Dioxirane Epoxidations of 1,1-Disubstituted Ethylenes. Probing for Radical Pathways by Computations and Experiments

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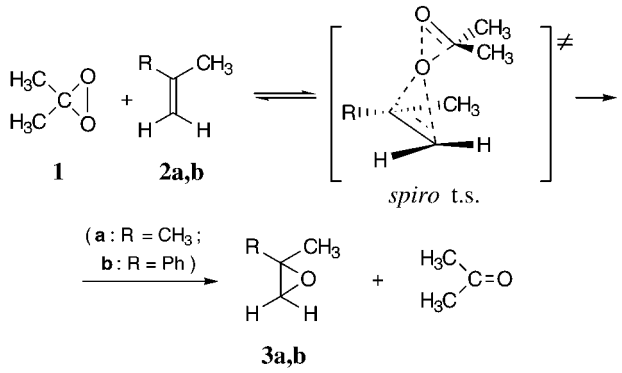
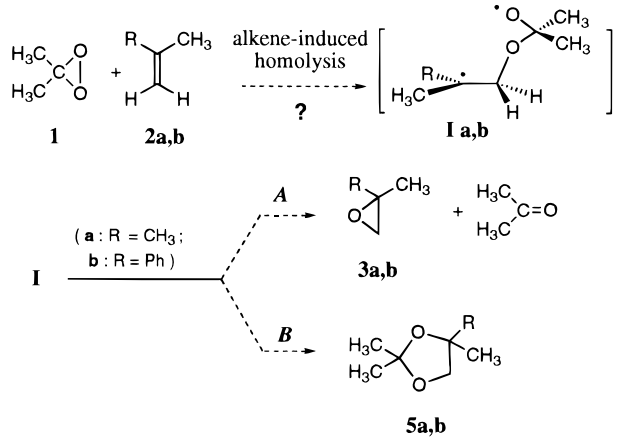
Introduction

The epoxidation of alkenes under extremely mild and neutral conditions using dioxiranes[1] is of particular interest due to the value of this transformation in synthesis. Dimethyldioxirane (DMD) (**1**)[2] and methyl(trifluoromethyl)dioxirane (TFD)[3] are frequently employed to carry out epoxidations of a variety of substrates, providing access to even highly sensitive epoxides.[1] Mechanistic studies of this reaction have continued unabated during the past decade; much experimental evidence, including the syn-stereospecific course of dioxirane epoxidations,[1] the greater reactivity of cis alkenes than their trans isomers,[4] kinetic H/D isotope effects,[5] and the outcome of radical-clock experiments,[6a] all have consinstently pointed to a concerted mechanism; a spiro transition state for dioxirane approach to the double bond was suggested to be consistent with these data (Scheme 1). Following the pioneering theoretical studies by Bach and co-workers,[7] increasingly accurate computational methods have provided support to the view of an essentially concerted mechanism for the dioxirane epoxidation of ethene, propene, and *cis*- and *trans*-2-butene.[7,8] This is well understood in terms of S_N2-like attack by the alkene at the dioxirane peroxide bond. FMO interactions provide a guide to the mechanism: the alkene HOMO interacts in a stabilizing fashion with the OO σ^* orbital, while the O lone pair interaction with the alkene LUMO strongly favors a spiro geometry in the transition state (TS).[1f,7,8] Unsymmetrical substitution of the alkene can cause the transition state to become unsymmetrical, but no intermediates were located on the potential surface.[8a]

Scheme 1. Concerted Epoxidation by Dioxiranes



Scheme 2. Stepwise Biradical Reaction of Alkenes with Dioxiranes



At odds with a concerted epoxidation mechanism, Minisci et al.[9a,b] recently envisaged a radical pair mechanism for the epoxidation of an unsymmetrically substituted alkene such as α-methylstyrene (**2b**) with DMD (Scheme 2); this conclusion was based on their detection of a minor amount of allylic oxidation byproducts, i.e., 2-phenylpropenol, PhC(=CH_2)CH_2OH (**4a**), and 2-phenylpropenal, PhC(=CH_2)CH=O (**4b**), along with epoxide **3b**. The proposed epoxidation mechanism involves alkene-induced homolysis of the dioxirane O−O bond and

