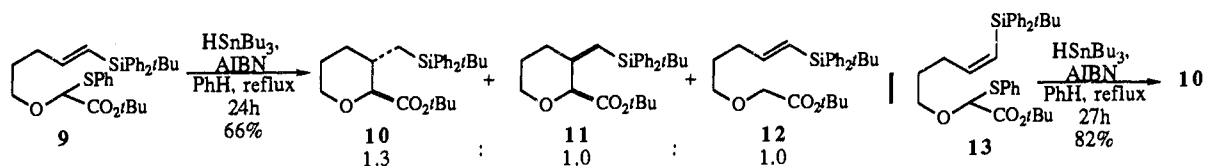
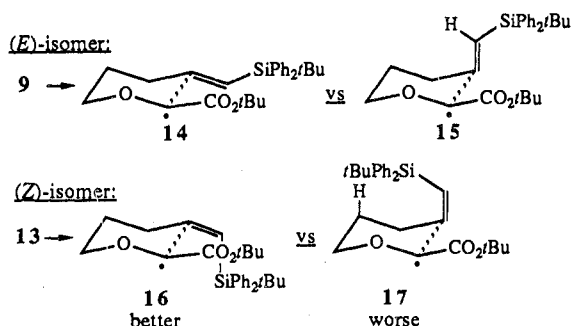


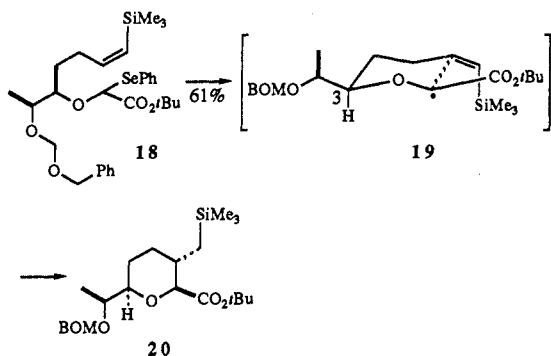
Scheme II



Scheme III



Scheme IV



The effects of silicon substituent identity and vinylsilane geometry are illustrated in Scheme II. Cyclization of the (*E*)-(tert-butylphenyl)silyl-substituted alkene **9** proceeded unselectively, yielding **10**, **11**, and **12** in nearly equal amounts. In contrast, radical cyclization of substrate **13**, containing a (*Z*)-(tert-butylphenyl)silyl-substituted alkene, led to the anti diastereomer **10** in 82% yield; no syn diastereomer **11** was detected.

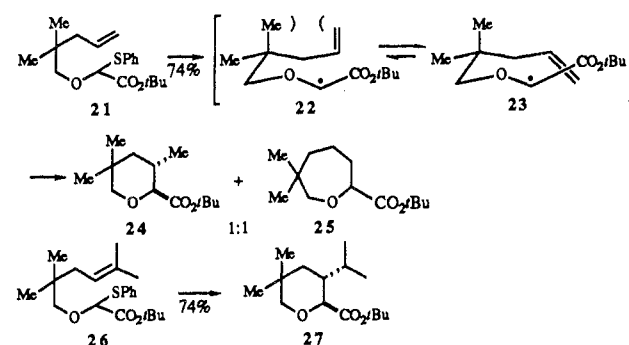
These observations can be explained by considering the cyclization conformers in Scheme III.¹⁰ There is little to energetically differentiate **14** and **15**; thus a 1.3:1 mixture of **10** and **11** results from **9**. However, conformer **16** has a substantial advantage over **17**, thus producing only **10** from **13**. Smaller silyl substituents, as in **6**, make the conformation analogous to **17** less disfavored, leading to production of a small amount of the syn isomer **8** along with **7**.¹¹

The additional effect of a substituent at C(3) on the stereochemical course of the cyclization is presented in Scheme IV. Homolytic cleavage of the carbon-selenium¹² bond in **18** resulted in a radical cyclization producing only diastereomer **20**. Equatorial

(10) Assumption of a chair-like transition state for these cyclizations is analogous to those invoked for the all-carbon systems analyzed by Houk^{6b} and by Beckwith^{6c} with their respective "flexible" and "rigid reactant" MM2 models. A similar model has been invoked for rationalizing the observed stereoselectivities in radical cyclizations of (*E*)- and (*Z*)-8-bromo-6-tert-butyl-2-octenoates: Hanessian, S.; Dhanoa, D. S.; Beaulieu, P. L. *Can. J. Chem.* **1987**, *65*, 1859.

