little higher spin-state contamination. The $\langle S^2\rangle$ values of 0.84 and 0.85 for the (vinylaza)methyl radicals **12** and **13** are somewhat higher, indicating some spin contamination by higher spin states. This is not unexpected in that these systems contain a more delocalized π system.

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(9) The calculations were carried out using the GAUSIAN 92 package of programs (Gaussian 92, Revision G.2, Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; 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, K. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. Gaussian, Inc., Pittsburgh, PA, 1992.).

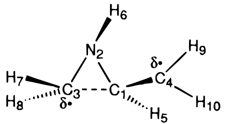
Table 2. Total and Relative Energies of the C_3H_6N Radical Species

structure	E_{tot}/6-31G* (Hartrees)	$\langle S^2 \rangle$	E_{rel} (kcal mol^{-1}	$E_{QCISD(T)}$ (Hartrees)	E_{rel} (kcal mol^{-1})
6	−171.448 55	0.7688	14.02	−172.033 34	11.58
7	−171.448 42	0.7660	14.10	−172.031 65	12.64
8	−171.470 85	0.7672	0.03	−172.046 61	3.25
10	−171.470 89	0.7781	0.00	−172.046 18	3.52
11	−171.470 16	0.7821	0.46	−172.049 52	1.42
12	−171.467 03	0.8439	2.42	−172.051 25	0.34
13	−171.468 15	0.8475	1.72	−172.051 79	0.00
14	−171.427 18	0.9579	27.42	−172.013 72	23.89
15	−171.427 31	0.9636	27.34	−172.012 73	24.51
16	−171.438 52	0.9162	20.31	−172.027 09	15.50
17	−171.435 60	0.9280	22.14	−172.023 37	17.83

Although nonplanarity is indicated in structures **10**–**13**, the extent of nonplanarity is minimal. The lowest-energy electronic configurations of **8** and **10**–**13** possess five π-electron systems (in **8**, **10**, and **11** the π-type CH_2 σ orbital contributes two electrons to the overall π-type system) in which the singly occupied molecular orbital is the highest-lying π MO highly localized on the nitrogen atom. Preliminary calculations on the six π-electron configuration for a structure similar to **8** (by interchange of the singly and doubly occupied nonbonding orbitals on the nitrogen atom) indicate that the six π-electron structure lies >40 kcal mol^{-1} above the five π-electron structure,[10] this undoubtedly being due to the promotion energy required to elevate an electron from an sp^2-hybridized AO on nitrogen to a 2p AO on nitrogen.

In contrast to the C_3H_5O radical system in which the allyloxy radical is calculated to be lowest in energy, in the C_3H_6N radical system the (vinylaza)methyl radicals **12** and **13** are calculated to be lower in energy at the QCISD(T)/6-31G* level. This reversal in relative energies of the ring-opened structures must be due to the greater stabilization of a carbon radical center provided by a nonbonded pair of electrons on an attached nitrogen atom (calculated to be ~11.3 kcal mol^{-1}),[8] as well as the decreased electronegativity of the nitrogen atom compared to that of the oxygen atom.

Calculations have also been carried out to locate the transition structures for C–N and C–C bond cleavage in **6** and **7**. Two transition structures for C–C bond cleavage have been located: one originating from the *cis*-aziridinylmethyl radical **7** shown as structure **14** (H_6–N_2–C_1–C_4 dihedral angle 11.47° and C_1–C_3 distance of 1.832 Å) and one originating from the *trans*-aziridinylmethyl radical **6** shown as structure **15** (H_6–N_2–C_1–C_4 dihedral angle of 142.05° and C_1–C_3 distance of 1.834 Å), both of which would appear to be capable of resulting in the formation of either **12** or **13**. The calculated structural parameters are provided in Tables 10 and 11 of the supporting information. The total and relative energies and $\langle S^2 \rangle$ values of **14** and **15** are given in Table 2. As in the case of the transition structures for C–C and C–O bond cleavage in the oxiranylmethyl radical, the $\langle S^2 \rangle$ values for the transtion structures **14** and **15** are significantly larger, indicating a greater extent of high spin-state contamination. Both transition structures possess one imaginary frequency (−755.25i and −753.12i cm^{-1}, respectively) involving the stretching mode of the C_1–C_3 bond.



