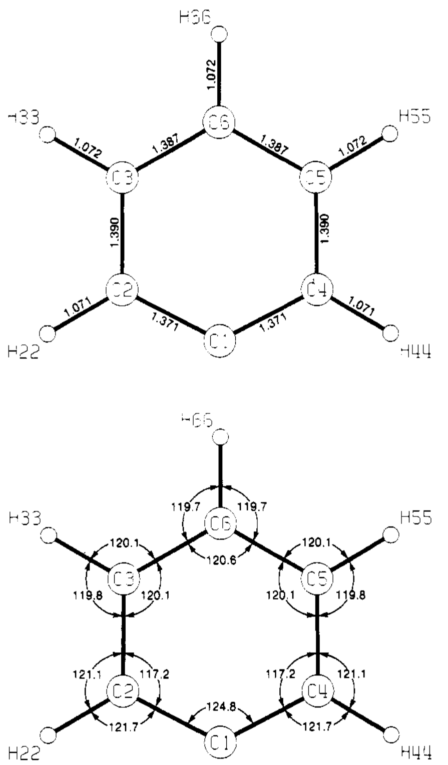

Figure 2. The ROHF-optimized geometry for the $^2A_1$ ground state of the phenyl radical; bond lengths in angstroms and bond angles in degrees; total energy = −229.725501 hartrees.

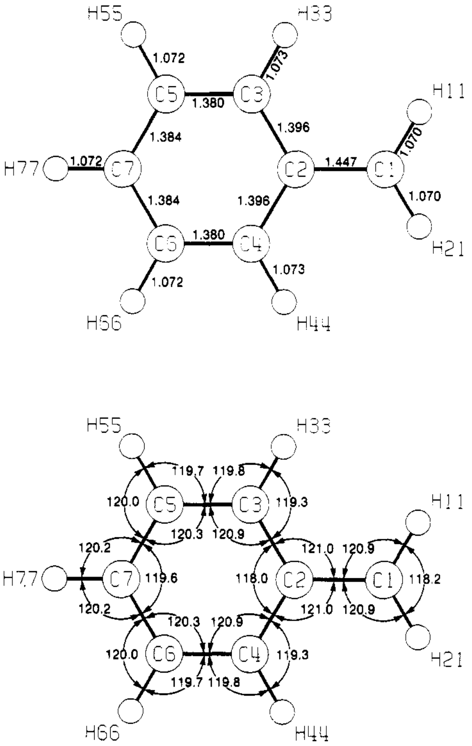

Figure 3. The ROHF-optimized geometry for the $^2B_2$ ground state of the benzyl radical; bond lengths in angstroms and bond angles in degrees; total energy = −265.837128 hartrees.

from a regular hexagon. In spite of this, however, the phenyl ring remains planar.

The phenyl radical geometry reported herein differs somewhat from the results reported by Johnson.[1] Although the bond angles are comparable the CH bond lengths given here are ≃0.03Å shorter, this is attributed to basis set differences.

The optimized geometry for the benzyl radical is illustrated by the computer drawing in Figure 3. Figure 3 shows that the phenyl ring is distorted in the molecular plane reflecting the presence of the unpaired electron on C1. The α-CH bond lengths, C1H11 and C1H22, are shorter than the other CH bond lengths in the system. The α-CC bond, C1C2, is the longest CC bond in the system but nevertheless it is very short for a CC single bond length.

The extent to which the phenyl ring interacts with the CH_2 group is revealed by comparing the geometry in the vicinity of the radical centers in the benzyl and ethyl systems.[12] The α-CH and α-CC bond lengths for the ethyl radical are 1.079 and 1.498 Å; these are considerably longer than those computed for the benzyl system listed in Figure 3. We attribute this to the interaction of the radical center with the phenyl ring.

Another feature is that the geometry tends to distort to a quinoidal type structure. Thus, the C1C2 bond length, as noted above, is much shorter than a CC single bond length (1.528 Å in ethane[12]) and, along with the shorter C4C6 and C3C5 bond lengths, it is tempting to represent the benzyl radical structure as one with alternating double and single CC bonds.