(11) *Z* α,β -unsaturated esters as acceptors have exhibited higher stereoselectivities than corresponding *E* isomers in radical cyclizations yielding five-membered^{11a,b} and six-membered^{11c} rings. Each example involves 1,3-allylic strain between the ester group and a branching γ -substituent. (a) Gaudino, J. J.; Wilcox, C. S. *Carbohydr. Res.* **1990**, *206*, 233. (b) Wilcox, C. S.; Thomasco, L. M. *J. Org. Chem.* **1985**, *50*, 546. (c) Ihara, M.; Yasui, K.; Taniguchi, N.; Fukumoto, K. *J. Chem. Soc., Perkin Trans. 1* **1990**, 1469. (12) Clive, D. L. J.; Chittattu, G. J.; Farina, V.; Kiel, W. A.; Menchen, S. M.; Russell, C. G.; Singh, A.; Wong, C. K.; Curtis, N. J. *J. Am. Chem. Soc.* **1980**, *102*, 4438.

Scheme V



deployment of the tether substituent and the conformational preference for the bracketed intermediate **19** explain the transfer of stereogenicity to the newly formed asymmetric centers.¹³

The employment of a *gem*-dimethyl moiety in **21** (Scheme V) provided a steric differentiation between cyclization conformers **22** and **23**, favoring the latter.¹⁴ Only the anti tetrahydropyran diastereomer **24** was formed, but with an equal amount of the 7-endo closure product **25**. Substitution on the alkene terminus suppressed this mode of closure, so that **26** gave the anti 6-exo product **27** as the sole tetrahydropyran diastereomer.

Acknowledgment. We gratefully acknowledge the National Institutes of Health, the Alfred P. Sloan Foundation, the National Science Foundation, and the Natural Sciences and Engineering Research Council of Canada for generous financial support.

(13) For recent additional examples of substituent effects in diastereoselective radical cyclizations yielding five- and six-membered carbocycles, see: (a) RajanBabu, T. V.; Fukunaga, T. *J. Am. Chem. Soc.* **1989**, *111*, 296. (b) Boger, D. L.; Mathvink, R. J. *J. Am. Chem. Soc.* **1990**, *112*, 4003.

(14) The rate-enhancing effects of substituents on the chain connecting the radical center and the acceptor are well-known. See refs 4a and 4e.

Unexpectedly Rapid Proton-Transfer Reactions of Weakly Acidic Cation Radicals

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Cation radicals¹⁻³ and dications⁴ of aromatic compounds often exhibit superacid thermodynamic properties, yet react with bases at moderate rates. An extreme example is the dication of (*p*-methoxyphenyl)diphenylmethane, which can be observed by cyclic

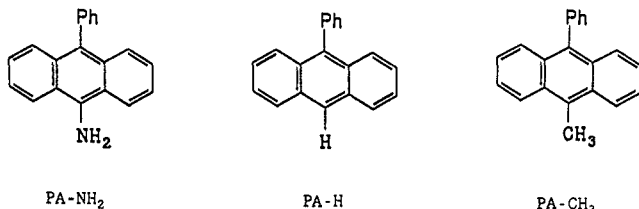
(1) Nicholas, A. M.; Arnold, D. R. *Can. J. Chem.* **1982**, *60*, 2165.
(2) (a) Bordwell, F. G.; Bausch, M. J. *J. Am. Chem. Soc.* **1986**, *108*, 2473.
(b) Bordwell, F. G.; Cheng, J.-P. *J. Am. Chem. Soc.* **1989**, *111*, 1792.
(3) (a) Schlessener, C. J.; Amatore, C.; Kochi, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 7472. (b) Masnovi, J. M.; Sankararaman, S.; Kochi, J. K. *J. Am. Chem. Soc.* **1989**, *111*, 2263.
(4) Parker, V. D.; Tilset, M. J. *J. Am. Chem. Soc.* **1988**, *110*, 1649.