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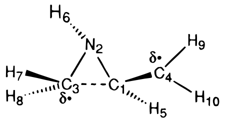

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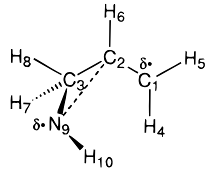

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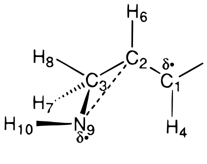

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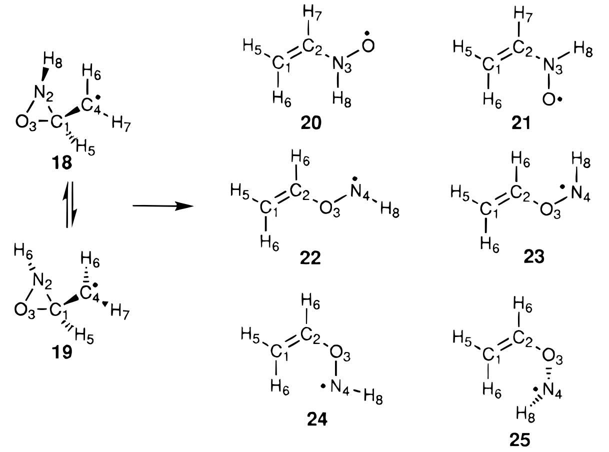
Two transition structures have been located for C–N bond cleavage: one originating from the *cis*-aziridinylmethyl radical shown as structure **16** (H_{10}–N_9–C_3–C_1 dihedral angle of −67.12° and C_2–N_9 distance of 1.736 Å), which would appear to be capable of resulting in the formation of either **8** or **9**, and one originating from the *trans*-aziridinylmethyl radical shown as structure **17** (H_{10}–N_9–C_3–C_1 dihedral angle of 119.74° with C_2–N_9 distance of 1.747 Å), which would appear to be capable of leading to the formation of either **10** or **11**. Transition structure **17** possesses one imaginary frequency (−801.54i cm^{-1}) involving predominantly C_2–N_9 stretching, while transition structure **16** possesses one imaginary frequency (−770.10i cm^{-1}) involving C_2–N_9 stretching along with some rotational movement of the methylene groups.

The C_2H_4NO Radical System. Calculations have been carried out on the *cis*- and *trans*-oxaziridinylmethyl radicals **18** and **19** and on the conformations of the C–O ring-opened (vinylaza)oxy radicals **20** and **21** and the C–N ring-opened (vinyloxy)aza radicals **22**–**25**. The calculated structural parameters are given in Tables 14–21 of the supporting information. Their total and relative energies and $\langle S^2 \rangle$ values are given in Table 3. The $\langle S^2 \rangle$ values for the *cis*- and *trans*-oxaziridinylmethyl radicals **18** and **19** indicate very little higher spin-state contamination. The $\langle S^2 \rangle$ values for the N-centered radicals average ~0.80, indicating some spin contamination, while the $\langle S^2 \rangle$ values for the O-centered radicals indicate a signifantly greater extent of spin contamination.



The lowest-energy electronic configurations of **20**–**25** possess five π-electron systems. Calculations on the six π-electron configurations of **21** and **22** indicate that these electronic configurations lie considerably higher in energy (ca. >50 kcal mol^{-1}).[10]

A search for the transition structures for C–O and C–N bond cleavage in the lower-energy *cis*-oxaziridinyl-

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(10) No attempts have been made to optimize the six π-electron structures.

