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A Theoretical Investigation of the 1,3-Migration in Allylperoxyl Radicals

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Abstract: Allylperoxyl radicals undergo a 1,3-transfer of oxygen, and both a concerted mechanism and a mechanism involving fragmentation of the peroxyl and readdition of oxygen have been previously proposed. In our theoretical study of this rearrangement, calculations were performed at the unrestricted Hartree-Fock, MP2, and MP3 levels: standard 6-31G(d) basis sets were used for geometry optimizations and pathway studies; single point energies for all optimized structures were obtained at the MP2/6-31G(d,p)//H-F/6-31G(d) level and for some structures at the MP3/6-31G(d,p)//HF/6-31g(d) level. A conformational energy map of the allylperoxyl radical was calculated, and a relatively flat energy surface was found; all of the conformations are accessible and populated under normal conditions. Attempts to find a transition-state structure for the rearrangement revealed a bound cyclic radical that is close in energy to the allylperoxyl. The lowest energy pathway from the acyclic allylperoxyl to the cyclic radical proceeds over a barrier of almost 170 kJ/mol. Fragmentation of allylperoxyl to give the allyl radical and oxygen requires only 90 kJ/mol, and the calculations therefore are interpreted to suggest that the rearrangement proceeds by this lower energy fragmentation–readdition mechanism. Calculations were also carried out on allyl and substituted allyl radicals. All of the radicals investigated were planar, so that the experimentally observed stereoselectivity of the rearrangement cannot be explained by arguing that the allyl radicals retain a pyramidal conformation after fragmentation of the allylperoxyl radical. The selectivity of the rearrangement thus must result from a cage effect wherein the diffusion of the allyl radical-oxygen pair is prevented due to caging by the solvent.

Introduction

Allylperoxyl radicals are intermediates in the radical autoxidation of unsaturated lipids of biological importance. The autoxidations of cholesterol and oleate esters, for example, proceed through intermediate peroxyls, and the chemistry of these intermediate radicals and the product allyl hydroperoxides has been the focus of investigations for over 30 years. Allylperoxyl radicals such as **1** are important intermediates in processes as diverse as the drying of paint and the peroxidative destruction of cell membranes, the latter being implicated in a number of degenerative diseases such as inflammation, heart disease, and cancer.

In pioneering studies, Schenck[1] and Brill[2] demonstrated that allyl hydroperoxides undergo a free radical rearrangement in which the peroxyl is transferred across the allyl system, i.e., a 1,3-migration, **1 → 2**, as shown below. The rearrangement is catalyzed

1   **2**
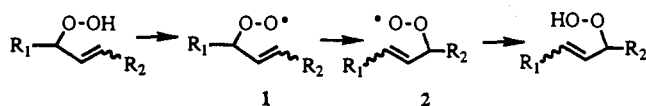
by free radical initiators or by light, and it is inhibited by phenolic antioxidants. The initial mechanism proposed for the rearrangement suggested that it proceeded through an intermediate 1,2-dioxolanyl-4-yl radical, **3**. Subsequent work by Brill[3] and

3   **4**

Porter[4,5] provided evidence against the intermediate **3** since authentic radicals like **3** undergo reactions (such as oxygen entrapment) to give products not observed in the rearrangement product mixture. Brill[3] subsequently suggested that the open peroxyl radicals were not intermediates in the rearrangement but that the hydroperoxide gave a common cyclic intermediate in which the unpaired electron was localized in an antibonding orbital

Scheme I. Free Radical Rearrangement of Oleate Hydroperoxide
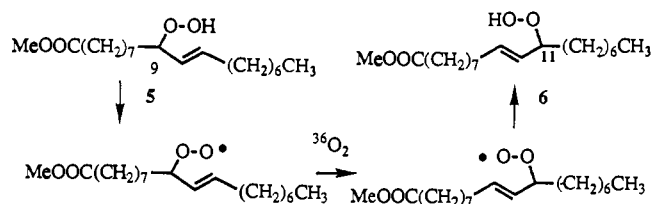
on oxygen. An EPR investigation of allylperoxyl radicals, however, did not support this suggestion.[6]

Porter and Wujek[5] proposed that the rearrangement proceeds from an open peroxyl radical through a transition state, **4**, with no intermediate like **3** being formed. Evidence to support this view is the fact that rearrangement proceeds without significant incorporation of atmospheric oxygen; also the rearrangement is highly stereoselective in acyclic systems.[7] Thus, rearrangement of the oleate hydroperoxide, **5**, under a [36]O₂ atmosphere gives an equilibrium mixture of **5** and **6** without significant incorporation of [36]O₂ into the hydroperoxide (Scheme I). The rearrangement is highly stereoselective; the rearrangement product is of the opposite configuration from the starting material; and even after extensive rearrangement when the 9 and 11 hydroperoxides are present in nearly equal amounts, both hydroperoxides are still significantly enriched in one enantiomer.[7] There is a temperature dependence on the observed selectivity: the product hydroperoxide is isolated with optical purities approaching 98% when the rearrangement is carried out at 20 °C, while 50 °C rearrangements lead to products with a greater loss of stereochemical integrity. As an example of the stereoselectivity of the rearrangement, 9-*R*-**5** with enantiomeric excess >99% rearranges at 22 °C to give a