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formation of the key diradical adduct **I** (Scheme 2); the allylic oxidation byproducts were envisaged to arise from the alternative formation of [PhC(═CH_2)CH_2•$^{•}$OC(CH_3)$_2$-OH] pairs.[9a] The molecule-induced homolysis mechanism has been proposed for other thermally induced radical processes.[9c,d]

The proposal[6a] that the diradical adduct **I**—if formed—would rather be expected to yield the cycloaddition product 1,3-dioxolane **5** (path B) was dismissed by Minisci et al.,[9b] because "entropic factors would favor the fragmentation" to epoxide (path A).

Therefore, further examination seemed in order to elucidate the actual mechanism of epoxidations by dioxiranes. We have reported[6a] on stereochemical evidence and application of a cyclopropylcarbinyl rearrangement radical probe ($k_r > 10^{10}$ s^{-1})[6b] that militate against the stepwise mechanism in Scheme 2. We now report on a mechanistic revisitation of the dioxirane epoxidation of unsymmetrical 1,1-disubstituted alkenes such as isobutene (**2a**) and α-methylstyrene (**2b**) by quantum mechanical computations and experiments. The results show that[9a,b] the previously established concerted mechanism is likely to apply even for these alkenes, which are prone to undergo asynchronous processes.

Results and Discussion

Reaction Products and Kinetics. The reaction of DMD with isobutene (**2a**) and with α-methylstyrene (**2b**) was examined under a variety of conditions. Rigorous scrutiny of products from the DMD oxidation of **2b** was performed, because of the reported formation of "circumstantial" radical byproducts.[9a,b] In this respect, the formation of 2-phenylpropanal, PhCH(CH_3)CH═O, in as much as 51% yield, initially reported[9a] by Minisci, has recently been recognized to be an artifact;[9b] with DMD and α-methylstyrene under N_2, the correct product distribution reportedly is 86% epoxide, 6% 2-phenylpropenol (**4a**), and 5% 2-phenylpropenal (**4b**).[9b] However, the presence of byproducts **4a** and **4b**, even in minor amounts, would suggest the circumstance of some radical pathway. To clarify this point, we carefully reexamined the oxidation of α-methylstyrene with DMD under conditions practically identical to those adopted by Minisci et al.[9b] Under oxygen-free N_2 at 20 °C in acetone, DMD and **2b** were reacted with initial concentrations of 0.005 M. Careful GC and GC/MS monitoring revealed that only epoxide **3b** was formed in greater than 98% yield during 30 min (Minisci et al. reported products after a reaction time of 6 h). We also synthesized authentic samples of fully characterized 2-phenylpropenol (**4a**) and of 2-phenylpropenal (**4b**) and determined their GC retention times (t_R) under the conditions of analyses. Deliberate addition of each reference compound to reaction mixtures showed that even amounts of **4a** and **4b** as low as 0.5% would have been revealed alongside epoxide **3b** in calibrated GC and GC/MS analyses (cf., Supporting Information). The absence of 2-phenylpropenol and 2-phenylpropenal in any detectable amount was confirmed by running ^{1}H and ^{13}C NMR spectra of reaction mixtures; in fact, these showed only the resonance signals of epoxide **3b** and of acetone (the solvent and reduction product of DMD), with only traces of methyl acetate and acetic acid.[10] To track another likely product of the biradical path (Scheme 2), we also compared reaction mixtures with an independently obtained authentic sample of dioxolane **5b**; again, calibrated GC retention times (t_R), GC/MS, and ^{1}H and ^{13}C NMR revealed no trace of this alternative byproduct. This confirms our previous observation[6a] that epoxide **3b** is the only product of α-methylstyrene oxidation by DMD under a variety of conditions.