Table 3. Total and Relative Energies of Structures of the C_2H_3NO Radical Species

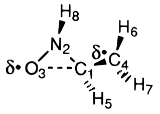
structure	E_{tot}/6-31G* (Hartrees)	$\langle S^2 \rangle$	E_{rel} (kcal mol^{-1})	$E_{QCISD(T)}$ (Hartrees)	E_{rel} (kcal mol^{-1})
18	−207.224 81	0.7672	33.98	−207.849 31	31.27
19	−207.224 499	0.7651	34.18	−207.847 54	32.38
20	−207.278 97	0.9898	0.00	−207.899 14	0.00
21	−207.278 00	0.9602	0.61	−207.899 07	0.04
22	−207.637	0.7947	14.18	−207.876 11	14.45
23	−207.245 45	0.8130	21.03	−207.866 39	20.55
24	−207.254 88	0.7982	15.12	−207.875 07	15.10
25	−207.245 96	0.7823	20.71	−207.866 94	20.20
26	−207.208 71	0.9453	44.09	−207.838 10	38.30
27	−207.205 83	0.9735	45.89	−207.832 74	41.66

Table 4. Energy Barriers and Reaction Energies for the Ring Opening of the Cyclopropyl and Heterocyclopropyl Radical Systems

system	bond cleaved	$\Delta E^{\ddagger}$ (kcal mol^{-1})	ΔE (kcal mol^{-1})
cyclopropylmethyl	C−C	7.05−7.26[a]	
		9.2[b]	−3.7
oxiranylmethyl	C−O	3.57	−5.40
	C−C	14.7	−3.51
aziridinylmethyl (*cis*)	C−N	3.92	−8.33
(*trans*)		5.20	−9.11, −11.21[c]
(*cis*)	C−C	12.27	−11.24, −11.58[d]
(*trans*)		11.87	−12.30, −12.64[e]
oxaziridinylmethyl (*cis*)	C−O	7.03	−31.27
	C−N	10.40	−16.17

[a] Experimental E_as from ref 5. Beckwith, A. L. J.; Bowry, V. W. *J. Org. Chem.* **1989**, *54*, 2681. Newcomb, M.; Glenn, A. G. *J. Am. Chem. Soc.* **1989**, *111*, 275. [b] CI/SVP calculation, see: ref 11. [c] To form **10** or **11**. [d] To form **12** and **13**. [e] To form **12** and **13**.

methyl radical **18** resulted in the structures shown as **26** and **27**. The calculated structural parameters are provided in Tables 22 and 23 of the supporting information, and their total and relative energies and $\langle S^2 \rangle$ values are given in Table 3. The $\langle S^2 \rangle$ values indicate significant spin contamination as observed in the transition structures for ring opening of the oxiranyl- and aziridinylmethyl radicals.



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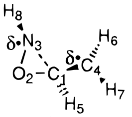

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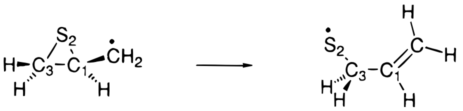
The C_3H_5S Radical System. All attempts to locate a local minimum-energy structure for the thiaranylmethyl radical **28** at the UHF 6-31G* level have failed; full geometry optimization calculations resulted in the spontaneous ring opening of **28** to produce the allylthiyl radical **29**. In another approach, the structure of methylthiarane was fully geometry optimized, and then geometry optimization calculations were carried out on **28** by maintaining the $C_1-S_2-C_3$ bond angle as calculated for methylthiarane. Further optimization, starting from the structural parameters thus calculated with a nonrestricted $C_1-S_2-C_3$ bond angle, again resulted in the immediate ring opening to form **29**.

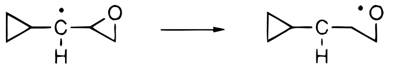


28 **29**

Discussion

Table 4 summarizes the experimentally observed and theoretically derived activation energies and overall changes in energy for the ring opening of the cyclopropylmethyl and heterocyclopropylmethyl radical systems determined in this study.