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(3) Brill, W. E. *J. Chem. Soc., Perkin Trans. II* **1984**, 621.
(4) Porter, N. A.; Zuraw, P. *J. Chem. Soc., Chem. Commun.* **1985**, 1472.
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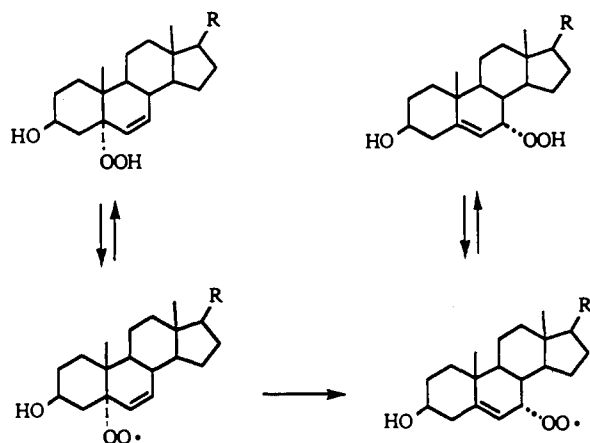(7) Porter, N. A.; Kaplan, J. K.; Dussault, P. H. *J. Am. Chem. Soc.* **1990**, *112*, 1266.

Scheme II. Free Radical Rearrangement of Cholesterol 5-α-Hydroperoxide

mixture of 9-*R*-5 and 11-*S*-6 with enantiomeric excess of 97.2% ± 0.5% if the product mixture is analyzed at the time when 5/6 = 1.7.

The stereochemical and oxygen labeling studies led to the proposal that the rearrangement proceeds by a concerted peroxyl radical transfer. Thus, a transition state with an envelopelike structure, 7, would result in both the transfer of chirality across the allyl system during rearrangement and the lack of incorporation of atmospheric oxygen during the course of rearrangement.
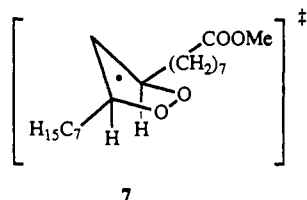

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Davies[8-12] and Beckwith[8] have reexamined the Schenck cholesterol hydroperoxide and related rearrangements in detail. Initial rearrangement of the 5-α-hydroperoxide gives the 7-α-hydroperoxide as shown in Scheme II. Subsequent to this rearrangement, the 7-α-hydroperoxide rearranges to the 7-β compound. The data show unequivocally that the 5-α to 7-α rearrangement occurs without incorporation of labeled oxygen (the reactions are carried out under [36]O₂). On the other hand, the epimerization of the 7-α to 7-β hydroperoxide occurs with incorporation of atmospheric oxygen, indicating that fragmentation must be important in the latter process. These two reactions thus represent the two extremes of the mechanism of peroxyl radical rearrangement.

In other peroxyl rearrangements, peroxyl fragmentation has also been unambiguously demonstrated. Thus, dienylperoxyl radicals rearrange with incorporation of atmospheric oxygen.[13] This supports a mechanism where the first-formed peroxyl radical undergoes fragmentation to a carbon radical. Readdition of oxygen gives the rearrangement hydroperoxide with atmospheric oxygen incorporation.

In an attempt to clarify how allylperoxyl radicals are rearranging, we have undertaken a theoretical investigation of the prototype 1,3-migration shown in Scheme III, using the simple allylperoxyl radical. As part of this study we examined the rotational potential energy surface, including all rotational con-

Scheme III. Rearrangement of Allylperoxyl[a]
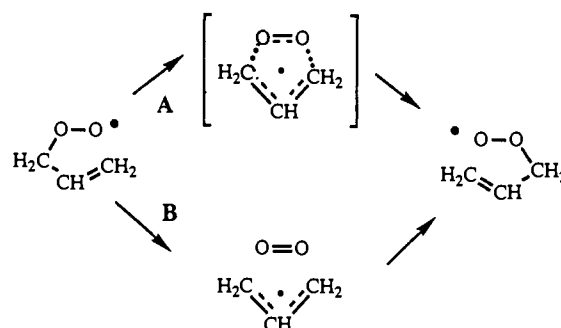
[a] (A) concerted path and (B) stepwise path.

formers, transition states, and second-order transition states between these conformers, for the allylperoxyl radical. The large number of variables in the system makes this a particularly interesting study. We then examined the reaction with special emphasis on whether the rearrangement proceeds via a concerted free radical pathway, A, in Scheme III, or by a fragmentation-readdition route, B. Our gas-phase results suggest that in fact the dissociative mechanism appears the more likely.