Table 1. Rates and Activation Energies for α-Methylstyrene and Isobutene Epoxidation by Dimethyldioxirane (1) in Acetone[a]

entry	substrate	T (°C)	atmosphere	$10^2 \times k_2$[b] (M^{-1} s^{-1})	E_a[c] (kcal M^{-1})
1	isobutene (**2a**)	0	air	7.00 ± 0.20	9.3 ± 0.2
2	isobutene (**2a**)	0	N_2	7.40 ± 0.20	
3	isobutene (**2a**)	−10	air	3.77 ± 0.15	
4	isobutene (**2a**)	−20	air	1.80 ± 0.10	
5	α-methylstyrene (**2b**)	20	air	102. ± 3.0	10.2 ± 0.1
6	α-methylstyrene (**2b**)	20	N_2	112. ± 5.0	
7	α-methylstyrene (**2b**)	20	Ar	108. ± 4.0	
8	α-methylstyrene (**2b**)	0	air	21. ± 1.0	
9	α-methylstyrene (**2b**)	−10	air	13. ± 0.5	
10	α-methylstyrene (**2b**)	−20	air	6.2 ± 0.4	
11	α-methylstyrene (**2b**)	−20	air	6.0 ± 0.4[d]	

[a] In all runs initial concentrations of alkene and of DMD were kept in the range (6−7) × 10^{-3} M, unless noted otherwise. [b] Kinetic constants calculated from integrated second-order rate law plots which were linear to over 80% reaction; average values shown are from two or more independent runs agreeing within ±5%. [c] Activation energy estimated from Arrhenius plots. [d] Second-order rate constants were estimated as (k_1/[**2b**]$_0$); the k_1 values were obtained from pseudo-first-order kinetic runs with [**2b**]$_0$ = 0.124 M and [DMD]$_0$ = 0.006 M.

Parallel to these studies, we also verified that the reaction of isobutene **2a** with DMD in acetone—either in air or under N_2—cleanly proceeds to give the corresponding epoxide **3a** in greater than 98% yield, with no trace of dioxolane **5a**, or other byproducts (GC, GC/MS analyses).

Kinetic studies also gave no indication of a radical pathway. The rates of the reaction of DMD with α-methylstyrene (**2b**) and the structurally related isobutene (**2a**) were performed in acetone at various temperatures by following the decay of dioxirane concentration (by iodometry)[6a,11] with time. The reactions were found to follow a clean overall second-order rate law (first order each in dioxirane and alkene); integrated second-order rate law plots were found to be linear to over 80% reaction, yielding reproducible rate constants. Control experiments were run involving monitoring the decay of α-methylstyrene concentration with time by GC; these experiments yielded the same value of k_2 (M^{-1} s^{-1}) within ±5%. Representative data are collected in Table 1.

Inspection of these data reveals that rates for both substrates **2a** and **2b** are of the same order of magnitude and that the estimated activation energy for α-methylstyrene oxidation is actually *higher* than that of isobutene. Were the reaction to proceed according to the stepwise process in Scheme 2, one would instead expect for **2b** an E_a lower than **2a**, because of the phenyl group stabilization at the C-2 terminus of the diradical intermediate.

In each case, either under air and in acetone purged with *oxygen-free* N_2 (or Ar),[9a,b] a smooth decay of dioxirane concentration with time was recorded, yielding practically identical second-order constant values (Table 1). In no

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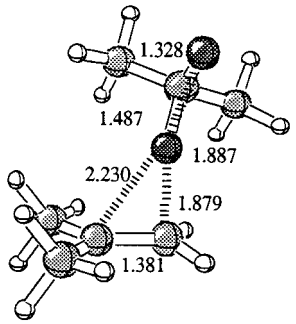

TS 1

Becke3LYP/6-31G* ΔE_a=15.3kcal/mol

Figure 1. Transition structure (B3LYP/6-31G*) for the epoxidation of isobutene (**2a**) by dimethyldioxirane (**1**).

case could we monitor the complex kinetic behavior that manifests itself when DMD radical decomposition is initiated.[11,12]