It is first necessary to compare the results of the experimental and theoretical studies on the rates of ring opening of the cyclopropyl- and oxiranylmethyl radicals. The experimental $\Delta E^{\pm}$s for the ring opening of the cyclopropylmethyl radical range from 7.05 to 7.26 kcal mol^{-1}, with a theoretically calculated value at the optimized CI/SVP level of 9.2 kcal mol^{-1}.[11] The lowest-energy pathway for the ring opening of the oxiranylmethyl radical by C−O bond cleavage is calculated to be associated with an energy barrier of 3.57 kcal mol^{-1}. The quantitative comparison of the calculated energy barriers is complicated by the fact that very different calculational methods have been used on the two systems; as has been pointed out earlier in this article, the higher spin-state contamination of the UHF QCISD(T)/6-31G* transition structure **4** must result in a lowering of the total energy of the transition structure **4**, with a concomitant lowering of the energy barrier for the ring opening of the oxiranylmethyl radical **1**. Qualitatively, however, the calculational results are in agreement with the experimental observation that the ring opening of the cyclopropyloxiranylmethyl radical (**30**) sets an *upper* limit on the relative rate of ring opening of the oxiranylmethyl portion of **30** of ~10^2 times faster than the ring opening of the cyclopropylmethyl portion of **30**. (The true magnitude of the rate difference in the two modes of ring opening of **30** may be even higher.) The strong preference for ring opening of the oxiranylmethyl radical by C−O bond cleavage over C−C bond cleavage is also consistent with experimental observations. Finally, the overall reaction energies calculated for the ring opening of the cyclopropylmethyl and oxiranylmethyl radicals are very similar, suggesting that the very small changes in $\langle S^2 \rangle$ values in going from **1** to **2** or **3** do not have a significant impact on the calculated reaction energies.



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The ring opening of the *cis*- and *trans*-aziridinylmethyl radicals **6** and **7** presents an interesting contrast between the kinetically and thermodynamically favored modes of ring opening. The energy barriers for the lowest-energy pathways for the ring opening of **6** and **7** by C−N bond cleavage are calculated to be slightly greater in magnitude than the energy barrier for C−O bond cleavage in the oxiranylmethyl radical and substantially less than the calculated energy barriers for ring opening by C−C bond cleavage. Again, the significant high spin-state contamination of the transition structures for cleavage of either C−N or C−C bonds would indicate that the calculated energy barriers might be somewhat low compared to those for the pure doublet states. However, the overall reaction energies thermodynamically favor the formation of products by C−C bond cleavage. These calculational results suggest that reversibility of product formation via **8**, **10**, and **11** versus **12** and **13** might be

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(11) Quenemoen, K.; Borden, W. T.; Davidson, E. R.; Feller, D. *J. Am. Chem. Soc.* **1985**, *107*, 5054.

readily observed by appropriate substitution to affect the relative energies of the ground and transition states.

The calculational results derived on the C_2H_4NO radical system indicate ring opening by C−O bond cleavage is both kinetically and thermodynamically favored over C−N bond cleavage. This is consistent with the combination of the calculational results derived on the oxiranyl- and aziridinylmethyl radical systems.

An overall analysis of these results indicates that the introduction of a heteroatom into the three-membered ring of the cyclopropylmethyl radical results in a lowering of the energy barrier for ring opening via cleavage of the carbon−heteroatom bond and an increase in the energy barrier for cleavage of the C−C bond. The overall reaction energies increase with increasing total electronegativity of the heteroatoms in the three-membered ring. Experimental studies are under consideration to gain further data on the ring-opening modes of these heterocyclopropylmethyl radical systems and on their potential for equilibration.

Supporting Information Available: Tables of calculated structural parameters for structures **4**−**8** and **10**−**27** (23 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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