Table I. Rate Constants and pK_a Differences for the Proton-Transfer Reactions of 9-Amino-10-phenylanthracene Cation Radical with Substituted Pyridines

base	ΔpK_a^a	$k^b/m^{-1} s^{-1}$
2,6-dimethylpyridine ($pK_a^B = 15.4$) ^c	2	1.0×10^7
pyridine ($pK_a^B = 12.3$) ^c	5	1.2×10^6
2,6-di- <i>tert</i> -butylpyridine ($pK_a^B = 11.8$) ^c	5	4.3×10^5

^aThe difference in pK_a of the cation radical and that of the conjugate acid of the base in acetonitrile at 298 K. ^bSecond-order rate constants in acetonitrile containing Bu_4NPF_6 (0.1 M) at 298 K. ^c pK_a^B values in acetonitrile from ref 3a.

voltammetry even though the pK_a has been estimated to be of the order of -57 .⁴ We now report unexpectedly low reaction barriers during strongly endergonic proton transfer reactions between 10-amino-9-phenylanthracene (PA-NH₂) cation radical and pyridine bases.



In contrast to the methylarene cation radicals, protons attached to heteroatoms of cation radicals are only weakly acidic.^{2b} For example, the pK_a of aniline cation radical in DMSO is 6.5. This translates to a value of about 15.5 in acetonitrile since pK_a 's of monocharged acids have been observed to be 9 units greater in acetonitrile than in DMSO.⁵ This suggested PA-NH₂^{•+} as a weakly acidic cation radical for proton-transfer studies. Previous work⁶ has shown that PA-NH₂^{•+} is sufficiently long-lived in acetonitrile to be observed by cyclic voltammetry at low sweep rates.

The rate constants for the reactions between PA-NH₂^{•+} with pyridine derivatives in acetonitrile at 298 K determined by derivative cyclic voltammetry⁷ are summarized in Table I. The corresponding ΔpK_a values are defined in eq 1, where pK_a^B refers to the dissociation constant of the conjugate acid of the base. The positive values of ΔpK_a imply that all three of the proton-transfer reactions are endergonic.

$$\Delta pK_a = pK_a(HA^{•+}) - pK_a^B \quad (1)$$

Under the same conditions, 9-methyl-10-phenylanthracene (PA-CH₃) cation radical was observed to react with 2,6-di-*tert*-butylpyridine (TBP) more than 4 orders of magnitude more slowly than PA-NH₂^{•+}, with a second-order rate constant equal to $27 M^{-1} s^{-1}$. 9-Phenylanthracene (PA-H) cation radical has previously been reported⁹ to undergo transfer of the 10-aryl proton upon reaction with TBP under these conditions with a rate constant equal to $130 M^{-1} s^{-1}$. Second-order rate constants for the reactions with TBP, $pK_a(HA^{•+})$'s, and reduction potentials in acetonitrile are gathered for the three cation radicals in Table II.