Computational Methods

As in our previous study,[14] calculations were performed at the unrestricted Hartree–Fock, and at second- and third-order Møller–Plesset perturbation theory levels, by using the GAUSSIAN 86[15] and GAUSSIAN 90[16] computer programs. Standard 6-31G(d) basis sets[17] were used for all geometry optimizations and pathway studies: full 6-31G(d) optimizations were performed for all minimum energy structures and for all first-order transition-state structures; "second-order" transition-state structures were obtained by restricting two parameters, which held the structure in an eclipsed conformation at two locations, then optimizing the remaining 22 parameters. In addition, single point energies with electron correlation incorporated were obtained for all minima, transition states, and second-order transition states, at the MP2/6-31G(d,p)//HF/6-31G(d) level, and for selected structures at the MP3/6-31G(d,-p)//HF/6-31G(d) level.[18] All structures were further characterized by frequency analysis: minimum energy conformers showed no imaginary frequencies, first-order transition structures yielded a single imaginary frequency, and second-order transition structures gave two imaginary frequencies.

Results and Discussion

Allylperoxyl Rotational Conformations. The structures of the nine conformational minima for the allylperoxyl radical, A → I, were optimized at the HF/6-31G(d) level; their relative 6-31G(d) and MP2/6-31G(d,p)//HF/6-31G(d) energies are presented in Figure 1. Of the nine, four structures exist as mirror images, while one is unique: A (C), B, D (I), E (H), F (G). D is the structure with minimum energy at the HF/6-31G(d) level, but, not surprisingly, correlation effects cause a slight shifting of relative minima, so that F is the minimum energy structure at the MP2/6-31G(d,p)//HF/6-31G(d) level; structure F is therefore assigned an energy of zero, and energies of other structures throughout this work are given relative to F. All other MP2// 6-31G(d,p)//HF/6-31g(d) minima lie within 5.2 kJ/mol of structure F. The structures of the 18 transition states between these minima (eight of which exist as mirror images, with two

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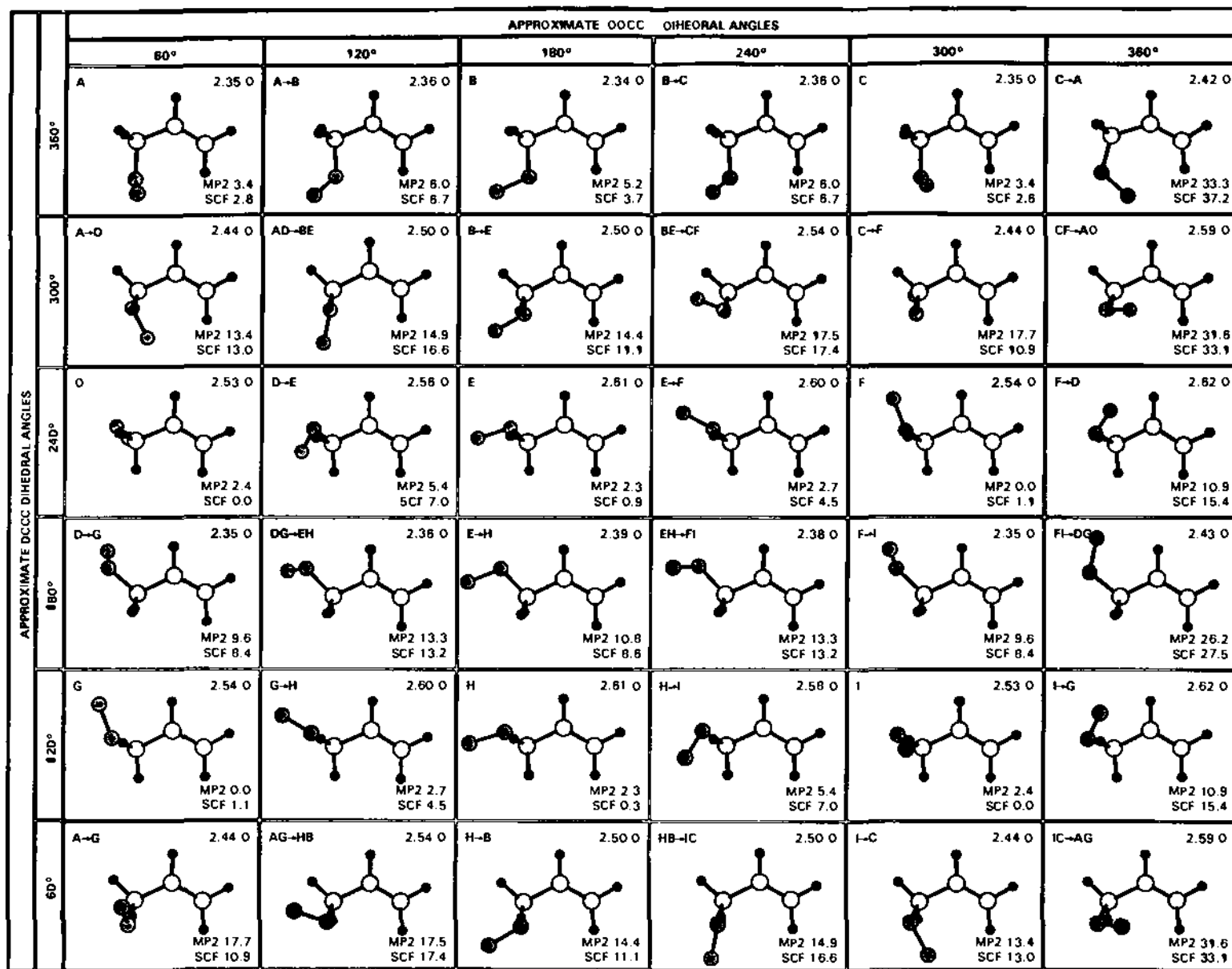
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(18) Reference 17, p 90.