Computational Studies. For the DMD epoxidation of ethene, propene, and *cis*- and *trans*-2-butene (as well as other substituted ethenes), several detailed studies at a high level of theory have examined the energetics of transition states having the spiro vs planar geometry;[7,8] also, the question of synchronous and asynchronous[8a] (i.e., symmetrical and unsymmetrical)[7b] transition-state geometries has been addressed. In the present study, reactions of dimethyldioxirane with isobutene and α-methylstyrene with dimethyldioxirane have been investigated using Hartree−Fock theory with the 3-21G basis set and with the B3LYP DFT method with the 6-31G* basis set. Previous studies by Bach et al. and by Houk et al. have demonstrated that calculations performed by using density functional theory with the Becke3LYP/6-31G* method yield accurate reaction energetics for dioxirane reactions.[7,8]

(a) Transition Structures for Epoxidation. The transition structure for oxygen transfer from dimethyldioxirane to isobutene was located by the Becke3LYP/6-31G* method (Figure 1). It has an asynchronous spiro geometry with the more fully forming C−O bond on the less substituted carbon of isobutene, similar to that for oxygen transfer to propene and butadiene.[8]

The B3LYP/6-31G* activation energy is 15.3 kcal/mol, which is notably less than the O−O bond dissociation energy (BDE) of ca. 20.6 kcal/mol estimated[13] for dimethyldioxirane. Then, B3LYP/6-31G* predicts that the concerted epoxidation is easier than O−O bond homolysis to form a diradical. The transition structure is an early transition state. The O−O bond (1.887 Å) in dioxirane is breaking when the dioxirane approaches the alkene. This is a typical S_N2 type reaction, although the substituents of the alkene make the transition state asynchronous. The S_N2 attack of the π electrons of the alkene HOMO on the σ^* orbital of O−O does not induce formation of the bisoxymethylene diradical.[7a] When the unrestricted B3LYP/6-31G* method was used, the energy for the transition state is the same as with the restricted method, indicating no appreciable diradical character. An intrinsic reaction coordinate (IRC) calculation shows that no diradical intermediates are present on this reaction pathway.

(b) Reaction Channels for Diradical Intermediates. The diradical adduct structures **Ia** and **Ib** were fully optimized by open shell unrestricted Hartree−Fock calculations with the 3-21G basis set. The optimized diradical structures are shown in Figure 2. The energies of these optimized diradical intermediates were evaluated by single-point calculations using the unrestricted B3LYP/6-31G* method. Two minima for the diradical formed from isobutene were located on the potential surface with different C−O−C−O dihedral angles. **Ia′** with a 0° C−O−C−O dihedral angle is 9.3 kcal/mol lower in energy than **Ia** with a 180° C−O−C−O dihedral angle. Steric repulsions in **Ia** between the two methyl groups on the dioxirane and the isobutene terminus cause **Ia′** to be more stable. Biradical **Ia** is 9.7 kcal/mol higher in energy than the reactants, while **Ia′** is just 0.4 kcal/mol higher in energy than reactants, according to UHF calculations. However, these generally make diradicals much too stable compared to closed shell species. The regioisomeric diradical, resulting from the attack of the dimethyldioxirane on isobutene at the more substituted terminus, is 17.1 kcal/mol higher in energy than **Ia′**.

To find out the barrier between the diradical intermediates and the products for path A and B (Scheme 2), two transition structures, TS2 and TS3 (shown in Figure 3), leading to ketal product and epoxide, respectively, have been located at the UHF/3-21G level. IRC calculations have been carried out, and it has been confirmed that TS2 connects the biradical intermediate **Ia** and the ketal product (path B), and TS3 connects **Ia** and the epoxide product (path A). The activation energy for TS2 is 1.1 kcal/mol with UHF/3-21G and −16.9 kcal/mol with the UB3LYP/6-31G* single point, which indicates that there is almost no barrier for the diradical intermediate to form the ketal product. The activation energy for TS3 is 24.2 kcal/mol with UHF/3-21G and 6.7 kcal/mol with UB3LYP/6-31G*. There is a significant barrier for the formation of epoxide product from the biradical intermediate. TS3 is about 23 kcal/mol higher in energy than TS2 with both methods. The activation energies for path A and path B predict that if the biradical intermediate **Ia** is formed in the reaction of dioxirane with isobutene, kinetically the ketal instead of epoxide would be the major product. The reaction through path B (TS2) is a combination of two radical centers, a process generally having no barrier. The reaction through path A (TS3) needs to form a strained three-membered ring and has a higher activation energy.