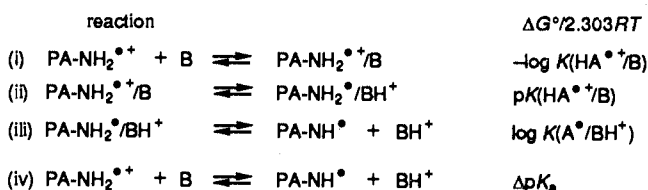
The pK_a of PA-H^{•+} has not been reported and was estimated from the PhH^{•+} value¹ by the following procedure. The pK_a difference for two cation radicals in solution is given by eq 2, adapted from that presented by Nicholas and Arnold.¹ The

$$\Delta pK_a(HA^{•+}) = \Delta BDE(H-A)/2.303RT - (F/2.303RT)\Delta E^{ox}(HA) \quad (2)$$

Table II. Rate Constants, Oxidation Potentials, and pK_a 's of Cation Radicals of 9-Amino-10-phenylanthracene and Related Anthracene Derivatives

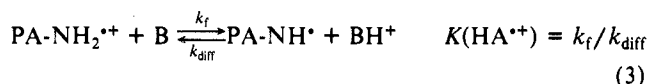
	cation radical (PA-X ^{•+})		
	PA-CH ₃ ^{•+}	PA-H ^{•+}	PA-NH ₂ ^{•+}
$k/M^{-1} s^{-1}$ (2,6-TBP) ^a	27	130 ^b	4.3×10^5
$pK_a(HA^{•+})$ ^c	3 ^e	≈ 17 ^f	17 ^g
E^{red}/V vs Fc/Fc ^{•+} ^d	0.748	0.848	0.048

^aSecond-order rate constant for the reaction of the cation radical with 2,6-TBP in acetonitrile containing Bu_4NPF_6 (0.1 M) at 298 K. ^bValue reported in ref 10. ^cSee text for pK_a estimates of the cation radicals. ^dLinear sweep voltammetry peak potentials for the reduction of the cation radicals in acetonitrile containing Bu_4NPF_6 (0.1 M) at 298 K. ^eValue from J.-P. Cheng, Ph.D. Dissertation, Northwestern University, 1987, adjusted to acetonitrile by adding 9 units. ^fSee text. ^gUnpublished DMSO value provided by Professor F. G. Bordwell adjusted to acetonitrile by adding 9 units.

Scheme I

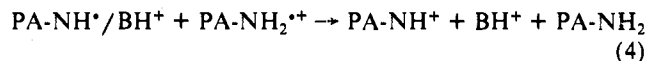
differences [$\Delta pK_a(HA^{•+})$, $\Delta BDE(H-A)$, and $\Delta E^{ox}(HA)$] refer to the value for the 9-phenylanthracene derivative minus that for the corresponding benzene derivative. The PA-H BDE is not known, and it was assumed that substituting PA for Ph lowers the BDE, relative to Ph-H, to the same degree as this substitution does for PA-CH₂-H and PA-NH-H BDEs (7 kcal/mol for PA-CH₃ and 8 kcal/mol for PA-NH₂).¹⁰

The second-order rate constants observed for the reactions of PA-NH₂^{•+} are as much as 12 times greater than predicted from equilibrium 3, taking into account the ΔpK_a and assuming that the back-reactions are diffusion controlled with rate constants of $10^{10} M^{-1} s^{-1}$. This discrepancy is a minimum value since there



is no reason to believe that reverse reactions 3 should be diffusion controlled.¹¹ The second-order rate constant for the reaction of PA-NH₂^{•+} with pyridine is only about 3 times greater than when the base is sterically hindered TBP. This relative rate constant appears to be somewhat lower than expected since TBP has been found to react significantly more slowly than pyridine in other acid-base reactions.¹³

A likely reason for the anomalous high proton-transfer rates is apparent from a consideration of the thermochemical cycle (Scheme I) which takes into account hydrogen bonding between PA-NH₂^{•+} and the bases. The mechanism of the proton transfer reaction need not involve all three (i-iii) of the steps shown in Scheme I. The third step can be circumvented by rapid electron transfer (eq 4). Under these nonequilibrium conditions, step ii



can be rate determining and result in an apparent rate constant considerably greater than predicted from consideration of ΔpK_a for equilibrium iv.