Figure 1. Conformational minima (A–I), transition states (A → B, etc.), and second-order transition states (AD → BE, etc.) for the rotational conformers of the allylperoxyl radical, $C_3H_5O_2$, as a function of the OCCC and OOCC dihedral angles: (O) carbon, (◉) oxygen, and (●) hydrogen. The HF/6-31G(d) energies (kJ/mol) are relative to the minimum energy conformation D, and the MP2/6-31G(p,d)//HF/6-31G(d) energies are relative to the minimum energy conformation F. Also listed are the dipole moments of the conformers in debyes (D).
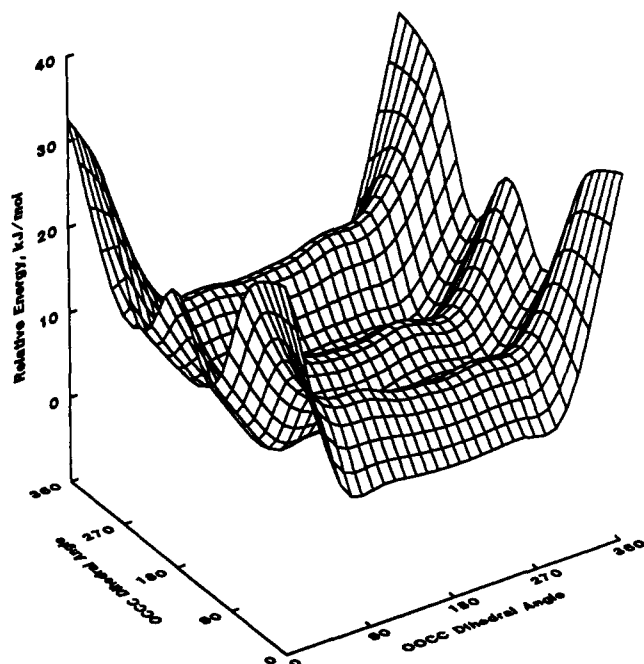
Figure 2. The potential energy surface for the rotational conformations of the allylperoxyl radical as a function of the OCCC and OOCC dihedral angles. Energies are those from the MP2/6-31G(d,p)//HF/6-31G(d) calculations and are relative to the minimum energy conformation F.

Reaction Coordinate

Figure 3. The rearrangement pathway via the "rearrangement transition structure", N, (--). Energies are MP2/6-31G(d,p)//HF/6-31G(d) and are relative to the acyclic allylperoxyl radical conformer, F. Point S (△) corresponds to the allyl radical and O_2 at infinite separation.

unique ones) are presented in Figure 1. These are denoted **A →
B**, etc. and show rotational barriers which range from 2.7 to 33.3
kJ/mol from the minimum energy conformation, **F**. Finally the
"second-order transition states", which are partially optimized
structures obtained by restricting the dihedral bond angles in two
locations within the structure, are also presented (denoted **AD →
BE**, etc.); their energies range from 13.3 to 31.6 kJ/mol. Therefore
all conformations are accessible and populated under normal
conditions. The potential energy surface is illustrated in Figure
2, and geometrical parameters of two representative conformations
(**F** and **C → A**) are given in Table I. MP3/6-31G(d,p) energies
were calculated for selected species to ascertain whether the
relative energies had "settled down". Some of these are also
reported in Table I and are essentially the same as the MP2
energies.