A graphical summary of the relative energies involved in the evolution of biradical **Ia** and **Ib** along path A and path B (Scheme 2) is presented in Figure 4. The energies for products are from fully optimized structures by B3LYP/6-31G*, while those for the intermediate and TS are UB3LYP/6-31G*//UHF/3-21G energies.

For the reaction of DMD plus α-methylstyrene (**2b**), the diradical intermediate has been optimized by unrestricted Hartree−Fock calculations with the 3-21G basis set; a single-point calculation with UB3LYP/6-31G* gave more accurate energies. For the evolution of **Ib** along

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(13) (a) Estimated by R. D. Bach et al. (private communication to R.C.) as the energy difference between dimethyl bis(oxy)methylene and dimethyldioxirane; the total energy of these species was determined as *E*(QCISD(T)/6-311G**//QCISD/(6-31G*) + *E*(MP2/6-311+G(2df,p)//QCISD/6-31G*) − *E*(MP2/6-311G(d,p)//QCISD/(6-31G*); see also ref 7b. (b) Cremer, D.; Kraka, E.; Szalay, P. G. *Chem. Phys. Lett.* **1998**, *292*, 97; these authors have estimated an activation energy of 23.1 kcal/mol for cleavage of the O−O bond of dimethyldioxirane using B3LYP/6-31G(d,p).

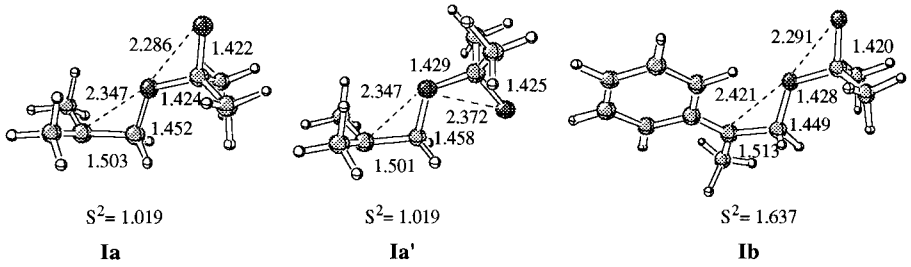


Figure 2. Structures for diradical intermediates optimized at UHF/3-21G.

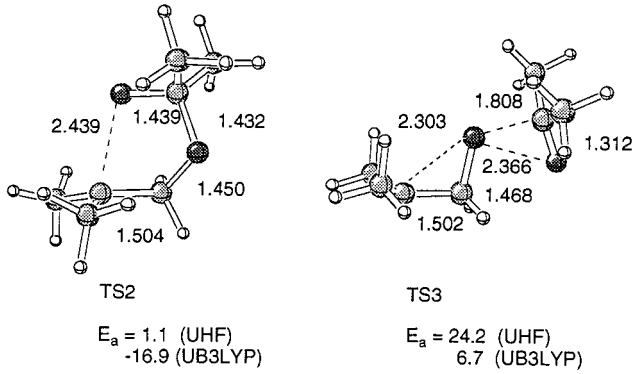


Figure 3. Transition structures leading to the ketal product (TS2) and to epoxide (TS3). Geometries were optimized with the UHF/3-21G method, and energies were evaluated by the UB3LYP/6-31G* method.