Summary

The computed equilibrium geometries are reported for the phenyl and benzyl radicals. The structures are calculated by using restricted open-shell Hartree–Fock calculations in conjunction with gradient optimization routines. The symmetry of each radical is C_{2v}. The phenyl radical structure distorts from the D_{6h} symmetry of benzene with the shortening of the CC bonds α to the carbon atom containing the unpaired electron. The benzyl radical contains α-CH and α-CC bonds shorter than those found in the ethyl radical. We attribute this to the interaction of the singly occupied orbital on the radical center with the phenyl ring, a phenomenon certainly consistent with the planar character of the system.

Registry No. Phenyl radical, 2396-01-2; benzyl radical, 2154-56-5.

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[12] Pacansky, J.; Dupuis, M. J. *Chem. Phys.* **1978**, *68*, 4276.

Nucleophilic Trapping of Intermediates in the Singlet Oxygenations of Isomeric 1,4-Di-*tert*-butoxy-1,3-butadienes

Edward L. Clennan* and Kathleen K. Lewis

Department of Chemistry, University of Wyoming, Laramie, Wyoming 82071

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We have previously reported the reactions of (*E*,*E*)-**1**, (*E*,*Z*)-**2**, and (*Z*,*Z*)-1,4-di-*tert*-butoxy-1,3-butadiene (**3**) with singlet oxygen[1] (Scheme I). Especially noteworthy in this previous study was the dramatic effect of solvent on the product composition in the reaction of diene **3** and the insensitivity of the product ratio over the same solvent range in the reaction of diene **1**.[2] A a result of this observation, it was suggested that a perepoxide intermediate

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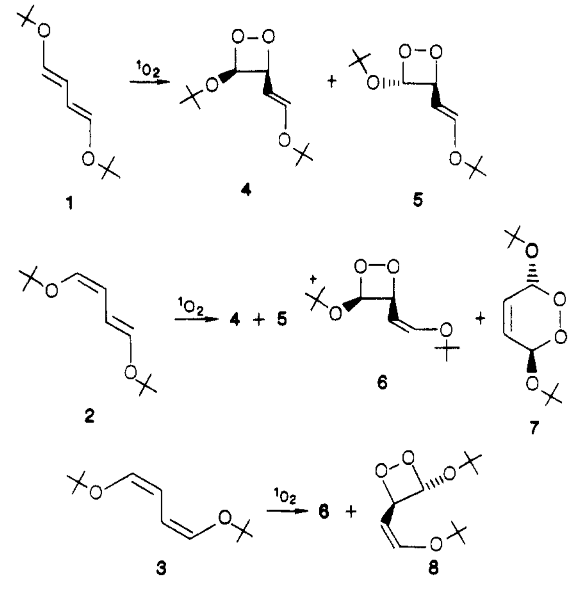
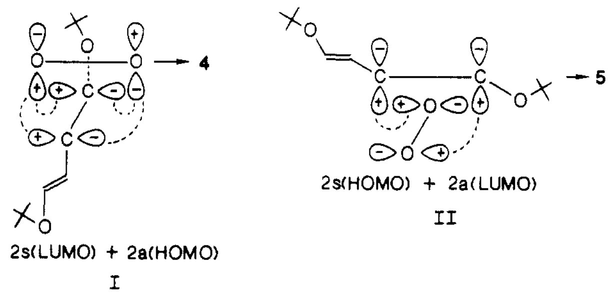
[1] Clennan, E. L.; L'Esperance, R. P. *J. Am. Chem. Soc.* **1985**, *107*, 5178.

[2] Clennan, E. L.; L'Esperance, R. P. *J. Org. Chem.* **1985**, *50*, 5424.