The allylperoxyl conformers are all polar, with dipole moments
ranging from 2.35 D for **A** to 2.61 D for **E**, as shown in Figure
1. Mulliken population analysis indicates that the majority of
the negative charge resides in the internal oxygen atom, as has
previously been reported for a wide variety of peroxyl radicals.[14]
On the other hand, the spin density of the allylperoxyl radical is
associated primarily with the terminal oxygen.[14]

Allylperoxyl Rearrangement Pathway. In view of the concerted
free-radical pathway (Scheme III, pathway A) which has been
suggested by Beckwith[6] and Porter,[7] the structures of possible
five-membered ring intermediates with symmetries C_{2v} (**J**), C_2
(**K**), and C_s (**L**) were investigated and are presented in Table II.
(It is interesting that these cyclic structures are substantially more
polar than the acyclic allylperoxyl radicals, with dipole moments
between 3.35 and 3.67 D. In all three cases, the negative charge
resides primarily on the oxygens, as would be expected, while the
spin density is mainly associated with the central carbon atom.
J and **K** are planar but **L** is slightly pyramidal at the radical site.)
The structure with C_2 symmetry (**K**) has the lowest energy; at
the MP2/6-31G(d,p) level, **K** is actually 4.8 kJ/mol lower in
energy than the acyclic conformer of lowest energy, **F**. (Note that
K is higher in energy than **F** by 23.2 kJ/mol at the HF/6-31G(d)
level but only by 2.1 kJ at the MP3/6-31G(d,p) level; the cor-
relation correction significantly shifts the relative energies of the
cyclic vs the acyclic peroxy radical, but further change due to
higher level calculations is small.) While **K** is the symmetrical
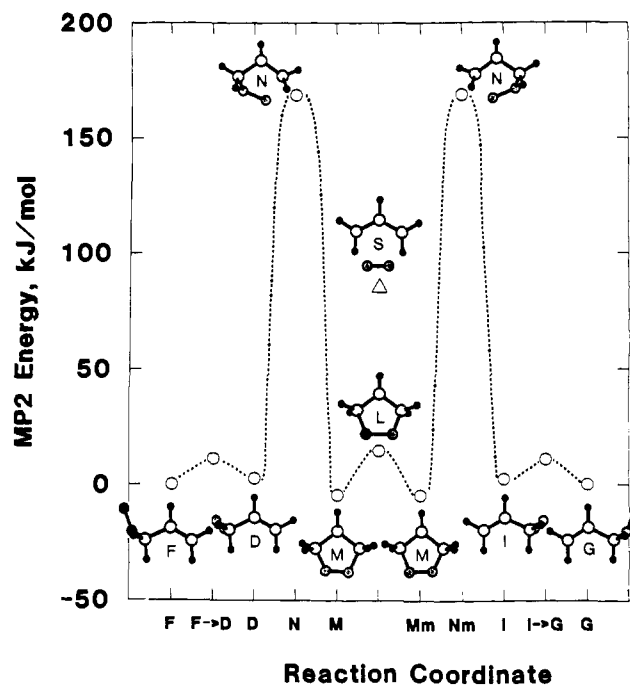
cyclic structure of lowest energy, it is not a true minimum energy
structure at the SCF level, as revealed by frequency analysis; when
all symmetry restrictions are removed, **K** flexes to a C_1 confor-
mation, **M**. **M** is a further 0.6 kJ/mol lower in energy at the
HF/6-31G(d) level than **K**; at the MP2/6-31G(d,p)//HF/6-
31G(d) and MP3/6-31G(d,p)//HF/6-31G(d) levels, however,
M is very slightly higher in energy (0.03 and 0.02 kJ/mol, re-
spectively) than **K**. Structure **M** shows no imaginary frequencies
and is therefore a minimum energy conformation at the SCF level.
M also has its spin density primarily at the central C and is slightly
pyramidal at this site; it is a bit less polar than **K** (Table II).
Structural parameters for **K** and **M**, either of which could be
considered to be the dioxolanyl radical **3**, are given in Table I.

Other possible intermediate structures, including four-membered
ring C_{2v}, C_2, and C_s structures were sought, but no structures of
reasonable energy were found: in general, they dissociated to the
free allyl radical and O_2.

Structure **F** and the various other acyclic conformers of the
allylperoxyl radical clearly do not collapse directly to **K** or **M** or
vice versa; thus there must be some energy barrier between the
acyclic and the cyclic conformers. An asymmetric "rearrangement
transition structure", **N**, with one imaginary frequency, was found.
Intrinsic reaction coordinate calculations with the STO-3G basis
set show that **N** collapses in one direction to the C_1 structure, **M**,
and in the other direction to the acyclic allylperoxyl radical, **D**.
N has a MP2/6-31G(d,p)//HF/6-31G(d) relative energy of 168.6
kJ/mol (Figure 3 and Table I). No other transition structure
between the cyclic and acyclic radicals has been located despite
numerous attempts.