We estimate, from shifts in the reversible potential for the oxidation of PA-NH₂ when the base is present, $K(HA^{•+}/B)$ to

(10) Bordwell, F. G., private communication.

(11) A number of thermodynamically favorable proton transfers between nitrogen and oxygen acids and bases have been observed to have rate constants considerably below the diffusion-controlled limit.¹²

(12) Lu, S.; Ritchie, C. D. *J. Am. Chem. Soc.* **1989**, *111*, 8542.

(13) Bernasconi, C.; Carré, D. *J. Am. Chem. Soc.* **1979**, *101*, 2707.

(5) Kolthoff, I. M.; Chantooni, M. K., Jr.; Bhowmik, S. *J. Am. Chem. Soc.* **1968**, *90*, 23.

(6) Billon, J. P.; Cauquis, G.; Raison, J.; Thibaud, Y. *Bull. Soc. Chim. Fr.* **1967**, 199.

(7) Rate constants were obtained by using derivative cyclic voltammetry measurements on solutions containing substrate/base in 1/2 molar ratios, typically using substrate concentrations ranging from 0.5 to 2.0 mM.⁸

(8) Parker, V. D. *Electroanal. Chem.* **1986**, *14*, 1.

(9) Reitsdøen, B.; Parker, V. D. *J. Am. Chem. Soc.* **1990**, *112*, 4968.

be of the order of 10^3 M^{-1} at 298 K when B is 2,6-dimethylpyridine.¹⁴ Since the hydrogen-bonding equilibrium is expected to be exceedingly rapid, these data support the interpretation presented in the previous paragraph for the rapid proton-transfer reactions.

The second-order rate constant (Table II) for the reaction of PA-NH_2^{*+} with TBP exceeds that for the transfer of a benzylic proton from PA-CH_3^{*+} to TBP by more than 10^4 even though the latter reaction is thermodynamically more favorable by a factor of 10^{14} . A similar comparison for the reactions of PA-H^{*+} and PA-CH_3^{*+} with TBP reveals that the former reacts 5 times as fast in spite of the fact that the equilibrium constant is 14 orders of magnitude less favorable. This apparent inverse dependence of kinetic on thermodynamic acidities further illustrates the complexities of cation radical deprotonation reactions. Likewise, there is no direct relationship between cation radical reduction potential and kinetic acidities in this series of reactions.

We suggest that charge distribution and the identity of the atom to which the proton is attached are important features in determining the relative kinetic acidities in this series of cation radicals. In both PA-NH_2^{*+} and PA-H^{*+} there is considerable charge on the atom to which the acidic proton is attached while this is not the case for PA-CH_3^{*+} .

Acknowledgment. This research was supported by the National Science Foundation (CHE-8803480) and the donors of the Petroleum Research Fund, administered by the American Chemical Society. We thank Professor F. G. Bordwell for providing unpublished $\text{p}K_a$ data.

(14) Hydrogen-bonding equilibrium constants have been determined from reversible electrode potentials in a number of cases; for example, see: Parker, V. D. *Acta Chem. Scand.* **1984**, *B38*, 125, 189. Eliason, R.; Parker, V. D. *Acta Chem. Scand.* **1984**, *B38*, 741. Svaan, M.; Parker, V. D. *Acta Chem. Scand.* **1985**, *B39*, 401. Svaan, M.; Parker, V. D. *Acta Chem. Scand.* **1986**, *B40*, 36.