Scheme I



Scheme II



or transition state which subsequently opens to a zwitterion is energetically inaccessible in the reaction of the (*E*,*E*)-diene **1** but is stabilized by interaction with cis substituents[3] in the (*Z*,*Z*)-diene **3**. A 2s + 2a mechanism was considered attractive for the reaction of $^1O_2$ with the (*E*,*E*)-diene because a concerted reaction is not expected to exhibit a dramatic solvent effect. The stereochemistry of the reaction can also be conveniently attributed to a substantial frontier[4] orbital interaction in the 2s + 2a transition state which can only occur when the LUMO, singlet oxygen, is the suprafacial component (I in Scheme II). Much less stabilization is available from the opposite frontier orbital interaction (II in Scheme II) which leads to dioxetane **5**.

In this study we have examined the reactions of **1** and **3** with singlet oxygen in CD_3OD in order to gain additional evidence for the different character of these ostensibly similar reactions.

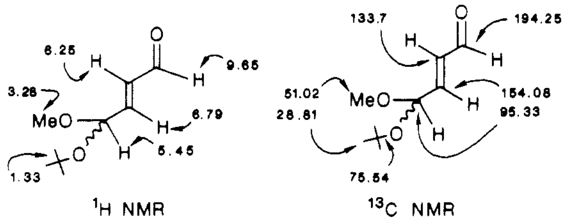
Results and Discussion

Methanol-d_4 solutions from 0.008 M to 0.0098 M in diene were placed in 5-mm NMR tubes and saturated with oxygen for 20 min at −78 °C. The progress of the singlet oxygen reactions was monitored by low-temperature NMR after purging the samples of oxygen with an argon stream for 25 min.[5] Higher concentrations of the dienes were avoided because of the concentration-dependent formation of an unidentified byproduct. At these lower concentrations, control experiments in argon atmospheres demonstrated that in methanol, as in the other solvents investigated, less than 2% dye initiated isomerizations of the dienes could have occurred during the course of the reactions. The absence of any isomerized diene in the reaction mixtures after partial photooxidation also argues against any singlet oxygen induced isomerization.[6] The product compositions using methylene blue or eosin were identical with those observed with rose bengal, verifying that singlet oxygen was the reactive intermediate in these reactions.

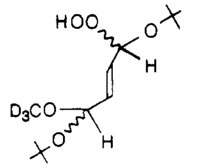
Table I. Product Percentages in the Reaction of Singlet Oxygen with 1 and 3 as a Function of Solvent Composition

		yield, %					
diene	solvent (v:v)	4	5	6	7	8	9
1	CD_3OD	54	7				39
	acetone-d_6	84	16				
	acetone-d_6/CD_2Cl_2 (4:1)	88	12				
	CD_2Cl_2	91	9				
	THF-d_8	82	18				
3	CD_3OD			30		15	55
	acetone-d_6			73		27	
	acetone-d_6/CD_2Cl_2 (4:1)			71		29	
	acetone-d_6/CD_2Cl_2 (1:1)			39		61	
	acetone-d_6/CD_2Cl_2 (1:4)			12		88	
	CD_2Cl_2			10		90	
	THF-d_8	7	10	38	14	31	

Scheme III



Methanol addition product **9** was formed at −78 °C along with the previously reported dioxetanes in the singlet oxidations of both dienes **1** and **3**. The product ratios in both reactions were determined by integration and by cutting and weighing appropriate proton NMR peaks from six independent reactions and are accurate to ±5%. These data are reported in Table I along with product distributions in other solvents for comparison. The proton NMR spectrum of the addition product (see Experimental Section) was assigned by a series of single-frequency decoupling experiments. This hydroperoxide was indefinitely stable in solution at room temperature. The dioxetanes, however, slowly decomposed to form the acrolein decomposition products and *tert*-butyl formate.[1] As a further verification of the structure of the addition product triphenylphosphine was added to the reaction mixtures after decomposition of the dioxetanes.[7] After 5 h the hydroperoxide completely disappeared concomitant with formation of aldehyde **11** (eq 1). The ratio of this new aldehyde to the dioxetane decomposition products indicated



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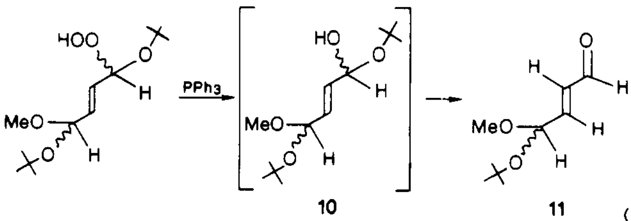
[3] Orfanopoulos, M.; Grdina, M. B.; Stephenson, L. M. *J. Am. Chem. Soc.* **1979**, *101* 275.