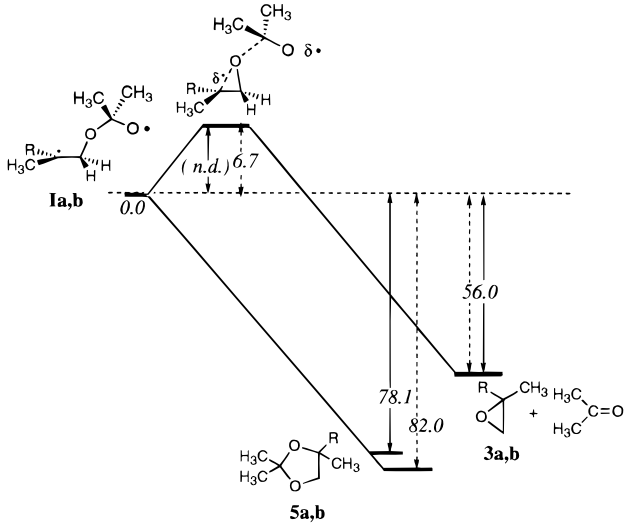


Figure 4. Relative energetics (B3LYP/6-31G*) for the reaction of DMD with isobutene (R = CH_3) and with α-methylstyrene (R = Ph). Energy differences are in kcal/mol; values for isobutene are shown by dashed arrows.

paths A and B, transition structures were not located due to excessive CPU time requirements.

Inspection of Figure 4 reveals that for both cases the 1,3-dioxolane product is *preferred* in energy with respect to the epoxide by about 26 kcal/mol from diradical **Ia**[14] and 22 kcal/mol from diradical **Ib** due to the strain of the three-membered epoxide. Calculations indicate that, if a diradical intermediate such as **Ia** were to arise from the reaction of DMD with isobutene, the formation of the corresponding 1,3-dioxolane (path B) would be preferred also *kinetically* because there is practically no barrier for its formation. While the cleavage to epoxide plus acetone will be favored entropically[9b] (as much as 12 kcal/mol at room temperature), little of this will be manifested in activation energies, since both transition states are relatively tight. In any case, the entropic advantage of cleavage is insufficient to make epoxide formation better than dioxolane formation.

Conclusion

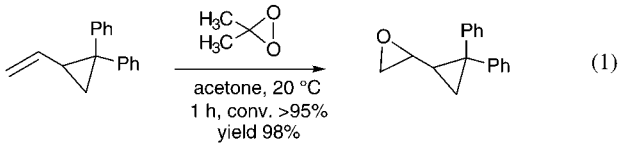
Careful scrutiny of the reaction of representative 1,1-disubstituted alkenes **2a** and **2b** with DMD failed to reveal even traces of the allylic oxidation products. Instead, the corresponding epoxides were formed in almost quantitative yield. This is in line with the outcome of DMD oxidation of a number of alkenes having widely varied structural features, as recorded in others' and our own laboratories.[1,4−6a] It is likely that the allylic oxidation products claimed by Minisci et al. derive from the adventitious triggering of dioxirane radical decomposition.[11] It was also argued by Minisci[9b] that "*small amounts of dioxolane...formed during the epoxidation of simple alkenes, such as cis-3-hexene, represent...a significant evidence of the induced homolysis*". However, in the original article by Murray at al.[15] it was clearly demonstrated that the dioxolanes detected in those early epoxidation experiments came from acetone solvent, and *not* from dioxirane. Thus, it seems that the only authentic 1,3-dioxolane formation in DMD oxidation of unsaturated compounds has been recorded (albeit in 6% yield only) by Foote et al.[16] during epoxidation of fullerene C_{60}; this involved low conversions and exceedingly long reaction times, during which—as for the reported polycyclic aromatic hydrocarbons case[17]—the radical decomposition of the dioxirane could be triggered. At any rate, careful analyses and comparison with authentic samples verified that no traces of dioxolanes are formed during the efficient DMD epoxidation of the substrates at hand.

At variance with rough thermochemical estimates,[9b] our computations clearly predict that the dioxolane should form preferentially over epoxide, if the claimed diradical adduct were to intervene in the reaction of DMD

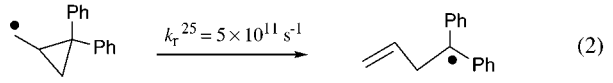
(14) While the present article was being completed, professor R. D. Bach informed us (private communication to R.C.) that his B3LYP/6-31G* computations on DMD oxidation of isobutene also indicate that, if diradical **Ia** were formed, formation of 1,3-dioxolane **5a** is thermodynamically favored over epoxide **3a** by 23.7 kcal/mol.