Transition Structure for the Epoxidation of Alkenes with Peroxy Acids. A Theoretical Study

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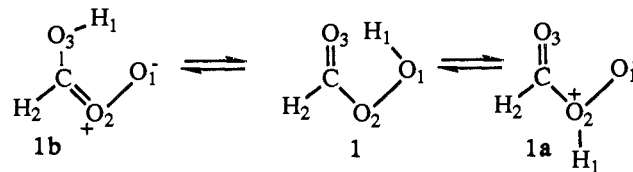
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Despite the importance of chemical transformations involving organic peroxides, the mechanistic details of oxygen transfer remain obscure. We recently employed hydrogen peroxide as a model oxidant for ab initio studies on the oxidation of ammonia.¹ The potential energy surface for oxygen atom transfer was dominated by the 1,2-hydrogen shift in H_2O_2 forming water oxide, $\text{H}_2\text{O}^+-\text{O}^-$ (56.0 kcal/mol barrier), followed by a facile $\text{S}_{\text{N}}2$ like displacement by NH_3 on $\text{H}_2\text{O}^+-\text{O}^-$ (1.7 kcal/mol barrier) to afford $\text{H}_3\text{NO} + \text{H}_2\text{O}$. Oxidation by a peroxy acid could potentially occur by a similar pathway involving either a 1,2- or a 1,4-hydrogen shift prior to or after oxygen atom transfer. Enthalpic considerations suggest that breaking both the O-H and O-O bonds of the peracid in the transition state (TS) would be energetically unfavorable. We now report that epoxidation of ethylene by peroxyformic acid proceeds by a distinctly different mechanism

than that found for hydrogen peroxide.¹

We first examined the relative energies of the two zwitterionic species arising from 1,2- and 1,4-hydrogen shifts in peroxyformic acid (**1**). Dioxygen ylide **1a** and hydroxycarbonyl oxide **1b** are



calculated to be 55.5 and 28.8 kcal/mol higher in energy than **1**, but the barrier for reversion of **1b** to **1** is only 1.7 kcal/mol ($\text{HF}/6\text{-}31\text{G}^*$).² As in $\text{HOOH} \rightarrow \text{H}_2\text{OO}$, the barrier disappears when MP4 correlation corrections are included.³ With geometry optimization at the $\text{MP2}/6\text{-}31\text{G}^*$ level, water oxide does exist as a local minimum:^{1a} by contrast, zwitterion **1b** is not a local minimum at $\text{MP2}/6\text{-}31\text{G}^*$ and optimized directly to **1**.⁴ When the $\text{O}_3\text{-H}_1$ bond in **1b** was constrained (0.98 Å), it was 33.4 kcal/mol higher in energy than **1**. Although this energy difference is considerably higher than the magnitude of a typical activation barrier for epoxidation (15–18 kcal/mol),⁵ we could not exclude a protonation-deprotonation sequence like that noted^{1b} for H_2O_2 because the intrinsic barrier for oxygen atom transfer from the parent carbonyl oxide ($\text{H}_2\text{C}=\text{O}^+-\text{O}^-$) to ethylene is only 13.9 kcal/mol ($\text{MP4}/6\text{-}31\text{G}^*/\text{MP2}/6\text{-}31\text{G}^*$).

In the only previous ab initio study of alkene epoxidation, Plesnicar examined five plausible transition states and reported a barrier of 16 kcal/mol (STO-4G) for an unsymmetrical TS where peroxyformic acid was directly over one of the methylene carbons of ethylene.⁶ Our search at the $\text{HF}/3\text{-}21\text{G}$ level led to only one first-order saddle point, TS-2, resulting from oxygen atom transfer from hydroxycarbonyl oxide **1b**. This TS exhibits a single imaginary frequency both at $\text{HF}/3\text{-}21\text{G}$ and at $\text{HF}/6\text{-}31\text{G}^*$. However, the $\text{MP4}/6\text{-}31\text{G}^*/\text{HF}/6\text{-}31\text{G}^*$ activation barrier of 41.4 kcal/mol was disturbingly high.^{5,7} Prior experience with the calculations involving O-O bond cleavage¹ prompted a search of this potential energy surface at $\text{MP2}/6\text{-}31\text{G}^*$. In an attempt to locate spiro TS-2, we constrained the $\text{O}_3\text{-H}_1$ bond distances at 0.99 and 1.09 and reoptimized the transition state in the space of the remaining parameters. These structures were 39.4 and 34.7 kcal/mol above isolated reactants, respectively. In each case release of that geometry constraint resulted in hydrogen transfer (H_1 to O_1) affording TS-3a. Although TS-3a is a second-order saddle point at $\text{HF}/3\text{-}21\text{G}$, a frequency calculation ($\text{HF}/6\text{-}31\text{G}^*$) established the validity of this TS at geometries optimized at both the $\text{HF}/6\text{-}31\text{G}^*$ and $\text{MP2}/6\text{-}31\text{G}^*$ levels; the corresponding MP4 barriers of 15.7 and 16.5 kcal/mol are in excellent agreement with experiment (Figure 1).^{5,8} We also find that spiro TS-3a is 9.2