[4] Houk, K. N. *Acc. Chem. Res.* **1975**, *8*, 361.

[5] Purging the oxygen from solution resulted in proton NMR spectra with better resolution.

[6] Gollnick, K.; Griesbeck, A. *Tetrahedron Lett.* **1983**, *24*, 3303.

[7] Manring, L. E.; Foote, C. S. *J. Am. Chem. Soc.* **1983**, *105*, 4710.



(1)

that this reaction was quantitative and that no polymeric materials undetectable by NMR were formed. The aldehyde presumably formed from decomposition of the hemiacetal **10**. The aldehyde was isolated by flash chromatographic treatment of reactions mixtures isolated from photooxidation of diene **3** in protiomethanol. The proton NMR spectrum of **11** (Scheme III) was assigned by single-frequency decoupling experiments and the ^{13}C NMR spectrum (Scheme III) by selective decoupling.

The formation of 16% more addition product in the reaction of the (*Z*,*Z*)-diene **3** than in the reaction of the (*E*,*E*)-diene **1** is another verification of the very different character of these two reactions. Mechanistic interpretation of these results, however, is more difficult. The distinction between trapping of zwitterions,[8] perepoxides,[9] or charge-transfer intermediates by nucleophilic solvents[10,11] in singlet oxygen reactions of electron-rich substrates is currently impossible. The formation of an addition product in the reaction of the (*E*,*E*)-diene **1**, however, is unexpected in view of the previously suggested[1] lack of intermediates on the concerted pathway for its reaction. This apparent discrepancy can be alleviated by either (1) suggesting that a charge-transfer intermediate preceding the concerted 2s + 2a cycloaddition was trapped or by (2) proposing a change in mechanism in the protic solvent methanol. Hydrogen bonding to the pendant oxygen of the perepoxide may provide the extra stability to allow the formation of this intermediate to compete with the concerted 2s + 2a cycloaddition in protic media.

The formation of only one and the same diastereomeric methanol addition product in both the reactions of the (*E*,*E*)- and (*Z*,*Z*)-diene indicate that both reactions are exclusively syn- or exclusively anti-1,4-diene additions. Unfortunately, the concentration limitations and the reactivity of the hydroperoxide precluded its isolation for further stereochemical analysis. We anticipate, however, in analogy to the addition of chlorine to several dienes[12] that syn addition of methanol and oxygen occurred.

Experimental Section

Preparative gas chromatographic separations were carried out on a GOW-MAC gas chromatograph utilizing a 0.25 in. by 20 ft column packed with 20% Carbowax 20M on Chromosorb W, 60/80 mesh NAW. The retention time for the (*E*,*E*)-diene **1** was 54 min when the column was 140 °C, the injector 180 °C, the detector 200 °C, the collector 180 °C, and the flow rate set to 120 mL/min. The proton NMR spectra were obtained on a JEOL FX270 spectrometer and the chemical shifts referenced to Me_4Si.

Triphenylphosphine (Aldrich) was purified by recrystallization from chlorobenzene. Methanol-d_4 (Aldrich), rose bengal (Aldrich), eosin B (Aldrich), and methylene blue (Baker) were used as purchased.

(*E*,*E*)-1,4-Di-*tert*-butoxy-1,3-butadiene (1) was synthesized by the method of Hiranuma and Miller[13] and purified by gas chromatography: ^{1}H NMR (CD_3OD) δ 6.46 (dd, J = 8, 3 Hz, 2 H), 5.56 (dd, J = 8, 3 Hz, 2 H), 1.28 (s, 18 H).