That there is a large energy barrier between the cyclic and
acyclic radicals is consistent with the chemistry observed for the
cyclic radical. Generation of cyclic dioxolanyl radicals like **M**
in the presence of oxygen results in products of addition of oxygen
at the radical center.[3,4] No such cyclic peroxide products are
observed from the allylperoxyl **F**, indicating that the cyclic and
acyclic radicals do not interconvert under rearrangement con-
ditions. The experimental results are thereby supported by the
calculations with regard to this important point; the dioxolanyl
radical **M** is a bound species and cannot be an intermediate on
the rearrangement reaction pathway. In fact, the 168.6 kJ/mol
barrier at **N** that separates **M** from **F** is unreasonably large for
any free radical propagation step, and one would not expect

Table I. Optimized Structural Parameters

parameter					
Bond Lengths (Å)					
C_1–C_2	1.318	1.318	1.496	1.497	1.421
C_2–C_3	1.499	1.504	1.496	1.500	1.506
C_3–O_1	1.427	1.428	1.411	1.412	1.409
O_1–O_2	1.301	1.292	1.400	1.399	1.381
C_1–H_1	1.077	1.069	1.083	1.083	1.076
C_1–H_2	1.075	1.076	1.088	1.088	1.074
C_2–H_3	1.077	1.080	1.071	1.072	1.076
C_3–H_4	1.082	1.084	1.083	1.083	1.080
C_3–H_5	1.081	1.084	1.088	1.087	1.085
Bond Angles (deg)					
$C_1C_2C_3$	123.76	133.92	105.46	104.93	109.51
$C_2C_3O_1$	111.88	121.99	102.72	103.15	102.91
$C_3O_1O_2$	111.23	116.67	104.95	104.86	106.25
$H_1C_1C_2$	121.99	124.18	114.50	114.54	119.72
$H_2C_1C_2$	121.58	118.92	112.83	112.63	119.23
$H_3C_2C_3$	115.83	108.74	127.27	125.32	118.26
$H_4C_3C_2$	111.66	108.48	114.36	114.36	112.17
$H_5C_3C_2$	111.52	108.48	114.50	112.59	114.52
$C_1C_2C_3O_1$	−123.48	0.0	13.18	11.34	−52.50
$C_2C_3O_1O_2$	−74.25	0.0	−35.40	−34.41	49.07
$H_1C_1C_2C_3$	1.18	0.0	−105.70	−103.66	−63.12
$H_2C_1C_2C_3$	−178.44	180.0	128.57	130.65	145.71
$H_3C_2C_3O_1$	57.59	180.0	−166.82	−145.38	90.20
$H_4C_3C_2C_1$	115.81	121.99	−105.70	−107.47	66.24
$H_5C_3C_2C_1$	6.82	−121.99	128.57	126.97	−167.51
symmetry	C_1	C_S	C_2	C_1	C_1
dipole moments (D)	2.54	2.42	3.35	3.29	2.95
SCF energy (H, (kJ/mol⁻¹)	−266.08221, 0	−266.06844, 36.1	−266.07339, 23.2	−266.07362, 22.6	−266.02129, 159.9
MP2 energy (H, (kJ/mol⁻¹)	−266.82650, 0	−266.81282, 33.3	−266.82831, −4.75	−266.82830, −4.73	−266.76228, 168.6
MP3 energy (H, (kJ/mol⁻¹)	−266.85896. 0	−266.84645, 32.8	−266.85816, 2.1	−266.85810, 2.3	−266.79585, 165.7
	F	C → A	K	M	N

interconversion of these species under most conditions of free radical propagation. N therefore similarly cannot be on the reaction pathway.
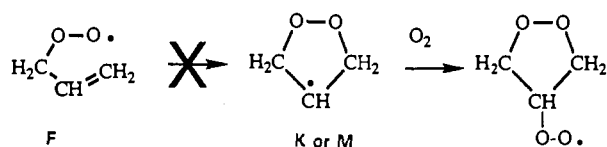
Another important result of the calculations is that we find no low-energy cyclic transition state, 4, like that suggested in pathway A, Scheme III, which would involve a C_{2v} structure such as J, with a planar distribution of the five annular atoms. Structure J exhibits two imaginary frequencies, indicating that it is neither a minimum energy structure nor a transition state between minima; when its C_{2v} symmetry restrictions are relaxed at the HF/STO-3G level, it collapses either to the C_2 structure, K, or all the way to the C_1 structure, M. L (C_s), whose five annular atoms have an envelopelike structure, has one imaginary frequency, indicating that it is a transition structure. L also collapses to K or M at the HF/STO-3G when its C_s symmetry restrictions are relaxed partially or completely; intrinsic reaction coordinate calculations at the STO-3G level show that L is a transition structure between M and the mirror image of M, not a transition structure for the peroxyl rearrangement. No other low-energy cyclic transition structures are observed.