(2) (a) Molecular orbital calculations have been carried out using the GAUSSIAN 88 program system^{2b} utilizing gradient geometry optimization.^{2c} (b) M. J. Frisch, M. Head-Gordon, H. B. Schlegel, K. Raghavachari, J. S. Binkley, C. Gonzalez, D. J. DeFrees, D. J. Fox, R. A. Whiteside, R. Seeger, C. F. Melius, J. Baker, R. L. Martin, L. R. Kahn, J. J. P. Stewart, E. M. Fluder, S. Topiol, J. A. Pople, Gaussian, Inc., Pittsburgh, PA, 1988. (c) Schlegel, H. B. *J. Comput. Chem.* **1982**, *3*, 214. (d) Gonzalez, C.; Schlegel, H. B. *J. Phys. Chem.* **1990**, *94*, 5523. Step size of $0.2 \text{ amu}^{1/2}\text{bohr}$ used.

(3) DeFrees, D. J.; Raghavachari, K.; Schlegel, H. B.; Pople, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 5576.

(4) (a) The $\text{MP2}/6\text{-}31\text{G}^*$ geometry of peroxyformic acid is in excellent agreement with microwave spectral data (in parentheses)^{4b} where $\text{O}_1\text{-O}_2 = 1.46 \text{ \AA}$ (1.45), $\text{C-O}_2 = 1.35 \text{ \AA}$ (1.34), $\text{C-O}_3 = 1.22 \text{ \AA}$ (1.20), $\text{O}_1\text{-H}_1 = 0.99 \text{ \AA}$ (1.02), and $\angle\text{O}_2\text{O}_1\text{H}_1 = 100.3^\circ$ (99.2). (b) Oldani, M.; Ha, T.-K.; Bauder, A. *J. Am. Chem. Soc.* **1983**, *105*, 360.

(5) Dryuk, V. G. *Tetrahedron* **1976**, *32*, 2855.

(6) The TS geometry, optimized with the STO-2G basis prior to the availability of gradient optimization, was a higher order saddle point that differed significantly from the first-order TS that we now report. Plesnicar, B.; Tasevski, M.; Azman, A. *J. Am. Chem. Soc.* **1978**, *100*, 743.

(7) $\text{HF}/6\text{-}31\text{G}^*$ calculations incorrectly predict TS-2 to be 12.1 kcal/mol more stable than TS-3a. The major effect of electron correlation is the improvement of the description of the O-O bond in TS-3a.

(8) Although the HF wavefunction to TS-3a is UHF unstable, there was no significant change in the barrier calculated at the UMP4 level with spin projection (18.9 kcal/mol, $\text{PMP4}(\text{SDTQ})/6\text{-}31\text{G}^*/\text{RMP2}/6\text{-}31\text{G}^*$) or at the RQCISD(T)/6-31G*/MP2/6-31G* level (19.7 kcal/mol).

(1) (a) Bach, R. D.; McDouall, J. J. W.; Owensby, A. L.; Schlegel, H. B. *J. Am. Chem. Soc.* **1990**, *112*, 7064, (b) 7065. (c) Bach, R. D.; Owensby, A. L.; Gonzalez, C.; Schlegel, H. B.; McDouall, J. J. W. *J. Am. Chem. Soc.*, submitted.