(15) Murray, R. W.; Ramachandran, V. *Photochem. Photobiol.* **1979**, *30*, 187.
(16) Elemes, Y.; Silverman, S. K.; Sheu, C.; Kao, M.; Foote, C. S.; Alvarez, M. M.; Whetten, R. L. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 351.
(17) Mello, R.; Ciminale, F.; Fiorentino, M.; Fusco, C.; Prencipe, T.; Curci, R. *Tetrahedron Lett.* **1990**, *31*, 6097.

with alkenes. The fact that no dioxolane products are observed in the reaction also militates against the intermediacy of diradical adduct **I** and the invoked stepwise mechanism (Scheme 2) for DMD epoxidations. Additional evidence ruling out the involvement of radical pair intermediates is already found in the higher E_a recorded for the oxidation of α-methylstyrene than isobutene (Table 1). This further supports the conclusion reached upon the application of the ultrafast (2,2-diphenyl)cyclopropylcarbinyl rearrangement radical probe (eqs 1 and 2).[6]



(1)



(2)

In summary, the concordance of experimental and theoretical results presented herein renders a molecule-assisted homolysis pathway extremely unlikely for the reaction of the alkene substrates examined with DMD. This is in accord with the conclusion of the overwhelming majority of studies on the mechanism of dioxirane epoxidations.[1−6a]

Experimental Section

Equipment. Boiling points and melting points were not corrected. The ^{1}H NMR spectra were run using a 500 or 200 MHz instrument, while the ^{13}C NMR spectra were taken at 125 MHz. Mass spectra and GC/MS were run employing a mass selective detector with 70 eV EI. The GC analyses were performed using a Vocol column [60 m × 0.53 mm, 3.0 μm i.d., temp prog. 60 °C (2 min), 60−220 °C, 10 °C/min] or SE 30 capillary column (30 m × 0.25 μm i.d.). Other equipment and analytical methods have been previously described.[6a]

Materials and Reagents. Commercial acetone was purified by standard methods, stored over 5 Å molecular sieves at 4−8 °C, and routinely redistilled prior to use. Curox triple salt $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$ (a gift by Peroxid-Chemie GmbH, Münich, Germany) was our source of potassium peroxymonosulfate employed in the synthesis of dioxiranes. Solutions of 0.08−0.16 M dimethyldioxirane (**1**) in acetone were obtained by adopting procedures, equipment, and precautions that have been already described in detail.[2] Solutions of **2a** were prepared upon condensation at −20 °C of high-purity 2-methylpropene gas (Aldrich): t_R = 2.11 min; ^{1}H NMR ($CDCl_3$) δ 4.64 (s, 2 H), 1.71 (s, 6 H). Commercial (Aldrich) α-methylstyrene (**2b**) was further purified by distillation (bp 60 °C/760 Torr; t_R = 10.15 min).

General Procedure for Alkene Epoxidations by Dimethyldioxirane. The alkene (200−500 mg) was dissolved in acetone (5−15 mL), and 1.0−1.1 equiv of dimethyldioxirane (0.05−0.10 M solution in acetone) was rapidly added at the given temperature (Table 1). The reaction solution was monitored by GC or GC/MS and kept under stirring until the peroxide test (KI/starch paper) indicated that the dioxirane had been consumed.