Earlier calculations[14] indicate that the CO bond energy of the allylperoxyl radical is about 90 kJ/mol, significantly lower than the barrier calculated for the rearrangement through N. Since we find no low-energy transition state for the concerted rearrangement, we conclude that the rearrangement must involve a

fragmentation–readdition mechanism. We have not however investigated this dissociative mechanism in detail: while MP2/6-31G(d) studies yield an adequate description of the reaction surfaces for systems such as the unimolecular decomposition of the ethyloxonium ion in which there is no change in multiplicity during the reaction,[19] a thorough theoretical investigation of the mechanism for the allylperoxyl → allyl + O_2 dissociation requires higher level calculations because of the substantial electronic rearrangement during the conversion of the doublet allylperoxyl radical to the doublet allyl radical plus the triplet oxygen molecule. MP2 calculations are known to yield bond dissociation energies with accuracies of 10 kJ/mol or better,[20] but it is unlikely that a method based on a single determinant wave function can provide an adequate description of the allylperoxyl dissociation surface. Indeed, an SCF study of a similar (though smaller) system, the nitromethane dissociation and rearrangement,[21] gave a high-energy transition state which was described as an artifact of the SCF computational model; MCSCF calculations were found on the other hand to yield satisfactory results[22] for the reaction and showed that the transition-state energy for the nitromethane → methyl + NO_2 dissociation was essentially the same as the bond dissociation energy. We anticipate that the MCSCF results for the dissociation of the allylperoxyl radical would be similar to those of the nitromethane dissociation,[22] i.e., that the transition state for the dissociation has approximately the same energy as the bond
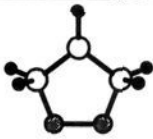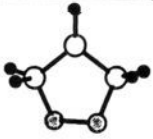
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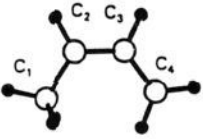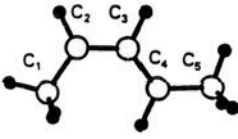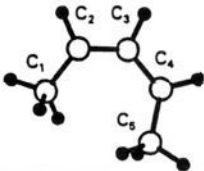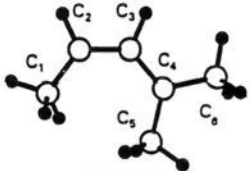
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Table II. Structures of the Cyclic Allylperoxyl Radicals

parameters				
MP2 energy (kJ/mol)	17.3	-4.8	14.5	-4.8
SCF energy (kJ/mol)	39.9	23.2	38.3	22.6
dipole moments (D)	3.67 D	3.35 D	3.66 D	3.29 D
symmetry	C_{2v}	C_2	C_S	C_1
electronic state	$^2B_1$ (π)	^2B (π)	$^2A_2$ (σ)	
no. of imaginary frequencies	2	1	1	0
	J	K	L	M

Table III. Structures of Allyl Radicals

parameters				
basis set	HF/6-31G(d)	HF/6-31G(d)	HF/6-31G(d)	HF/STO-3G
SCF energy (hartrees)	-155.50493	-194.54335	-194.53764	-230.80267
symmetry	C_1	C_S	C_2	C_1
bond lengths (Å)				
C_1C_2	1.505	1.505	1.506	1.522
C_2C_3	1.396	1.397	1.396	1.411
C_3C_4	1.388	1.389	1.396	1.415
C_4C_5		1.501	1.506	1.527
C_5C_6				1.527
	O	P	Q	R

dissociation energy. This, together with the experimental observations discussed above, therefore, leads us to suggest that the allylperoxyl rearrangement does not proceed via the concerted pathway **A** in Scheme III but instead proceeds via the dissociative mechanism, **B**.

The proposed dissociative mechanism bears an interesting resemblance to the 3,2-rearrangement of β-acyloxylalkyl radicals for which experimental evidence[23-25] and calculations[26] have been given supporting a charge-separated anion-radical cation pair.

There are problems with this mechanistic interpretation. The high stereoselectivities observed in the rearrangement[7] and the lack of significant incorporation of atmospheric oxygen into the product hydroperoxide in the oxygen labeling experiments[5,6] indicates that the allyl radical-triplet dioxygen pair has unusual properties for a radical-pair species. Indeed, this is an unusual radical pair. Pairs of doublet radicals may have either singlet or triplet multiplicity and the chemistry of such radical pairs is influenced by their diffusion in solution. The well-known radical pair cage effect[27] is a result of radical pair coupling competing with diffusion of the pair into solution.[28] Radical pairs generated

from ground state singlet precursors are formed as singlet radical pairs initially and these radicals typically undergo recombination reactions with loss of stereochemistry.[28]

In contrast to the chemistry of pairs of free radicals, fragmentation of a doublet peroxyl radical generates a doublet radical-triplet oxygen pair, and this pair can have either doublet or quartet multiplicity. Since the peroxyl radical precursor is a doublet, the intermediate pair would presumably be formed as a doublet, and the chemistry of this pair would also be influenced by diffusion of the pair from the initial encounter. The peroxyl dissociation-readdition mechanism involves a peroxyl precursor that generates a doublet intermediate pair which can collapse to the doublet rearrangement radical or diffuse into solution. There is no precedent in the literature to support this notion, but the stereochemistry and oxygen-labeling results of the peroxyl rearrangements, along with the calculations reported here, suggest that the allyl radical-oxygen pair undergoes pair collapse to give peroxyl radicals with stereochemical control and with little diffusional escape, if any, from the initial encounter. The mechanism that emerges from experiment and theory is presented in Scheme IV. The intermediate pair is a caged pair with doublet multiplicity as indicated by the bar and 2 above this species.