(*Z*,*Z*)-1,4-Di-*tert*-butoxy-1,3-butadiene (3) was synthesized by the method of Hiranuma and Miller[13] and purified by recrystallization from cold pentane: ^{1}H NMR (CD_3OD) δ 6.16 (dd, J = 4, 2 Hz, 2 H), 5.42 (dd, J = 4, 2 Hz, 2 H), 1.31 (s, 18 H).

(*E*)-1,4-Di-*tert*-butoxy-4-(trideuteriomethoxy)-1-hydroperoxy-2-butene (9): ^{1}H NMR (CD_3OD) δ 5.86 (ddd, J = 15.7, 4.4, 1.1 Hz, 1 H), 5.80 (ddd, J = 15.7, 3.7, 1.1 Hz, 1 H), 5.50 (d, J = 3.7 Hz, 1 H), 5.16 (d, J = 4.4 Hz, 1 H), 1.32 (s, 9 H), 1.29 (s, 9 H).

(*E*)-4-*tert*-Butoxy-4-methoxy-2-butenal (11). A solution of 42 mg of the (*Z*,*Z*)-diene **3** and rose bengal in methanol was irradiated at −78 °C. The reaction was complete as determined by TLC after 8.5 h. After sitting for 24 h at room temperature, 1 equiv of triphenylphosphine was added. The aldehyde was isolated after an additional 48 h by flash column chromatography[14] on silica gel: ^{1}H NMR (acetone-d_6) δ 9.65 (d, J = 7.9 Hz, 1 H), 6.79 (ddd, J = 15.9, 4.2, 1.3 Hz, 1 H), 6.25 (ddd, J = 15.9, 7.9, 1.3 Hz, 1 H), 5.45 (dd, J = 4.2, 1.3 Hz, 1 H), 3.28 (s, 3 H), 1.33 (s, 9 H); ^{13}C NMR (acetone-d_6) δ 194.25 (d, J = 173 Hz), 154.08 (d, J = 157 Hz), 133.7 (d, J = 161 Hz), 95.33 (d, J = 160 Hz), 75.54 (s), 50.45 (q, J = 142 Hz), 28.81 (q, J = 124 Hz). **4-(Trideuteriomethoxy)-11** ^{1}H NMR (CD_3OD) δ 9.62 (d, J = 7.7 Hz, 1 H), 6.80 (ddd, J = 15.7, 4.4, 1.1 Hz, 1 H), 6.30 (ddd, J = 15.7, 7.7, 1.1 Hz, 1 H), 5.45 (dd, J = 4.4, 1.1 Hz, 1 H), 1.32 (s, 9 H).

Photolysis Conditions. Methanol-d_4 solutions of dienes **1** and **3** were placed in 5-mm NMR tubes with enough rose bengal to make the solutions 1 × 10^{-5} M in dye. These samples were saturated with oxygen for at least 20 min at −78 °C while being protected from room light. The reaction mixtures were then irradiated at −78 °C with a WIKO 750W-250V projector lamp through a 0.5% $K_2Cr_2O_7$ filter solution which is opaque to all irradiation below 500 nm. The (*E*,*E*)-diene **1** was irradiated for 35 min and the (*Z*,*Z*)-diene **3** for 30 min. Overoxidation products were not observed in any reaction. Each solution was purged with argon to facilitate tuning of the high-resolution NMR. All single-frequency decoupling experiments were conducted at −80 °C.

These samples were then warmed to room temperature and allowed to sit in the dark for 24 h at which time proton NMR indicated complete decomposition of the dioxetanes. Triphenylphosphine was then added and the reduction of the hydroperoxide monitored by proton NMR. In all cases the reactions were complete within 5.5 h. The amount of aldehyde formed was independent of the number of equivalents of triphenylphosphine utilized as long as at least 0.5 equiv was used.

Acknowledgment. we are grateful to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation (CHE-8418603) for support of this research.

Registry No. 1, 86528-14-5; **3**, 79989-51-8; **9**, 103669-06-3; **11**, 103669-07-4; 4-(trideuteriomethoxy)-**11**, 103669-08-5.

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