2,2-Dimethyloxacyclopropane (3a). An authentic sample was synthesized upon reaction of 2-methylpropene (**2a**) with methyl(trifluoromethyl)dioxirane in 1,1,1-trifluoropropanone (TFP, both the solvent and the reduction product of the oxidant); the dioxirane was obtained according to described protocols.[3] Gaseous 2-methylpropene (**2a**) (0.34 g, 6.1 mmol) was condensed (−25 °C) and added to a solution of methyl(trifluoromethyl)-dioxirane in TFP (0.61 M, 10 mL);[3] after 2 min GC monitoring revealed complete conversion of the substrate. Careful distillation at atmospheric pressure allowed removal of TFP solvent (bp 22 °C) and isolation of **3a** (0.44 g, 6.1 mmol, yield 99%+): colorless oil, bp 52−53 °C/760 Torr; ^{1}H NMR ($CDCl_3$) δ 2.58 (s, 2 H), 1.29 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 54.94, 54.70, 23.00; MS (EI, 70 eV), *m*/*z* (rel int) 72 (31, M^+), 43 (40), 42 (74), 41 (100); IR (neat) 2984, 1289, 1172, 1089 cm^{-1}; t_R = 4.12 min.

2-Methyl-2-phenyloxacyclopropane (3b) was obtained from 2-phenylpropene according to the general procedure given above. The solvent was removed in vacuo (20 °C, 20−100 Torr) to afford epoxide **3b** in high purity: colorless oil, bp 76−78 °C/10 Torr; ^{1}H NMR ($CDCl_3$) δ 7.24−7.48 (m, 5 H), 2.95 (d, *J* = 5.40 Hz, 1 H), 2.78 (d, *J* = 5.40 Hz, 1 Hz), 1.70 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 140.50, 128.40, 127.40, 125.40, 56.70, 52.01, 25.33; MS (EI, 70 eV), *m*/*z* (rel int) 134 (9, M^+), 106 (11), 105 (100); t_R = 16.00 min.

Kinetic Measurements. Runs were performed by following the decay of dioxirane concentration (by iodometry) with time, according to a reported procedure.[1f,11] All experiments were carried out under air (or under a N_2 blanket) in second-order conditions, with the dioxirane and alkene initial concentrations kept in the range (5−7) × 10^{-3} M, and differing by 8−20%. At zero time an aliquot (0.5−1.0 mL) of a thermostated dioxirane **1** acetone solution was added to 10−20 mL of a solution (also thermostated) of α-methylstyrene (**2b**) in the same solvent; aliquots (1.0 mL) of the reaction solution were withdrawn periodically and quenched with excess KI/EtOH, and the liberated I_2 was determined by iodometry. In runs performed by following the decay of α-methylstyrene substrate by GC, the internal standard Freon A112 was also present in the reaction solutions; at time intervals, aliquots (5−10 μL) were withdrawn and quenched with 0.1 mL of ca. 0.15 M n-Bu_2S in CH_2Cl_2, and the substrate concentration was determined on the basis of a previously constructed calibration curve. Linear $\ln[(a - x)/(b - x)]$ vs time plots were obtained to over 80% reaction, with correlation coefficient ≥ 0.999; from these k_2 (M^{-1} s^{-1}) values could be estimated. In each case, at least two independent runs were performed and the k_2 values averaged (estimated error ≤ ±6%).

Computational Methodology. Calculations reported herein were conducted with the Gaussian 94 program.[8] The restricted Becke3LYP/6-31G* or HF method is suitable for the closed shell species, while the unrestricted Becke3LYP/6-31G* or HF method is necessary to compute open shell radical structures. Full geometry optimizations for closed shell species were carried out by using density functional theory with the Becke3LYP functional and the 6-31G* basis set. The unrestricted HF/3-21G method was used for the geometry optimization of open shell diradical species and transition structures, and the energies were evaluated with single-point calculation with the UB3LYP/6-31G* method. Frequency calculations have been carried out for transition structures to ensure the presence of only one imaginary frequency corresponding to C−O bond forming and O−O bond breaking. The optimized reactants were also checked by frequency calculations to confirm that they are minima.

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Supporting Information Available: Physical constants and spectral characteristics of reference compunds **4a**, **4b**, **5a**, and **5b**; GC of the reaction mixture of α-methylstyrene (**2b**) oxidation by DMD and of reference compounds **4a** and **4b**; ^{1}H MNR of the reaction mixture above (3 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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