While there is little precedent for the high stereoselectivity and pair reactivity proposed, there are tests which can be applied based on this mechanism. Cage effects are dependent on solvent viscosity and on temperature, and the chemistry described here may also depend on these factors. Thus, oxygen labeling and stereochemical studies of the rearrangement as a function of solvent viscosity and temperature might provide useful mechanistic evidence. It is interesting to note, in this regard, that we have reported significantly greater loss of stereochemistry in the oleate

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Scheme IV. Pair Mechanism for Allylperoxyl Rearrangement
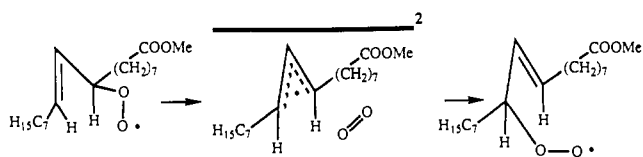
rearrangement at 40 °C compared to that observed at room temperature[7], an observation which is consistent with pair escape competing successfully with pair collapse.

The pair mechanism suggested by theory and the stereochemistry observed in the experiments stimulated us to investigate the structure of allyl radicals in some detail. A pyramidal allyl or one that had an energy barrier separating a pyramidal allyl and a planar structure might give rise to a facial bias in the addition of oxygen to the radical, especially if inversion of the radical were slow relative to encounter and reaction with atmospheric oxygen. The structures of several different allyl structures were calculated (Table III). Sterically hindered radicals such as **Q** and **R** exhibit

slight twisting of the plane containing the radical center, i.e., the $C_2C_3C_4C_5$ dihedral angle is about 2°. But each radical investigated was planar at the radical center(s): the sum of the bond angles around the carbons with high spin density was 360°. No pyramidization of the radical center was therefore observed. In general, both C_2 and C_4 exhibit spin densities of essentially equal magnitudes, with a very slightly greater density on the more substituted carbon (e.g., in structure **O**, C_2 has spin density of 1.023, while C_4 has 1.014.)

Thus our conclusion remains that the selectivity of the rearrangement of the allylperoxyl radical results from a cage effect wherein the diffusion of the allyl radical-oxygen pair is prevented due to caging by the solvent.

Magic Angle (54.7°) Gradient and Minimal Surfaces in Quadruple Micellar Helices

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Abstract: The first self-organized quadruple helices consisting of nonpolymeric material have been obtained from *N*-octyl- and *N*-dodecyl-D-gluconamides in water. They have been characterized by electron microscopy, image analysis, and computer modelling. The pitch of the helices is equal to $(2\pi \times$ molecular bilayer diameter); their gradient conforms with the magic angle (54.7°). The quadruple helices rearrange in aqueous gels to a single helix made of circular 4-fold layers of molecules, a pitch of 7.4 nm, and a gradient of 82 ± 3°. This quadruple layer may already contain head-to-tail oriented molecules, which are exclusively found in the final crystal sheets. The process of crystallization, from highly curved micellar fibers to planar crystal sheets, proceeds on minimal surfaces.

Molecular assemblies of amphiphiles in water are organized by the same physical forces that enforce order in proteins, namely, the hydrophobic effect, hydrogen bonding, steric repulsion, and charge interactions. Similar molecular shapes are therefore observed in molecular assemblies[1] and proteins,[2] in particular globules, sheets, and helical fibers. The tightness of the arrangements in assemblies and proteins, however, is different. The relative arrangement of the monomers in proteins is largely determined by the covalent backbone; e.g., the smallest possible loop is usually preferred in helices. The loose attachment of the monomers in assemblies, on the other hand, reflects more directly the impact of repulsive and attractive physical forces. From detailed analysis of complex structures of such assemblies, one may therefore learn more about the action of physical forces between molecules. We report here for the first time on micellar quadruple helices, which incline at the magic angle, thereby minimizing the dielectric energy associated with order electric polarization of oriented quadrupolar systems. Furthermore, we have evaluated a rearrangement of these quadruple helices to a single right-handed helical tube made of

a molecular 4-fold layer, which has the appearance of elongated staples of toroids in electron micrographs.

Results

Electron Microscopy. Micellar fibers made of *N*-alkylglyconamides have been characterized by us earlier with the aid of electron microscopy.[3,4] *N*-Octyl- and *N*-dodecylgluconamides[3] (**1a,b**) as well as *N*-octadecylmannonamides[5] were supposed to produce double helices with bulges and knots ("bulgy helices") at room temperature in the presence of 1% phosphotungstate. Addition of other electrolytes usually leads to the formation of microcrystalline platelets. A new series of negative stain electron

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